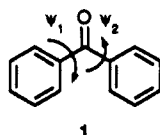# Hindered Internal Rotation in Benzophenone

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Contribution from the Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada. Received January 22, 1990

Abstract: Quantum chemical calculations have been performed for structures on the rotational potential energy surface for benzophenone. A Fourier expansion for this surface in terms of torsional angles ψ_1 and ψ_2 about the C_6H_5-CO bonds has been obtained on a 15° grid. The series reproduces relative energies from semiempirical calculations with Austin Model 1 (AM1). Ab initio calculations with the STO-3G and 3-21G bases have been performed for the minimum energy conformation, the ($\psi_1 = 0°$, $\psi_2 = 90°$) conformation at the top of the barrier to internal rotation, and the (90°,90°) conformation. The optimum STO-3G conformation is of C_2 symmetry with $\psi_1 = \psi_2 = 33°$, in agreement with the crystal structure. The optimum geometry and the minimum energy path on the surface are determined by a balance between steric interaction of the phenyl groups and π-conjugation of the phenyl and keto groups. The dihedral angle between the phenyl rings remains near 60° along most of the minimum energy path. Apparently, crystal packing forces have a minor influence on the conformation in the crystal. On the basis of the combined results, the barrier to internal rotation is estimated to lie between 3.0 and 5.6 kJ·mol⁻¹. The frequencies of the antisymmetric and symmetric torsions are estimated to be 23 and 56 cm⁻¹, respectively, from the semiempirical calculations and 32 and 57 cm⁻¹ from the STO-3G calculations.

Introduction

Photoenolization/reketonization and biradical reactions of various o-alkyl-substituted aromatic ketones and o-alkylbenzo-phenones have been subjects of continuing interest.[1-21] Conformational dynamics appears to play an important role in the determination of the rates of these processes. In particular, we have been interested in the mechanism of the reketonization process and in the relative importance of vibrationally assisted tunneling for a series of structurally related ketones, including benzophenone (1).[21] In the literature, conflicting values have been

reported for the location of the minimum on the ground-state potential energy surface and for the barriers to internal rotation for benzophenone. Because we require this information in order to understand the reketonization process, we have undertaken a computational study to clarify the conformational behavior and to provide a comparison between results from a reliable semiempirical method and from an ab initio calculation.

The benzophenone molecule has C_2 symmetry in the crystal.[22] The dihedral angle made by the phenyl rings is about 56°, from which the twist angles ψ about the exocyclic CC bonds are about 33° with respect to the plane of the keto group. The conformation with all heavy atoms coplanar has $\psi_1 = \psi_2 = 0°$. Estimates of ψ for the preferred conformer generally lie in the range from 30° to 45° for benzophenone[23-25] and for its 4-substituted or 4,4'-disubstituted derivatives.[25-28] Electronic structure calculations at various levels of sophistication have been performed for benzophenone. These presumably relate to the structure of the isolated molecule in the vapor rather than in a condensed phase. Early extended Hückel calculations indicated that $\psi = 38°$ in the minimum energy conformation.[29] Semiempirical calculations at the MINDO and MNDO levels[30] yielded twist angles between 70° and 90°, but such large angles may be attributed to the MNDO overestimation of repulsions between atoms that approach van der Waals contact.[31] An ab initio calculation[32] with the minimal STO-3G basis and geometry optimization provided $\psi = 33°$, which is in excellent agreement with the experimental estimates.

To our knowledge, no direct experimental estimate of the barrier to internal rotation in benzophenone has been reported. Lines in the $T_1 \leftarrow S_0$ absorption spectrum of a single crystal have been tentatively assigned to torsional modes of the triplet at 85 and 100 cm⁻¹.[33] A computational estimate[32] of the barrier height from

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Table I. Potential Energy Coefficients (kJ·mol⁻¹) That Describe the AM1 Surface for Benzophenone

$V_{0,0}$	6.832	$V_{4,6}$	0.805	$V_{2,10}$	−0.215
$V_{2,0}$	0.786	$V'_{4,6}$	−0.890	$V'_{2,10}$	−0.022
$V_{2,2}$	6.892	$V_{8,0}$	−0.080	$V_{4,10}$	−0.081
$V'_{2,2}$	−5.249	$V_{8,8}$	0.719	$V'_{4,10}$	−0.073
$V_{4,0}$	0.745	$V'_{8,8}$	−0.734	$V_{6,10}$	0.147
$V_{4,4}$	2.522	$V_{2,8}$	−0.097	$V'_{6,10}$	−0.174
$V'_{4,4}$	−2.354	$V'_{2,8}$	−0.088	$V_{8,10}$	0.500
$V_{2,4}$	2.034	$V_{4,8}$	0.069	$V'_{8,10}$	−0.413
$V'_{2,4}$	−2.441	$V'_{4,8}$	−0.186	$V_{12,0}$	−0.074
$V_{6,0}$	0.075	$V_{6,8}$	0.485	$V_{12,12}$	0.289
$V_{6,6}$	0.959	$V'_{6,8}$	−0.579	$V_{2,12}$	−0.118
$V'_{6,6}$	−1.020	$V_{10,0}$	−0.129	$V_{4,12}$	−0.048
$V_{2,6}$	0.196	$V_{10,10}$	0.756	$V_{6,12}$	0.036
$V'_{2,6}$	−0.168	$V'_{10,10}$	−0.438	$V_{8,12}$	0.159
				$V_{10,12}$	0.415

Figure 1. Sections through the AM1 potential surface for internal rotation in benzophenone. The torsion angle ψ_1 is on the abscissa. The solid line corresponds to rotation of the phenyl groups in the same sense such that $\psi_2 = \psi_1$. The dashed curve describes a section through $\psi_2 = -\psi_1$ or equivalently through $\psi_2 = 180° - \psi_1$.

STO-3G calculations is inappropriate because it presupposes that the molecule retains C_2 symmetry throughout the internal rotation, i.e. on the minimum energy path across the rotational potential energy surface $V(\psi_1,\psi_2)$, the phenyl groups rotate in the same sense with $\psi_1 = \psi_2$. The results of the extended Hückel[29] calculations on benzophenone indicate that the minimum energy pathway between preferred conformers involves concerted rotation of the phenyl groups not such that $\psi_1 = \psi_2$ but along a path through $(\psi_1,\psi_2) = (0°.90°)$.

A compensation for overestimation of repulsive van der Waals interactions by MNDO has been included in the superior semiempirical procedure Austin Model 1 (AM1).[31] In our experience, AM1 tends to underestimate rotational barriers in similar aromatic ketones[21] while ab initio calculations with the STO-3G basis probably overestimate these barriers.[34] Herein we report some results of semiempirical calculations with AM1 and of ab initio calculations with the minimal STO-3G basis and the split-valence 3-21G basis for comparison with the semiempirical results.
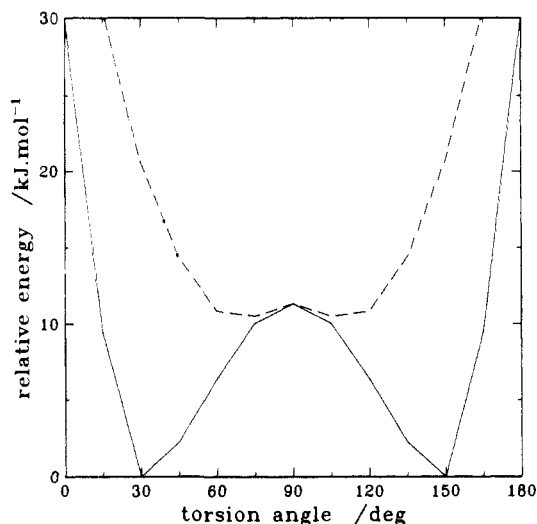
Computational Method

Ab initio calculations were performed with Gaussian86[36] and the standard STO-3G and 3-21G bases. Because computations on a molecule the size of benzophenone (14 heavy atoms) are cpu-intensive and memory-intensive, the 3-21G results were obtained at the STO-3G optimum geometries (3-21G//STO-3G) rather than at the 3-21G geometries. The initial STO-3G geometry of the preferred conformer was taken from the work of Schaefer and Penner.[32] where the atoms within each phenyl groups were held coplanar. The present optimization with planar phenyl groups and C_2 symmetry provided a total energy 2.95 × 10⁻⁴ au lower than that previously reported.[32] A complete geometry optimization allowing slight puckering in the phenyl groups resulted in a further decrease (1.74 × 10⁻⁴ au) in the total energy. For all other ab initio computations in the present work, the phenyl groups were kept planar. Other conformations of interest were the (90°,90°) conformation of C_{2v} symmetry, the minimum energy conformation (0°,~60°) in which only one phenyl ring is coplanar with the keto group (C_1 symmetry), and the (0°,90°) conformation that corresponds to the lower barrier to internal rotation (C_s symmetry).

A complete potential energy surface for internal rotation was obtained with AM1[31] with use of AMPAC (Version 2.10). Full geometry optimizations were performed for fixed values of the torsion angles ψ_1 and ψ_2 on a grid at 15° intervals.

Results and Discussion

AM1 Calculations. From the symmetry of the benzophenone molecule, the potential surface for internal rotation is symmetric with respect to inversion and with respect to reflection through $\psi_2 = \psi_1$ and through $\psi_2 = -\psi_1$ (or equivalently through $\psi_2 = 180° - \psi_1$). The minimum energy conformer has $\psi_1 = \psi_2 = 33°$, and

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the angle between the ring planes is 54°, in excellent agreement with the crystal structure[22] and with the earlier ab initio result.[32] In order to assess the importance of potential coupling and high-order terms, the AM1 results may be described by a two-dimensional Fourier series approximation of the form

$$V(\psi_1,\psi_2) = V_{0,0} + \sum_{n=1}^{6} \{V_{2n,0}(\cos 2n\psi_1 + \cos 2n\psi_2) +$$

$$\sum_{m=1}^{n-1} [V_{2m,2n}(\cos 2m\psi_1 \cos 2n\psi_2 + \cos 2n\psi_1 \cos 2m\psi_2) +$$

$$V'_{2m,2n}(\sin 2m\psi_1 \sin 2n\psi_2 + \sin 2n\psi_1 \sin 2m\psi_2)] +$$

$$V_{2n,2n} \cos 2n\psi_1 \cos 2n\psi_2 + V'_{2n,2n} \sin 2n\psi_1 \sin 2n\psi_2\} \quad (1)$$

where all of the $V'_{2m,12}$ coefficients vanish on the 15° grid. The coefficients from the AM1 energies are listed in Table I. According to this analysis, coupling between the 2-fold and 4-fold terms (and to a lesser extent, the 6-fold terms) has a strong influence on the surface features. These terms correspond to the largest coefficients in Table I.

There is a qualitative difference between eq 1 and the simple product of two 2-fold potentials as in

$$V_{2\times2}(\psi_1,\psi_2) = V_2(\psi_1)V_2(\psi_2)$$
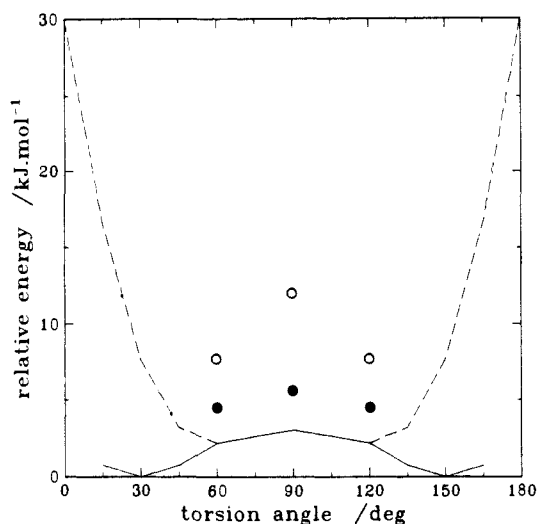$$= \{V_2[1 - \cos (2\psi_1)]/2\}\{V_2[1 - \cos (2\psi_2)]/2\}$$
$$(2)$$

where V_2 is the 2-fold barrier to internal rotation for a single phenyl group, as for benzaldehyde. From eq 2, coincident maxima in $V_2(\psi_1)$ and $V_2(\psi_2)$ give maxima in $V_{2\times2}$. Similarly, coincident minima in $V_2(\psi_1)$ and $V(\psi_2)$ give minima in $V_{2\times2}$. The occurrence of a maximum along one coordinate and a minimum along the other gives rise to a saddle point, corresponding to a barrier to internal rotation. The qualitative difference between eq 2 and the AM1 surface is that the positions of the minima have shifted along the diagonal $\psi_2 = \psi_1$ from $\psi_2 = \psi_1 = 0°$ and 180° to $\psi_2 = \psi_1 = 33°$ and 147°. Thus, maxima appear at (0°,0°), (0°,180°), (180°,0°), and (180°,180°) on the benzophenone surface. The AM1 potential energy surface resembles that obtained from extended Hückel theory.[29] A contour plot appears elsewhere in connection with a NMR study of the conformational behavior.[21]

Sections through the surface at $\psi_2 = \psi_1$ (solid curve) and at $\psi_2 = \psi_1$ (dashed curve) are shown in Figure 1. The AM1 results indicate that the (90°,90°) conformation (C_{2v}) lies 11.3 kJ·mol⁻¹ above the minimum. From the dashed curve, this conformation is a local maximum, but it lies only 0.8 kJ·mol⁻¹ above the symmetrically disposed saddle points. The lower barrier to internal rotation occurs on the $\psi = 0°$ axes, as shown by the dashed curve

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Figure 2. Sections through the AM1 potential surface for internal rotation in benzophenone. The torsion angle ψ_1 is on the abscissa. The solid curve corresponds to the minimum energy path for internal rotation. The dashed curve describes a section through $\psi_2 = 0°$. Solid circles indicate relative energies from STO-3G geometry optimizations. The open circles represent the 3-21G energies at the corresponding STO-3G geometries.

Table II. RHF Energies (au)[a] for Benzophenone

| conformer	STO-3G	3-21G//STO-3G
(33°,33°)	-565.877 249[b]	-569.783 634
	-565.877 423[c]	
(0°,60°)	-565.875 540	-569.780 713
(0°,90°)	-565.875 116	-569.779 069
(90°,90°)	-565.867 669	-569.761 858

[a] 1 au = 2625.5001 kJ·mol⁻¹. [b] Planar phenyl group. [c] Full geometry optimization including puckering of the phenyl groups.

in Figure 2. The approximate minimum energy pathway is indicated by the solid curve in Figure 2. It corresponds to a concerted motion of the phenyl groups in the opposite sense such that the angle between the ring planes is preserved until one ring is nearly coplanar with the keto group. The non-coplanar ring then rotates to 90°, which provides the (0°,90°) conformation that corresponds to the barrier maximum. This conformation lies 3.0 kJ·mol⁻¹ above the minimum. These results are strikingly similar to the pathway and energies from the extended Hückel surface.[29] for which the barriers are 4.9 kJ·mol⁻¹ at (0°,90°) and 14.1 kJ·mol⁻¹ at (90°,90°).

Ab Initio Calculations. Total energies from ab initio computations on the (33°,33°), (0°,60°), (0°,90°), and (90°,90°) conformations with planar phenyl groups are listed in Table II. Also listed is the total energy from a calculation on the (33°,33°) conformer in which puckering of the phenyl rings was allowed. This flexibility lowered the total energy by only 0.5 kJ·mol⁻¹ at the STO-3G level, thus the planarity constraint on the phenyl groups is not anticipated to affect seriously the relative energies of the various conformations.

The STO-3G optimum geometries of the (33°,33°), (0°,90°), and (90°,90°) conformations are given in Figures 3, 4, and 5, respectively. These may serve as useful starting points for more sophisticated calculations. The principal geometry changes between these conformations occur in the lengths of the CO and exocyclic CC bonds and in the OCC angles. As a phenyl ring loses conjugation with the keto group, the connecting CC bond lengthens, the CO bond shortens, and the OCC angle increases slightly.

In accord with the AM1 results, the (0°,60°) conformation is an energy minimum along $\psi_1 = 0°$, but not a stationary point. It lies 4.5 kJ·mol⁻¹ above the minimum energy conformer at the STO-3G level. The saddle point corresponding to the top of the rotational barrier is found at (0°,90°). Its relative energy is the lowest rotational barrier between the potential energy minima,
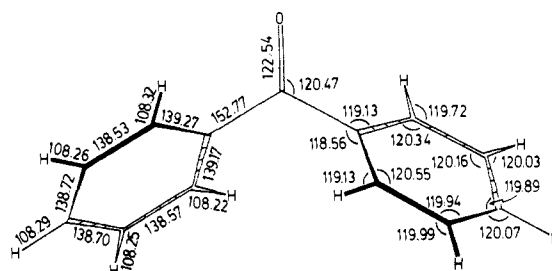
Figure 3. The STO-3G optimum geometry for the minimum energy conformation of benzophenone (C_2). Bond lengths are given in pm. Bond angles are in degrees. The torsion angles ψ_1 and ψ_2 about the C_6H_5-CO bonds are about 33.27°. Each phenyl group has been constrained to remain planar.
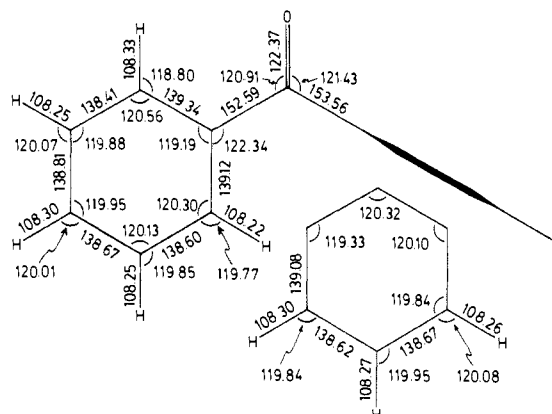
Figure 4. STO-3G optimum geometry for the (0°,90°) conformation of benzophenone (C_s) at the top of the barrier to internal rotation. Bond lengths are given in pm. Bond angles are in degrees. Each phenyl group has been constrained to remain planar.
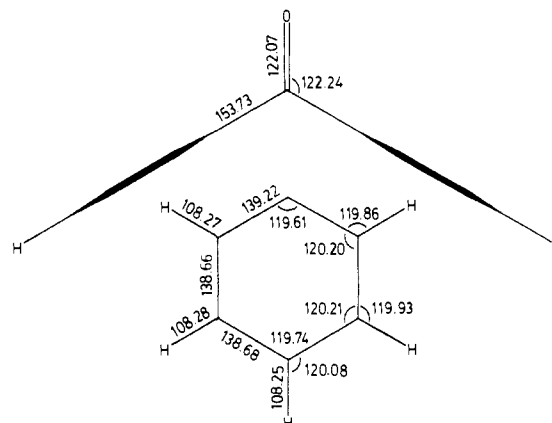
Figure 5. STO-3G optimum geometry for the (90°,90°) conformation of benzophenone (C_{2v}). Bond lengths are given in pm. Bond angles are in degrees. Each phenyl group has been constrained to remain planar.

which is 5.6 kJ·mol⁻¹ from the STO-3G energies and 12.0 kJ·mol⁻¹ from the 3-21G//STO-3G energies. These values are plotted for comparison in Figure 2. For benzophenone, the minimum energy path is determined by a balance between the avoidance of steric interaction between the phenyl rings and the maintenance of π-conjugation between the keto group and the phenyl rings. For the minimum energy conformer, neither phenyl group is coplanar with the keto group, although coplanarity is the most favorable orientation for π-conjugation. Instead both rings maintain some conjugation while avoiding mutual steric repulsion. The rings maintain a near-60° dihedral angle along most of the minimum energy path. Once one of the phenyl rings achieves coplanarity with the keto group, the second ring can adopt the unfavorable $\psi = 90°$ orientation at the barrier maximum. The imperative of avoiding close contact between the phenyl groups provides an indication of the relative importance of steric interactions over

conjugation and crystal forces in determining the preferred molecular geometry.

The (90°,90°) conformation lies 25.3 kJ·mol^{-1} above the minimum according to the STO-3G results. As mentioned previously,[32] this value is comparable to the barrier to internal rotation in benzaldehyde, which lies in the range 19.3–22.7 kJ·mol^{-1} for various experimental methods[37-40] and 24 kJ·mol^{-1} from an STO-3G calculation.[34,35] In both molecules, the origin of the barrier is presumably the loss of π-conjugation between the phenyl and keto groups. It is perhaps surprising therefore that the loss of conjugation between the keto group and one phenyl group in benzaldehyde should require as much energy as the loss of conjugation between the keto group and both phenyl groups in benzophenone. From the 3-21G//STO-3G results, the barrier is 57.2 kJ·mol^{-1}.

Although the more flexible split-valence basis provides a lower total energy, it leads to larger relative energies than the STO-3G basis. The 3-21G barrier heights are roughly twice the STO-3G values. Because the STO-3G barrier for benzaldehyde is in better agreement with experiment[37-40] than the estimates obtained from 4-21G, 4-31G, or 6-31G split-valence bases,[35] this is not unexpected. Presumably, this agreement is a result of a fortuitous cancellation of errors at the STO-3G level, perhaps associated with the compactness of the STO-3G basis functions.

Torsional Frequencies. Lines in the $T_1 \leftarrow S_0$ absorption spectrum have been tentatively assigned to torsional modes of the triplet state at 85 and 100 cm^{-1}, which would correspond to B and A modes, respectively, in C_2 symmetry.[33] Progressions in the $^1n\pi^*$ $\leftarrow S_0$ spectrum were assigned to the same A mode at 80 cm^{-1} because the B mode cannot form progressions. From semiempirical and ab initio calculations of the harmonic vibrational frequencies of the C_2 minimum energy conformer, the torsional frequency corresponding to the minimum energy path (B mode)

is 23 cm^{-1} from AM1 or 32 cm^{-1} from STO-3G. Torsion along the $\psi_2 = \psi_1$ diagonal (A mode) appears at 56 cm^{-1} according to AM1, or 57 cm^{-1} according to the STO-3G calculation. Although the calculated normal coordinates corresponding to these frequencies may be inaccurate, a harmonic approximation to the AM1 surface in the vicinity of the minimum supports these assignments. The third-lowest and fourth-lowest calculated vibrational frequencies are 85 and 133 cm^{-1} from AM1, or 97 and 152 cm^{-1} from STO-3G. According to the normal coordinate descriptions, these are skeletal modes of A and B symmetry, respectively, and not the torsions. Possibly, the observed vibrations[33] of the excited singlet and triplet correspond to these skeletal modes. Experimental investigation of these low-frequency motions would be helpful.

Conclusions

On the basis of AM1 and STO-3G calculations, the preferred conformation of benzophenone has C_2 symmetry. The angle between the planes defined by a phenyl ring and the keto group is about 33°, and the angle between the phenyl ring planes is about 56°. These results are in excellent agreement with crystallographic data. The barrier to internal rotation in benzophenone is probably between 3.0 and 5.6 kJ·mol^{-1}. The minimum energy path for conformational interconversion is determined by a balance between the maintenance of π-conjugation between the keto group and the phenyl rings and the avoidance of mutual repulsion of the phenyl rings. These findings are in agreement with early results from extended Hückel theory. With the 3-21G basis and the STO-3G optimum geometry, the rotational barrier is 12.0 kJ·mol^{-1}, which is probably an overestimate. From the AM1 and STO-3G results, the torsional frequency corresponding to the antisymmetric mode is estimated to be 23 and 32 cm^{-1}, respectively, and the torsional frequency corresponding to the symmetric mode is estimated to be 56 and 57 cm^{-1}, respectively. An experimental determination of the torsional frequencies would be valuable.

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Implementation of Nonadditive Intermolecular Potentials by Use of Molecular Dynamics: Development of a Water–Water Potential and Water–Ion Cluster Interactions

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Abstract: We present the results of simulations using water–water and water–ion models that include explicit nonadditive polarization energies. The water–water potential has been adjusted to fit the experimental water density and potential energy. The resulting potential is used in a simulation of liquid water. In addition to the density and potential energy, the model also fits the experimental radial-distribution functions and the diffusion coefficient well. Water–ion parameters are derived similarly and include, in addition to polarization nonadditivity, three-body exchange repulsion. The model is then used to compute the energy of ion–water clusters. The agreement with experimental energies of cluster formation is very good.

Introduction

The structure and properties of liquid water are critical to our existence, as well as being representative of an important polar liquid. Thus, understanding these structures and properties from

a physical–chemical point of view has inspired a very large number of statistical mechanical models as well as computer simulation approaches. The goal of the latter is, beginning with the intra- and intermolecular energies of a water molecule as a function of coordinate, to use Monte Carlo or molecular dynamics methods to derive observable structural, kinetic, and thermodynamic properties that are consistent with experiment.

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