Faculty Publications

2007-07-12

Potential energy surfaces for small alcohol dimers. II. Propanol, isopropanol, t-butanol, and sec-butanol

Richard L. Rowley
rowley@byu.edu

Christopher M. Tracy

Tapani A. Pakkanen

Follow this and additional works at: <https://scholarsarchive.byu.edu/facpub>

Part of the [Chemical Engineering Commons](#)

Original Publication Citation

Rowley, Richard L., Christopher M. Tracy, and Tapani A. Pakkanen. "Potential energy surfaces for small alcohol dimers. II. Propanol, isopropanol, t-butanol, and sec-butanol." *The Journal of Chemical Physics* 127 (27)

BYU ScholarsArchive Citation

Rowley, Richard L.; Tracy, Christopher M.; and Pakkanen, Tapani A., "Potential energy surfaces for small alcohol dimers. II. Propanol, isopropanol, t-butanol, and sec-butanol" (2007). *Faculty Publications*. 243.
<https://scholarsarchive.byu.edu/facpub/243>

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact ellen_amatangelo@byu.edu.

Potential energy surfaces for small alcohol dimers. II. Propanol, isopropanol, *t*-butanol, and *sec*-butanol

Richard L. Rowley and Christopher M. Tracy

Department of Chemical Engineering, Brigham Young University, Provo, Utah 84602

Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, FIN-80101 Joensuu, Finland

(Received 21 February 2007; accepted 14 May 2007; published online 12 July 2007)

Potential energy landscapes for homogeneous dimers of propanol, isopropanol, *tert*-butanol, and *sec*-butanol were obtained using 735 counterpoise-corrected energies at the MP2/6-311+G(2df,2pd) level. The landscapes were sampled at 15 dimer separation distances for different relative monomer geometries, or routes, given in terms of the yaw, pitch, and roll of one monomer relative to the other and the spherical angles between the two monomer centers (taken as the C atom attached to the O). The resultant individual energy surfaces and their complex topographies were also regressed using a site-site pair potential model using a modified Morse potential that provides a mathematically simple representation of the landscapes suitable for use in molecular simulations. Generalized Morse parameters were also obtained for this model from a composite regression of these energy landscapes and those previously reported for methanol and ethanol. The quality of fit for all these energy landscapes suggests that these site parameters have transferability for possible use on other alcohols. © 2007 American Institute of Physics. [DOI: 10.1063/1.2747244]

I. INTRODUCTION

In a companion paper,¹ we reported counterpoise-corrected dimer potential energy landscapes for rigid monomers of methanol and ethanol. These dimer energy surfaces were obtained from *ab initio* supermolecule calculations using MP2/6-311+G(2df,2pd). Similar calculations are used in this study to obtain the energy landscapes for dimers of alcohols containing three or four carbon atoms. Such potential energy surfaces are important in relating condensed-matter thermophysical properties to molecular interactions and for quantitative property predictions using those interactions in methods such as molecular dynamics and Monte Carlo simulations. We refer readers to the discussion and references cited in Ref. 1 for background on appropriate methods for obtaining dimer energy landscapes and their validation in simulation work.

Analytical representation of the potential energy surface is generally required for its use in simulations. In the companion paper, we showed that the multidimension, complex potential energy surfaces obtained for methanol and ethanol could be adequately modeled as the pairwise summation of site-site interactions,

$$U = \sum_{i=1}^{NS} \sum_{j=1}^{NS} u_{ij}(r_{ij}), \quad (1)$$

where U is the potential energy, NS is the number of sites on each monomer, and u_{ij} is a spherically symmetric site-site pair potential energy that is a function only of the separation distance between the sites r_{ij} . We have used an all-atom model in which NS is equal to the number of atoms in the monomer. A modified Morse model,

$$u_{ij} = -\epsilon_{ij}(1 - \{1 - \exp[-A_{ij}(r_{ij} - r_{ij}^*)]\})^2) + \frac{z_i z_j e^2}{4\pi\epsilon_0 r_{ij}}, \quad (2)$$

was used to represent the interatomic interactions. In this model, ϵ , A , and r^* are adjustable parameters representing the attractive well depth, well shape factor, and the location of the minimum in the potential well, respectively. Equation (2) uses fractional point charges z_i (e is electron charge and ϵ_0 is the free space permittivity) assigned to nuclear sites i to model Coulombic interactions within the molecule. The use of such point charges is a common means of separately modeling interactions due to permanent charge distributions and dispersion interactions. However, it should be remembered that point charge interactions are a rudimentary representation of the actual interactions between spatially complex electrostatic molecular surfaces. For example, a Mulliken population analysis assigns point charges based on a partitioning of the electron density between the atoms, while an electrostatic-potential (ESP) method, such as that used to obtain the point charges in this study, regresses a set of point charges that best reproduces the electrostatic potential at a grid of points surrounding the molecule. With this in mind, in Ref. 1 we regressed the *ab initio* methanol and ethanol energy landscapes to obtain parameters in Eq. (2) in two different ways, both of which adequately represented the complexity of the dimer energy surfaces. Using ESP charges and Eq. (2) as written, we obtained Morse potential parameters representing only the repulsion and dispersion interactions. In the second method, we obtained the parameters ϵ , A , and r^* by regressing the *ab initio* landscapes without the point charges. In this case, the Morse potential models the total interactions between the monomers. Interestingly, this

FIG. 1. Optimized geometry and ESP point charges (labeled on right-hand figure) for propanol (top) and isopropanol (bottom).

second model represented the *ab initio* energy landscapes of methanol and ethanol as well as, or arguably better than, the more traditional model of collapsing electron density information into point charges. See Ref. 1 for additional details and discussion of modeling polar molecules sans point charges.

The model shown in Eq. (2) has recently been used by several groups to regress *ab initio* potential energy surfaces. In our previous studies we found that the modified Morse model fits potential energy landscapes significantly better than Lennard-Jones and exp-6 models.^{2,5,6} Garrison and Sandler⁸ found that Gibbs ensemble simulations accurately reproduced the experimental vapor-liquid phase dome of acetylene using a site-site Morse-C6 model. Hayes *et al.*⁹ found better agreement between experimental and simulated thermodynamic data with a Morse potential model derived from an *ab initio* methane potential energy surface than that obtained with more commonly used parameter sets and models.

Models developed from *ab initio* calculated pair potentials are fairly recent. For example, transferable parameters for alcohols are available for OPLS (Ref. 10) and TRAPPE (Ref. 11) force field models. The parameters in these models have been regressed from experimental data to optimize them for use in simulations to predict thermophysical properties. Other models have also been developed, in which the model parameters have been tuned for specific properties.

For example, Zhang and Ely¹² used an anisotropic, united-atom, Buckingham-exponential-6 potential model with parameters optimized to pure alcohol viscosity data to simulate mixture viscosities. Boutard *et al.*¹³ used methanol and ethanol vapor-liquid equilibrium data to tune interactions for general phase equilibrium calculations involving alcohols. Models tuned with experimental data inherently contain multibody information, which can lead to higher accuracy for conditions and properties for which they have been tuned. Models obtained from *ab initio* dimer potential energy surfaces are true pair potentials and may need multibody corrections for accurate simulations at high densities. *Ab initio*-derived molecular pair potential models can also be scaled and supplemented with polarizability to take into account multibody effects and better represent experimental results.¹⁴

In our previous studies of small alkane dimers,²⁻⁷ we found that Eq. (2) with $z_i=0$ provides a reasonably good representation of the *ab initio* potential energy surface of nonpolar dimers. Moreover, the Morse parameters obtained were found to have a relatively high degree of transferability from one alkane molecule to the next. The generic C-C, C-H, and H-H interaction parameters regressed from dimer potential energy landscapes for neopentane, isopropane, propane, and ethane are referred to here as NIPE values,³ an acronym for the surfaces used in the regression.

An obvious advantage of modeling the energy land-

FIG. 2. Optimized geometry and ESP point charges (labeled on right-hand figure) for *t*-butanol (top) and *sec*-butanol (bottom).

scapes with Eqs. (1) and (2) is the reduction of independent spatial variables required to define the relative orientations of the monomers; only interatomic distances are required to obtain the potential energy for any given dimer configuration. The viability of such models in simulation studies is dependent only on how well it reproduces the actual potential energy surface. In this study we both examine the ability of the model to reproduce the *ab initio* dimer landscapes and the extent to which the model parameters can be taken as independent of the alcohol dimer from which they were regressed. Such parameter transferability suggests some physical underpinning of the model and the possible use of the interatomic parameters for use in predicting other alcohol dimer potentials. In conjunction with the companion paper, these surfaces also provide opportunity to qualitatively examine the effect of additional $-\text{CH}_x-$ character and structural branching on alcohol dimer interactions.

II. COMPUTATIONAL DETAILS

As in the companion paper, all calculations were made with MP2/6-311+G(2df,2pd) using GAUSSIAN 98.¹⁵ The level of theory and basis set size used in this study were the same in our previous studies in order to maintain consistency with those studies. That is, the transferable site-site interactions regressed from these combined studies all represent the landscapes generated with MP2/6-311+G(2df,2pd). Sev-

FIG. 3. Illustration of yaw, pitch, roll, r , θ , and φ coordinates to describe dimer approach routes (using methanol monomers to simplify diagram).

TABLE I. Propanol routes in terms of the approach axis (gray line) as defined by yaw, pitch, roll, θ , and ϕ coordinates. Multiple values represent the coefficients in Eq. (3) for yaw, pitch, roll, and θ or Eq. (4) for ϕ .

Approach	Number	Yaw	Pitch	Roll	θ	ϕ
1	181.89	-71.59	-2.62	179.13	35.806
2	358.22	17.42	179.73	179.13	-2.3746 2.1406 0.5796 -0.4247
3	178.25	0.00	180.00	-0.87	0.0018 0.9999 -1.4119
4	178.26	0.00	-180.00	-0.87	2.6105 0.3135 0.7073
5	180.64	54.16	1.24	-0.87	-0.0082 -0.9996 -0.4112
6	180.00	-16.79	-0.26584	179.128	0.9475 0.5849 3.5144
7	0.0128 -0.8265 217.74	0.0015 -0.9175 21.047	0.0068 -0.9396 -70.617	0.0248 0.4245 118.98	-2.4865 0.3818
8	178.26	0.00	180.00	0.00	-90.00
9	178.26	0.00	-180.00	-0.87	18.39
10	0.00	-0.60	0.00	-0.87	-1E-05 0.0092 0.3154
11	-0.0107 0.2163 320.05	-0.0092 1.2223 23.159	-0.0071 -0.5527 75.638	0.1163 -1.9975 140.83	2.7614 -1.6968 0.363 6E-05
12	178.26	0.00	180.00	179.13	-0.0183 -0.3257 4.8967
13	-0.0177 1.1527 134.01	0.0005 0.7717 -34.383	0.0112 -1.2728 122.68	0.0686 -1.043 134.66	-2.1607 0.3808 4.9335
14	0.0021 1.2178 85.371	0.0189 -1.9817 54.523	-0.0024 -0.8837 -129.43	0.0582 -0.78 131.53	-3.6937 0.3979 0.9909
15	181.94	-71.56	-2.68	179.13	-0.016 -0.9991 -0.3107
16	178.26	0.00	-180.00	-0.87	1.2879 0.3152 -0.3069
17	0.00	-0.60	0.00	-0.87	1.295 0.3153 2.8903
18	-0.0299 2.3652 278.95	0.0195 -0.1772 -53.226	0.0273 -2.6675 170.97	0.1881 -4.331 162.69	-1.1064 0.3501

eral studies found that the effect of electron correlation beyond an MP2 treatment was not large and that accurate potential energy surfaces can be obtained from MP2 calculations with reasonably large basis sets containing multiple polarization functions.^{16–18} Our own results with methane² showed that energies calculated with MP2/6-311+G(2df,2pd) differed from those calculated with MP4/aug-cc-pVTZ by less than 0.04 kcal/mol.

Optimized geometries of the isolated monomers and model point charges obtained from the ESP method are shown in Fig. 1 for propanol and isopropanol and in Fig. 2 for *t*-butanol and *sec*-butanol. These geometries were used without relaxation to determine *ab initio* data for unique dimer orientations.

All potential energies of the dimer pair were counter-

poise corrected. Potential energy scans were performed for the dimers along routes of fixed relative monomer orientations. The routes were defined in terms of an approach axis along which the distance between the two monomers was varied. Figure 3 defines the geometrical terms that are used throughout this paper to define the approach routes. In all cases, the origin for the coordinate system for each monomer is the primary alcohol C atom (labeled C_α). The standard monomer orientation, depicted in the left-hand drawing of Fig. 3, places the C_α –O bond along the z axis with the O–H bond parallel to the x axis. Dimer route orientations are defined in terms of the yaw, pitch, and roll angles of the second monomer relative to the standard orientation in which the first monomer is fixed. As shown in Fig. 3, yaw ($0^\circ \leq \text{yaw} < 360^\circ$) represents a right-hand rotation about the z axis,

TABLE II. Isopropanol routes in terms of the approach axis (gray line) as defined by yaw, pitch, roll, θ , and ϕ coordinates. Multiple values represent the coefficients in Eq. (4) for ϕ .

Approach	Number	Yaw	Pitch	Roll	θ	ϕ
1	180.00	-72.51	0.00	-180.00	36.26
2	180.00	-72.51	0.00	0.00	-36.26
3	0.00	0.03	0.00	-180.00	36.26
4	0.076	53.72	0.05	-180.00	-0.4144 0.9328 0.5912
5	62.58	-17.75	0.00	-180.00	-0.4563 0.9829 0.5913
6	0.07	-0.03	180.00	62.58	-89.93
7	260.67	-25.86	110.69	62.58	0.0006 -0.0602 -0.3177
8	305.19	-0.03	-180.00	62.58	0.0026 -0.1204 -0.3177
9	180.13	-72.51	-0.10	0.00	-0.3034 1.3044 0.2999
10	242.60	-1.04	0.00	0.00	-0.3263 1.3635 0.3001
11	0.00	-53.74	0.00	-180.00	-0.0131 -0.1698 0.5915

pitch ($-90^\circ \leq \text{pitch} \leq 90^\circ$) represents a right-hand rotation about the y axis, and roll ($-180^\circ \leq \text{roll} \leq 180^\circ$) represents a right-hand rotation about the x axis. The relative spatial location of each monomer origin is characterized by the spherical coordinate triplet (r, θ, ϕ) for the vector from the first monomer origin to the second. This is depicted in the right-hand diagram of Fig. 3, where it can be seen that θ ($-180^\circ \leq \theta < 180^\circ$) specifies the angle between the origin-to-origin vector and the x axis, ϕ ($-90^\circ \leq \phi \leq 90^\circ$) specifies the azimuthal angle between the vector and the x - y plane, and r specifies the distance between the origins.

The approach routes for the four dimers are defined in Tables I–IV. The thumbnail picture of the route shown in the left column depicts the approach axis (line) between the monomers. The central site in these thumbnails, represented

by a small sphere, is a dummy site used in the scans to vary r , the distance between the positions of the two C_α nuclei. The orientation of the second monomer relative to the first does not change in many of the routes; in this case the yaw, pitch, and roll of the second molecule do not vary with r , and a single value appears in the columns of Tables I–IV for the yaw, pitch, and roll of the second molecule. In all cases, the first molecule is maintained in the standard orientation shown in Fig. 3. For those cases in which the relative orientation of the second molecule changes with the approach distance r , yaw, pitch, and roll have been parametrized in terms of r and three entries appear in these columns instead of a fixed angle. These entries correspond to the a , b , and c , respectively, in the correlation

TABLE III. *t*-Butanol routes in terms of the approach axis (gray line) as defined by yaw, pitch, roll, θ , and ϕ coordinates. Multiple values represent the coefficients in Eq. (4) for ϕ .

Approach	Number	Yaw	Pitch	Roll	θ	ϕ
1	180.00	-72.27	0.00	-180.00	36.15
2	0.00	0.00	0.00	-180.00	36.15
3	0.00	72.29	180.00	-180.00	-1.9555 1.9462 0.5857
4	0.00	2.817	0.00	0.00	-0.3019 1.3044 0.304
5	0.00	-72.26	0.00	0.00	-0.3043 1.3051 0.3039
6	359.94	75.11	179.92	0.00	-90.00
7	180.00	0.00	180.00	-180.00	-14.89
8	180.00	0.00	180.00	0.00	-90.00
9	180.00	51.04	180.00	-180.00	-0.4127 0.9381 0.5897
10	0.00	0.00	0.00	0.00	90.00
11	180.00	53.86	0.030	-180.00	-0.4173 0.9393 0.5896
12	0.00	18.46	180.00	0.00	-1.2851 2.4714 0.3004
13	180.00	0.00	180.00	-180.00	-3.723 2.6563 0.5823

$$\begin{bmatrix} \text{yaw} \\ \text{pitch} \\ \text{roll} \\ \theta \end{bmatrix} = ar^2 + br + c. \quad (3)$$

Likewise, θ and ϕ , defining the relative angles of the origin-to-origin vector from the first monomer to the second, have been parametrized in terms of the separation distance r . The triple entries in Tables I–IV for θ are the coefficients a , b , and c in Eq. (3); the entries for ϕ correspond to the coefficients a , b , and c , respectively, in

$$\phi = \sin^{-1} \left(\frac{a}{r^2} + \frac{b}{r} + c \right). \quad (4)$$

Dimer energies were calculated at 15 different separation distances r along each route for a combined total of 735 counterpoise-corrected values: 270 for the propanol surface, 165 for the isopropanol surface, 195 for the *t*-butanol surface, and 105 for the *sec*-butanol surface.

III. POTENTIAL ENERGY LANDSCAPES

Results of the dimer potential energies for each of the routes are shown in Figs. 4–7. Route numbers defined in Tables I–IV are shown in the legends, but the routes are loosely grouped in the figures by the expected dominant site-site interaction. Routes grouped together tend to bring similar sites toward each other along the approach axis. For convenience, we will refer to routes in Figs. 4–7 using the nomenclature Cr where C represents the compound abbreviation (P=propanol, I=isopropanol, T=*t*-butanol, and S=*sec*-butanol) and r represents the route number. Thus, P2 represents propanol route 2, S3 represents *sec*-butanol route 3, etc.

As one might expect, the dominant attractive routes are those that bring the O and H_α atoms together for hydrogen bonding. The deep attractive wells for P2, P3, I3, I11, T12, and S4 are clearly dominated by the O– H_α interaction. These strong O– H_α attractive potential wells arise primarily from the Hartree-Fock portion of the *ab initio* calculation

TABLE IV. *sec*-Butanol routes in terms of the approach axis (gray line) as defined by yaw, pitch, roll, θ , and ϕ coordinates. Multiple values represent the coefficients in Eq. (3) for yaw, pitch, roll, and θ or Eq. (4) for ϕ .

Approach	Number	Yaw	Pitch	Roll	θ	ϕ
1	180.00	-72.00	0.00	-180.00	35.99
2	0.00	0.00	0.00	-180.00	35.99
3	0.00	-54.03	0.00	-180.00	-0.0121 -0.164 0.5877
4	0.00	17.97	180.00	-180.00	-2.3937 2.141 0.5823
5	180.00	0.00	180.00	0.00	18.02
6	291.92	0.00	180.00	55.98	0.0004 0.0426 -0.3711
7	0.0228 -1.5095 363.82	0.0009 0.0224 23.033	0.0036 -0.0157 17.851	-0.1417 -0.4241 0.8274	0.3956 1.108 -0.3703

and are dominated by strong permanent charge distribution within the monomers. Figures 1 and 2 show that increased branching at the C_α site produces larger negative charges on the O atom, consistent with the corresponding deeper potential wells (stronger hydrogen bonds) of the direct O– H_α routes in the order P2, I11, S4, and T12.

Routes P1, I1, T1, and S1 all feature the approach of the two O atoms together. The I1 and T1 routes are entirely repulsive as one might suspect from the electrostatics. S2 has a substantial attractive region at reasonably close distances despite the O–O approach. The two monomers are oriented in the same direction, so as they approach each other along this route there is considerable dispersion attractions from the alkyl chains before the two O atoms approach each other close enough for their mutual repulsion to impact the potential. Dispersion interactions between the alkyl chains also produce the attractive wells in routes P1 and S1. In this case, the ends of the two alkyl chains are directed toward each other, creating early opportunity for dispersion attractions as the monomers approach each other. We were surprised that P16 and T13 were entirely repulsive because both orientations appear to create the opportunity for double O– H_α interactions, but the repulsions of the more direct C_α – H_α interaction for P16 and the O–O interaction for T13 dominate. The repulsive nature of P4 is due to the head-to-head approach of the H_α atoms on the two monomers, both of which have a strong positive partial charge.

Routes P5, I4, T10, and T11 are of type O– C_α and exhibit deep attractive wells. The trends in these routes are consistent with the ESP charges listed in Figs. 1 and 2. The charges on the C_α atom are 0.2117, 0.6202, and 0.8174 for propanol, isopropanol, and *t*-propanol, respectively, and the

corresponding attractive minima for P5, I4, and T10 are -1.4 , -1.8 , and -2.5 kcal/mol. Routes P6, I5, and T9 also bring an O toward a carbon atom, but toward the C atom attached to the C_α atom, which we designate as C_1 in propanol (and ethanol) and as C_β in isopropanol and *t*-butanol. These routes also exhibit relatively strong attractive potential wells, but the minima are not as deep as those for the routes dominated by the O– C_α interaction. Again the relative magnitudes of these attractive wells are consistent with the ESP charges on these atoms. The minima in P5 and P6 are approximately equal as are the ESP charges on C_α and C_1 in propanol. However, the charges on the C_β atoms in isopropanol and *t*-butanol are negative (which is why we distinguish them as C_β instead of C_1) and the corresponding well depths for I5 and T9 are significantly attenuated relative to I4, T10, and T11.

The significant attractive well at about 3.8 Å on P9 followed by a repulsive hump at about 6 Å is interesting. This behavior seems to be due to C_α – C_α repulsions at the larger distances, where the O–H interactions are oriented too far away to contribute significantly. At closer distances the much deeper O–H well and the C– H_α attractions (see P18) successfully overcome the C_α – C_α repulsions, though they are not directly emphasized by this approach route. I2, T5, S1, and S5 also show small repulsions at larger r values followed by attractive wells at closer distances. Again competing interactions effective at different r values are likely the explanations of this behavior. For example, the O–O repulsions likely produce the longer-range repulsions in I2 and S1, while the dispersion interactions from the alkyl groups become effective at shorter C_α – C_α distances.

The attractive well for I3 is about half that of direct

FIG. 4. Dimer energies for propanol as a function of distance between C_α monomer sites from *ab initio* calculations (points) and from the site-site model without point charges (lines).

hydrogen bond interactions and considerably broader. In spite of the approach axis through the two O atoms, this orientation permits a pair of longer-range O-H $_\alpha$ interactions to compete with the O-O repulsion.

The C-C routes (P12-P14, I6-I8, T6-T8, and S5-S7) are characteristic of dispersion interactions, in which electron correlation provides the main attractive part of the potential. These routes are very similar in appearance to those obtained

in our alkane dimer studies, and this similarity suggests extending the NIPE model parameters developed from those studies to C interactions.

IV. PAIRWISE ADDITIVE ATOMIC POTENTIALS

To model the potential energy surfaces using Eqs. (1) and (2), interaction sites are located at each atomic center. As in the companion paper for methanol and ethanol, a satellite

FIG. 5. Dimer energies for isopropanol as a function of distance between C_α monomer sites from *ab initio* calculations (points) and from the site-site model without point charges (lines).

site X was placed on the vector bisecting the C_α -O- H_α angle of the alcohol, but on the side of the O opposite the C_α -O and O- H_α bonds, to represent the off-center high electron density of the electron pairs on the O atom. All interactions with the satellite site were assumed to be zero except for H_α -X and X-X. The H_α -X interaction was modeled with Eq. (2), but the X-X interaction was simplified to a purely repulsive interaction modeled with

$$u_{XX} = B_{XX} \exp(-C_{XX}r_{XX}). \quad (5)$$

Values of the parameters B_{XX} and C_{XX} (as well as the location of the X site in terms of the O-X distance) were regressed from the *ab initio* potential landscapes simultaneously with the site-site parameters of Eq. (2).

The purpose of representing the potential energy landscapes with site-site models is to provide a mathematical parametrization of the surfaces useful for molecular simulations. Such mathematical models are particularly useful if the site-site interactions are transferable between molecules because then the model can be used as a predictive equation for other molecules whose energy landscapes might also be modeled by the same set of site-site interactions.

Amongst the many site-site models that could be used, Eqs. (1) and (2) maintain consistency with the previous NIPE model that has been developed for alkanes and has shown considerable transferability. However, the most com-

mon representation of atom-atom dispersion interactions is with an r^{-6} term because this is the leading term obtained from long-range perturbation theory when used in conjunction with a multipole expansion.¹⁹ Accordingly, the dispersion energy is often written as a power series in r^{-n} , where $n=6, 8, 10, \dots$. The singularity as r approaches zero is incorrect and so damping functions, usually of an exponential nature in r (see, for example, Ref. 20), are used to allow an r^{-6} limit at infinite distance while suppressing the singularity at $r=0$. This series is unfortunately nonconvergent (or asymptotically convergent¹⁹). In the model represented by Eqs. (1) and (2), the molecule-molecule interactions are a linear combination of the many exponentials representing the atom-atom interactions and therefore can reproduce a variety of r -dependent behaviors, as shown in Figs. 4–7. However, individual atom-atom intermolecular potentials do not include the more traditional r^{-6} behavior, nor is there any theoretical basis for an exponential decay. These atom-atom interactions are a means to an end and one should not attribute too much physical significance to them individually. For example, there is some evidence that the spherical or isotropic approximation used here and in most atom-atom interaction models can be poor.¹² In this pragmatic view, representation of the energy landscape by the model and the model's potential for transferability is sufficient. That is, agreement be-

FIG. 6. Dimer energies for *t*-butanol as a function of distance between C_α monomer sites from *ab initio* calculations (points) and from the site-site model without point charges (lines).

tween the model and the *ab initio* potentials over intermolecular distances where the potential differs from zero more than the uncertainty of the calculations is the prime concern. Higher-level calculations and larger basis sets would likely be required to more accurately investigate the smaller potentials at larger separation distances, which Eqs. (1) and (2) may not adequately represent.

To maintain consistency and transferability with the NIPE site-site interactions developed for alkyl sites, all C atoms for which the absolute value of the ESP charge was

less than 0.3 and all H atoms except H_α were modeled as NIPE sites. With this definition, the model's set of interacting sites for all alcohols contains seven members: {O, C_α , C_β , C, H_α , H, and X}. C_α is always taken to be the carbon attached to the O, C_β is taken to be the carbon attached to C_α whenever the magnitude of its charge is greater than 0.3 (otherwise it is considered a C), and all other carbon atoms are considered to be C. Likewise, H_α is the hydrogen attached to the O and all other hydrogen atoms are considered to be H. There are 23 possible unique pair interactions between these

FIG. 7. Dimer energies for *sec*-butanol as a function of distance between C_α monomer sites from *ab initio* calculations (points) and from the site-site model without point charges (lines).

sites, as defined here; these are shown in Table V. As mentioned, the NIPE constants are used for the C–C, C–H, and H–H interactions, leaving 20 pair interactions to be parametrized.

Each alcohol energy landscape, except that for *sec*-butanol, was regressed separately to obtain a best set of site-site interaction parameters for that compound. Then a regression of all available alcohol energy surfaces, including those previously reported for methanol and ethanol, was performed to obtain a generalized set of alcohol site-site interaction parameters. The quality of the individual compound regressions serves as a best-case representation of the landscape using

this model, and the quality of the simultaneous fit of all the alcohols relative to these best-case values is indicative of the transferability of the generalized parameters. A simulated annealing program was used to perform all of the regressions. Convergence to a global minimum was verified by varying the “cooling” rate and by using different initial parameter values.

Table V shows which energy landscapes were used in the regression of the generalized model parameters. All the generalized parameters except those for the C_β –C interaction were obtained from a regression using the energy landscape data for methanol, ethanol, propanol, isopropanol, and

TABLE V. Pair interactions and the alcohol energy landscapes used to regress the generalized site-site interactions. NIPE parameters were used directly as constants; other interactions were obtained from energy landscapes for M (methanol), E (ethanol), P (propanol), I (isopropanol), T (*t*-butanol), and S (*sec*-butanol).

Site-site	O	C_α	C_β	C	H_α	H	X
O	M,E,P,I,T	M,E,P,I,T	I,T	E,P	M,E,P,I,T	M,E,P,I,T	...
C_α	...	M,E,P,I,T	I,T	E,P	M,E,P,I,T	M,E,P,I,T	...
C_β	...	...	I,T	S	I,T	I,T	...
C	...	...	...	NIPE	E,P	NIPE	...
H_α	...	...	...	...	M,E,P,I,T	M,E,P,I,T	M,E,P,I,T
H	...	...	...	...	...	NIPE	...
X	...	...	...	...	...	...	M,E,P,I,T

t-butanol. As the C_β -C interaction appears only in *sec*-butanol, its parameters were obtained from a single regression of the *sec*-butanol energy landscape with all the other pair interaction parameters fixed at their previously determined generalized values.

The two models mentioned earlier, Eq. (2) with and without point charges, were regressed separately using the scheme described above to obtain the model parameters. For the model that included point charges, the small charges on C and H sites treated with the NIPE parameters were set to zero, and the remaining charges in the monomer were normalized to the values listed near the bottom of Table VI. The results of the regression are shown in the bottom line of Table VI as a sum of squared errors (SSE) per point, and the resultant pair potential model parameters are given in the main rows of Table VI. The SSE values suggest a reasonably good fit of the isopropanol and *t*-butanol energy landscapes but a poor fit of the propanol energy surface. This model does not produce transferable site-site interactions as is evident by the very large SSE for the simultaneous regression of all the alcohol energy surfaces to obtain generalized model parameters. No set of model parameters for the model with point charges is capable of representing the energy surfaces of these alcohols.

Similar results of the regression of the energy landscapes using the second model without point charges are shown in Table VII. The individual regressions all yielded smaller SSE values than the first model with point charges. The fit of the propanol energy surface without point charges was substantially improved over that obtained with the first model, the SSE now comparable to that of the other alcohols. A generalized set of parameters for the site-site model without point charges was also found that represents all the alcohol energy surfaces quite well. The SSE for this simultaneous regression shown in Table VI was a factor of 14 smaller than the model with charges. As reported in our earlier paper, the SSEs for the individual regressions of methanol and ethanol were 0.030 and 0.017 kcal²/mol², respectively. The SSE value of 0.054 kcal²/mol² obtained for the generalized six-alcohol regression shows a relatively small degradation in quality of fit relative to the individual regressions, and this indicates a reasonable level of transferability of the resultant parameters.

Figures 4–7 compare the fitted site-site model (without charges) to the *ab initio* data. In general, the site-site model reproduces quite accurately the very complex energy surface between all of the dimers. The very attractive wells associated with routes experiencing hydrogen bonding all show good agreement between the model and the *ab initio* data. So also, energies for routes dominated by smaller dispersion interactions, such as those labeled C–C, are also well represented by the model. There are, however, some differences between the model and the *ab initio* data, particularly for the propanol routes which had the largest SSE of the four compounds. The propanol O–C routes tended to be the most problematic. Though the model correctly reproduces the shapes of the attractive wells and the location of the well minima for routes P5, P6, and P7, it underestimates the well depth for P5 and P6 and overestimates the well depth for P7. The O–C routes for the other dimer pairs do not have this

TABLE VI. Model parameters for Eq. (2) regressed with point charges. Parameter values are given in the order ε (kcal/mol), A ($\text{\AA}^{-1}$), and r^* ($\text{\AA}$), respectively, for Eq. (2) and in the order B (kcal/mol), C ($\text{\AA}^{-1}$), r_{ox} ($\text{\AA}$) for the X–X interaction.

Interactions	Propanol	Isopropanol	<i>t</i> -Butanol	Generalized
O–O	8.495 53	0.000 18	0.350 77	0.307 36
	0.925 58	1.305 55	0.985 37	1.542 41
	0.633 83	4.150 64	0.020 04	3.316 10
O–C $_\alpha$	3.22×10^{-5}	0.988 922 31	6.666 717 67	0.102 65
	0.770 14	1.815 955 45	4.711 306 17	1.442 51
	2.606 01	0.204 389 98	3.081 872 94	4.162 85
O–C $_\beta$		1.779 697 26	0.037 112 75	0.002 46
		1.421 892 88	0.948 511 22	1.328 72
		2.958 542 93	5.364 659 04	5.270 58
O–C	7.165 11			0.002 74
	1.460 58			1.303 28
	2.566 20			5.270 74
O–H $_\alpha$	3.624 99	15.954 4	1.135 35	19.511 94
	1.863 70	3.124 36	1.630 19	2.087 81
	1.935 70	0.065 99	1.032 79	0.017 32
O–H	5.25×10^{-5}	0.002 18	0.931 60	0.143 38
	0.946 77	1.889 85	1.844 94	1.749 85
	8.349 65	4.013 90	2.661 74	2.901 51
C $_\alpha$ –C $_\alpha$	4.595 98	2.290 09	1.521 59	1.438 77
	1.300 23	1.238 66	5.835 86	2.053 02
	2.919 05	3.426 22	2.081 82	3.147 99
C $_\alpha$ –C $_\beta$		0.024 79	3.539 50	0.070 73
		0.963 41	5.044 67	1.024 25
		5.907 75	0.342 03	3.847 76
C $_\alpha$ –C	0.009 88			0.285 923 22
	0.327 23			1.012 375 41
	10.862 97			3.906 176 26
C $_\alpha$ –H $_\alpha$	1.749 07	5.840 40	7.177 81	7.089 01
	2.827 68	1.800 52	12.582 6	13.295 73
	2.390 06	2.529 07	0.457 48	0.272 40
C $_\alpha$ –H	5.720 79	2.224 99	6.905 72	6.500 80
	4.847 76	3.254 52	5.086 35	5.296 26
	0.597 19	2.483 72	0.120 69	0.452 33
C $_\beta$ –C $_\beta$		0.011 09	7.20×10^{-5}	0.200 88
		1.302 11	1.622 63	1.218 55
		5.075 56	6.121 35	3.988 31
C $_\beta$ –H $_\alpha$		6.932 07	0.000 94	7.084 87
		1.447 81	2.238 37	6.922 91
		0.000 16	3.688 82	0.231 19
C $_\beta$ –H		0.624 21	0.402 28	6.457 14
		2.022 25	2.127 10	2.938 47
		2.480 69	2.829 67	1.521 04
C–H $_\alpha$	0.064 20			7.085 59
	10.01 54			6.922 56
	0.057 43			0.136 76
H $_\alpha$ –H $_\alpha$	5.70×10^{-11}	0.080 17	9.38×10^{-7}	0.000 32
	0.965 48	1.185 48	0.631 26	1.643 08
	15.312 58	4.530 90	9.412 65	4.620 52
H $_\alpha$ –H	0.685 95	0.002 88	1.04×10^{-6}	1.27×10^{-7}
	4.626 37	0.700 15	0.683 73	2.756 86
	0.000 15	6.941 92	11.922 50	4.190 78
X–X	1.010 03	6.712 52	10.889 15	10.679 09
	4.241 33	0.783 21	0.895 73	2.357 49
	0.448 39	1.105 59	1.016 28	1.180 84
H–X	0.000 93	0.374 93	1.385 40	0.086 50
	0.670 26	2.928 62	1.638 63	1.711 50
	7.775 37	0.823 49	1.394 15	2.302 29

TABLE VI. (Continued.)

Interactions	Propanol	Isopropanol	<i>t</i> -Butanol	Generalized
C-C	0.051 33			0.051 33
(NIPE)	1.459 85			1.459 85
	4.341 17			4.341 17
C-H	0.355 62			0.355 62
(NIPE)	2.111 74			2.111 74
	2.602 11			2.602 11
H-H	0.010 48	0.010 48	0.010 48	0.010 48
(NIPE)	1.260 72	1.260 72	1.260 72	1.260 72
	3.975 36	3.975 36	3.975 36	3.975 36
Normalized charges (no charge on NIPE sites)				
O	-0.626 4	-0.606 3	-0.610 1	See
C _α	0.225 5	0.729 6	0.945 8	individual
C _{β1}	0	-0.311 9	-0.324 7	alcohols
C _{β2}	0	0	-0.197 1	
H _α	0.400 9	0.500 5	0.510 9	
SSE ^a /point	0.115	0.019	0.033	0.789
	kcal ² /mol ²	kcal ² /mol ²	kcal ² /mol ²	kcal ² /mol ²

^aSSE=(1/*N*)Σ_{*i*=1}^{*N*}(*U*_{*i*,calc}−*U*_{*i*,qm})², where *N* is the number of potential energy points in the regression, *U*_{*i*,calc} is the site-site model potential energy [Eqs. (1) and (2)] and *U*_{*i*,qm} is the *ab initio* potential energy.

problem, likely because the C attached to the C_α is treated as a C_β site in the isopropanol and *t*-butanol routes but as a NIPE C site for propanol. Using a C_β site in propanol does not give better overall results because as the ESP charges indicate, the C attached to C_α in propanol is clearly different than the C_β sites. We chose not to define a separate C_β site for propanol, but rather to treat all C atoms with ESP charges of magnitude smaller than 0.3 as NIPE C sites. The P16 route is interesting with its gradual repulsive nature. The model reproduces this behavior reasonably accurately but has a small anomalous shoulder in the repulsion just beyond 4 Å. This is likely because of the competing O–O, O–H_α, and C–H_α site-site interactions along this route. The regressed site-site model replicates quite well the short-range attraction exhibited in P9, and while it does qualitatively show the interesting intermediate repulsive potential observed in the *ab initio* results, it does not quite capture all the subtleties of the competitive repulsions and attractions that produce the repulsive magnitude shown in the quantum mechanical results.

The *sec*-butanol landscapes were largely generated as a test set for the regressed model. As mentioned above, the only parameters regressed from this data were the C_β–C parameters; all others were fixed at the values obtained from the generalized regression that did not include *sec*-butanol data. Again the deep routes dominated by hydrogen bonding (S3 and S4) are reproduced very accurately. The model potential energies for routes S1, S3, S4, S6, and S7 in Fig. 7 accurately reproduce the *ab initio* data. The model predicts the correct attractive energy for route S5 and correctly models the repulsive portion of the potential energy curve, but it misses slightly the location of the minimum and it does not show the very small repulsion region at intermediate distances exhibited by the *ab initio* data. The worst prediction by the model is for route S1, in which the depth and breadth of the attractive well are overpredicted. Nevertheless, the

TABLE VII. Model parameters for Eq. (2) regressed without point charges. Parameter values are given in the order ϵ (kcal/mol), A (Å^{−1}), and r^* (Å), respectively, for Eq. (4) and in the order B (kcal/mol), C (Å^{−1}), r_{ox} (Å) for the X–X interaction.

Interactions	Propanol	Isopropanol	<i>t</i> -Butanol	Generalized
O–O	0.026 99	2.919 46	0.282 00	0.095 54
	1.552 97	0.917 53	0.670 01	1.306 86
	4.363 24	2.694 60	3.435 03	4.239 58
O–C _α	3.256 41	5.422 41	10.870 02	0.123 51
	1.752 39	2.037 29	3.429 71	1.434 15
	2.719 61	2.979 75	2.924 72	3.848 28
O–C _β		0.051 66	0.197 98	0.001 05
		1.061 83	1.013 80	2.007 42
		4.647 33	4.214 99	4.710 99
O–C	3.818 84			0.000 23
	1.637 11			1.843 53
	2.814 96			5.304 22
O–H _α	14.199 8	19.766 50	19.761 40	13.370 90
	1.593 53	1.293 81	1.548 88	1.514 62
	1.337 22	0.465 39	0.877 39	1.470 07
O–H	0.002 55	0.097 86	0.180 11	0.347 52
	0.929 00	1.627 39	2.200 34	1.456 96
	6.284 88	3.258 74	2.898 69	2.819 95
C _α –C _α	9.43 × 10 ^{−11}	0.397 28	0.397 32	0.276 08
	8.352 16	5.824 68	5.824 93	3.330 04
	3.493 36	2.077 39	2.078 25	3.118 63
C _α –C _β		3.547 17	3.547 27	8.19 × 10 ^{−11}
		5.038 52	5.037 39	2.359 39
		0.771 02	0.773 21	3.597 49
C _α –C	0.387 34			0.098 08
	2.393 94			1.669 35
	3.712 97			3.952 90
C _α –H _α	6.163 66	6.556 55	6.556 55	6.596 01
	12.806 02	12.271 97	12.272 01	12.507 21
	0.539 86	0.459 19	0.459 19	0.421 52
C _α –H	6.858 014 71	6.912 38	6.912 40	4.873 25
	9.449 658 87	5.100 36	5.103 47	13.643 87
	0.599 622 39	0.481 24	0.471 58	1.39 × 10 ^{−6}
C _β –C _β		0.008 58	0.004 11	0.104 93
		0.619 20	0.901 63	1.064 90
		8.699 04	6.734 89	4.711 93
C _β –C				0.046 60
				1.650 98
				4.286 72
C _β –H _α		5.849 02	3.049 55	1.085 67
		2.446 52	3.020 66	3.126 46
		1.941 71	2.064 88	2.151 10
C _β –H		2.197 52	0.656 20	0.702 62
		1.591 63	2.026 85	2.565 57
		2.364 34	2.685 76	2.467 89
C–H _α	0.016 40			1.811 04
	5.485 17			1.662 23
	0.098 33			1.668 75
H _α –H _α	5.20 × 10 ^{−5}	0.000 12	5.83 × 10 ^{−6}	0.002 03
	0.717 41	0.714 21	0.190 42	0.626 05
	10.270 10	10.318 46	9.199 59	8.650 18
H _α –H	8.95 × 10 ^{−7}	1.58 × 10 ^{−5}	8.20 × 10 ^{−6}	8.36 × 10 ^{−7}
	2.644 15	1.332 38	1.219 26	0.777 71
	4.359 93	6.375 14	6.939 35	10.945 59
X–X	4.897 52	8.144 75	19.999 3	14.193 10
	0.663 89	0.822 30	0.888 22	0.764 57
	1.321 30	1.499 19	0.849 07	0.901 43

TABLE VII. (Continued.)

Interactions	Propanol	Isopropanol	<i>t</i> -Butanol	Generalized
H-X	0.469 28	0.197 88	0.417 55	0.711 88
	0.750 41	0.901 63	1.406 85	0.603 78
	1.945 79	1.049 170	2.148 69	1.525 10
C-C (NIPE)	0.051 33			0.051 33
	1.459 85			1.459 85
	4.341 17			4.341 17
C-H (NIPE)	0.355 62			0.355 62
	2.111 74			2.111 74
	2.602 11			2.602 11
H-H (NIPE)	0.010 48	0.010 48	0.010 48	0.010 48
	1.260 72	1.260 72	1.260 72	1.260 72
	3.975 36	3.975 36	3.975 36	3.975 36
SSE/point	0.019	0.010	0.018	0.054
	kcal ² /mol ²	kcal ² /mol ²	kcal ² /mol ²	kcal ² /mol ²

site-site model without charges does a rather remarkable job of modeling the different and very complex *ab initio* energy landscapes of all of the dimers studied. Moreover, the quality of fit for the overall regression suggests that the transferability of the generalized parameters obtained is quite good.

V. SUMMARY

We have calculated 735 CP-corrected energies for homogenous dimers of propanol, isopropanol, *t*-butanol, and *sec*-butanol using MP2/6-311+G(2df,2pd). These points constitute 49 different approach routes that focus on specific types of intermolecular interactions, but as a whole provide comprehensive potential energy surfaces for the dimers. Routes providing opportunity for hydrogen bonding show deep attractive wells, but the dispersion interactions emphasized in other relative monomer orientations are also significant. Much of the qualitative complexity of each potential energy surface can be understood in terms of the charge distribution calculated within the rigid monomers. Interesting topography of the landscapes can be understood in terms of competing attractions and repulsions between different sites within the dimer.

The complexities of these energy landscapes provide a good challenge and validation opportunity for site-site models, employing spherical symmetry about atomic centers. We have successfully modeled the *ab initio* potential energy surfaces using a pairwise-additive, site-site model based on a modified Morse potential. A generalized set of parameters reproduces quite well the potential energy landscapes of all the small alcohols containing up to four carbon atoms. This suggests a fairly good level of transferability for the site-site

interactions to other alcohol molecules, though we have not yet tested the use of these model parameters in larger alcohols. A similar model that includes point charges to represent the permanent charge distribution was not as effective in modeling these surfaces and the resultant parameters were not transferable to other molecules. The transferable site-site model without charges provides a very good representation of the *ab initio* hydrogen bond potential wells. It also represents the energy scans of most of the routes, in which dispersion dominates the attraction between the pairs including some of the unusual and complex features of some of the routes. The most significant differences between the *ab initio* and model data are for the O-C-type routes for the propanol dimer. Treating the C atom attached to the C_α atom in propanol as a different site could perhaps improve these results, but we have not undertaken to improve the fit in this manner in order to maintain a clearly defined set of site interaction parameters that can be applied, at least in principle, to other alcohols.

- ¹R. L. Rowley, C. M. Tracy, and T. A. Pakkanen, J. Chem. Phys. **125**, 154302 (2006).
- ²R. L. Rowley and T. Pakkanen, J. Chem. Phys. **110**, 3368 (1999).
- ³J.-P. Jalkanen, T. A. Pakkanen, and R. L. Rowley, J. Chem. Phys. **120**, 1705 (2004).
- ⁴J.-P. Jalkanen, T. A. Pakkanen, Y. Yang, and R. L. Rowley, J. Chem. Phys. **118**, 5474 (2003).
- ⁵R. L. Rowley, Y. Yang, and T. A. Pakkanen, J. Chem. Phys. **114**, 6058 (2001).
- ⁶J.-P. Jalkanen, R. Mahlanen, T. A. Pakkanen, and R. L. Rowley, J. Chem. Phys. **116**, 1303 (2002).
- ⁷R. Mahlanen, J.-P. Jalkanen, and T. A. Pakkanen, Chem. Phys. **313**, 271 (2005).
- ⁸S. L. Garrison and S. I. Sandler, J. Phys. Chem. B **108**, 18972 (2004).
- ⁹J. M. Hayes, J. C. Greer, and D. A. Morton-Blake, J. Comput. Chem. **25**, 1953 (2004).
- ¹⁰W. L. Jorgensen, J. Am. Chem. Soc. **103**, 335 (1981).
- ¹¹B. Chen, J. J. Potoff, and J. I. Siepmann, J. Phys. Chem. B **105**, 3093 (2001).
- ¹²H. Zhang and J. F. Ely, Fluid Phase Equilib. **217**, 111 (2004).
- ¹³Y. Boutard, Ph. Ungerer, J. M. Teuler, M. G. Ahunbay, S. F. Sabater, J. Perez-Pellitero, A. D. Mackie, and E. Bourasseau, Fluid Phase Equilib. **236**, 25 (2005).
- ¹⁴A. K. Sum, S. I. Sandler, R. Bukowski, and K. Szalewicz, J. Chem. Phys. **116**, 7627 (2002).
- ¹⁵M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.6, Gaussian, Inc., Pittsburgh, PA, 1998.
- ¹⁶S. Tsuzuki and H. P. Luthi, J. Chem. Phys. **114**, 3949 (2001).
- ¹⁷S. Tsuzuki, T. Uchimaru, and K. Tanabe, Chem. Phys. Lett. **287**, 202 (1998).
- ¹⁸S. Tsuzuki, T. Uchimaru, M. Mikami, and S. Urata, J. Chem. Phys. **121**, 9917 (2004); J. Phys. Chem. A **107**, 7962 (2003).
- ¹⁹A. J. Stone, *The Theory of Intermolecular Forces* (Clarendon, Oxford, 1996).
- ²⁰R. Ahlrichs, P. Penco, and G. Scoles, Chem. Phys. **19**, 119 (1977).