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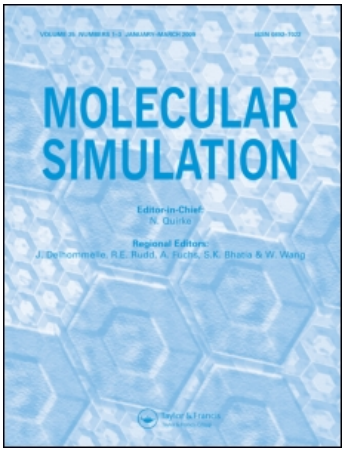

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Intermolecular Potential Variation due to Intramolecular Rotation in Molecules

Anders Wallqvist[a]
[a] Physical Chemistry 2, Chemical Center, Lund, Sweden

To cite this Article Wallqvist, Anders(1991) 'Intermolecular Potential Variation due to Intramolecular Rotation in Molecules', Molecular Simulation, 7: 3, 195 — 204
To link to this Article: DOI: 10.1080/08927029108022153
URL: http://dx.doi.org/10.1080/08927029108022153

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Molecular Simulation, 1991, Vol. 7, pp. 195–204
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INTERMOLECULAR POTENTIAL VARIATION DUE TO INTRAMOLECULAR ROTATION IN MOLECULES

ANDERS WALLQVIST

Physical Chemistry 2, Chemical Center, POB 124, S-221 00 Lund, Sweden

(*Received October 1990, accepted October 1990*)

The changes in charge and polarization densities of ethane, methanol and formamide upon internal rotation is studied using SCF-HF calculations. For formamide the charge density changes with dihedral angle are seen in the rapidly varying molecular dipole moment, whereas these changes are only moderate in the methanol molecule. In ethane the quadrupole moment variation is about 15%. The barriers to rotation are found to be 3.47 kcal/mole for ethane, 0.84 kcal/mole for methanol and 14.94 kcal/mol for formamide. The total molecular polarizability, which is estimated using perturbation theory, is varying slowly with rotation angle, but the individual atomic components change rapidly for all three molecules investigated. The calculations indicate that solvent effects upon intramolecular configuration are reflected in variations of intermolecular interactions. These implications are discussed in connection with modelling internally flexible molecules for use in molecular dynamics and Monte Carlo simulations. Similarly, water–water interactions are affected by small vibrations which alter the equilibrium charge density and polarizability of the individual molecule.

KEY WORDS: Internal rotation, multipole moment variations, intermolecular interactions.

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1. INTRODUCTION

The rapid spread of applications for molecular modelling [1] warrants constant reexamination of the underlying approximations in the force fields used [2], and even the type of functions best able to reproduce potential data [3]. An almost universal assumption is that of the independence of the intermolecular interaction on intramolecular configuration. In a simulation of a polyatomic liquid with internal degrees of freedom the system will consist of an ensemble of molecules with different intramolecular configurations. The distribution of rotational isomers will depend on temperature and rotation barriers. In gas phase the barrier energy arises from the cost of creating a new electron distribution but in a solution this energy can be modified by an energetic coupling to the surrounding media. Thus if a rotation causes the molecular dipole moment to increase, favourably oriented neighboring molecules can lower the transition state energy. The reverse might also be true. Likewise changes in polarizability can locally alter the electrostatic interaction of e.g. a hydrogen bond and cause variations in the dispersion energy. In a dense liquid the connection between intramolecular motion and intermolecular interaction are non-trivial as single molecule properties such as electrostatic moments and polarization are determined by its intramolecular configuration.

In a complex, many atom molecule the range of intramolecular motion can be large, stretching from bond and angle vibrations, dihedral rotation to even slower motion

involving whole subunits of the molecule. If the frequency of this motion is not well separated energy will flow between the different modes. In molecular simulations high frequency intramolecular motion, like bond vibrations, is often frozen as it is only weakly coupled to other degrees of freedom in the system [4]. In simulations where bond flexibility is incorporated the intramolecular potential is normally just grafted on top of the rigid intermolecular potential, but for accurate calculations of spectral shifts it has been found important to include conformation dependent charge densities [5]. Freezing of the dihedral motion does not lend itself to realistic simulation of larger molecular assemblies. Potential functions for dihedral barriers to rotation are constructed from experiments using diffraction, spectroscopical and relaxation techniques or calculated using quantum chemical methods [6]. This work is aimed at investigating the charge and polarization variation due to low frequency dihedral rotation in small molecules that can be thought of as templates for typical rotations in larger molecules.

Three molecules with an internal rotational degree of freedom were selected; the non-polar ethane, methanol as an intermediary polar molecule and the strongly polar formamide with a dipole moment of 4.3D. In ethane and methanol the bond between heavy atoms is dominated by σ-bonding whereas in formamide the NCO fragment has π-bonding character. The NCO unit is also of more general interest as it is common to all polypeptides. The dipole moments (quadrupole moment for ethane) and polarization were calculated as a function of rotational angle. These variations in charge and polarization densities will affect intermolecular interaction differently, e.g. attractive interactions are dominated by dispersion forces in ethane vapour and by electrostatic interactions in a formamide liquid. The properties of a water molecule were also investigated with regards to small vibrations in the bond and angle.

For ethane it is found that the quadrupole moments changes by -0.2DÅ from the eclipsed to the staggered configuration, but as ethane interaction is dominated by dispersion forces this would only lead to a few percent deviation in the total intermolecular ethane ethane potential. The magnitude of the total dispersion variation is similar. For methanol the rotation of the hydroxyl group is only associated with small changes in charge and polarization densities. In formamide the breaking of the favourable planar configuration of the molecule leads to 15% decrease of the dipole moment at the transition state. Individual atoms also experience large shifts in polarization. This would lead to large changes in intermolecular potentials if the barrier state is significantly occupied. Studying processes of this kind in simulations or molecular modelling will require models of variable charge, polarization and dispersion functions. The construction of such models and the appropriate treatment of charge reorganization is discussed with the outlook of investigating such systems using molecular simulation techniques.

2. METHODS

Selfconsistent field Hartree-Fock calculations were carried out on the equilibrium configuration of ethane, methanol and formamide. The coordinates for ethane and methanol were taken from Snyder and Basch [7] and those of formamide from Stenkamp and Davidson [8]. Note that in formamide the nitrogen are not equivalent in the minimum energy configuration. The SCF energies of the these configurations are given in Table 1. Successive rotations around the dihedral angle were then done

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Table 1

SCF energies in atomic units		
Ethane	CH_3CH_3	−79.25374904
Methanol	CH_3OH	−115.08355515
Formamide	$HCONH_2$	−168.98782258

without varying the bond lengths or angles. The SCF calculations were performed as in the calculation of the NEMO force field [9] using Gaussian-type contracted basis sets derived from atomic natural orbitals. For the carbon, nitrogen and oxygen atoms 10*s*, 6*p* and 3*d* functions were contracted to 4*s*, 3*p* and 1*d* respectively. Two sets of functions were used for the hydrogen atoms depending on whether they were connected to a carbon or either a nitrogen and oxygen. Hydrogens connected to carbons used 6*s* and 3*p* functions contracted to 3*s* and 1*p*, otherwise the basis set was augmented with an extra diffuse *p* function. As the ANO basis set is not explicitly optimized with regards to electrostatic moments it is our experience that these tend to be overestimated in the HF approximation. In the NEMO potential calculation scheme [9] these basis functions represent an adequate and realistic set for potential calculations of larger molecules. In the energy calculations and molecular simulations using these potentials bond lengths and angles are kept fixed.

Apart from calculating the molecular dipole and quadrupole moment a local charge distribution was also investigated. The total molecular charge distribution is written as the sum over all basis functions.

$$\rho = \sum_{ij} D_{ij}\chi_i\chi_j \tag{1}$$

where D_{ij} is a density matrix element and χ_i a basis function centered on a nucleus. A local pair contribution [10] can be formed by summing only over those basis functions belonging to a specific pair of nuclei K and L.

$$\rho_{KL} = \sum_{i\in K}\sum_{j\in L} D_{ij}\chi_i\chi_j. \tag{2}$$

Charges between non-bonded atoms in a molecule were divided up to their respective constituent atoms with a weight factor proportional to the distance to the charge center between them [10, 11].

The polarization tensor was calculated using perturbation theory with one component given as [12].

$$\alpha_{xx'} = 4\sum_{ij} \langle\psi_i|x|\psi_j\rangle\langle\psi_i|x'|\psi_j\rangle/(\varepsilon_j - \varepsilon_i) \tag{3}$$

where ψ_i is an occupied orbital, ψ_j a virtual orbital and the ε's are the corresponding orbital energies. In general it is found that this scheme gives unconstrained HF-limit polarizabilities to within 10%. In order to study the polarization changes on an atomic scale we divide up the total polarization into local contributions [13]. To proceed the orbitals are written as linear combinations of a set of basis functions, χ, centered on nuclei N, with expansion coefficient c,

$$\psi_i = \sum_N \sum_{k(N)} c_{i,k(N)}\chi_{k(N)} \tag{4}$$

where the summation runs over all nuclei and all basis functions of the molecule. The polarization in Equation (3) can then be split up into four center contributions

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Table 2 Ethane, CH_3CH_3

Rotation (degrees)	V_{excess} *(kcal/mole)*	Q_{zz} *(DÅ)*	α_{mol} *(Å³)*	α_C *(Å³)*	α_H *(Å³)*
0	0.00	−1.237	3.200	0.714	0.296
20	0.85	−1.285	3.192	0.730	0.289
40	2.59	−1.382	3.174	0.736	0.284
60	3.47	−1.432	3.166	0.740	0.281
Exp	2.93[15]	−1.00[16]	4.44/4.50[17]		

associated with the nuclei of the molecule. Summing up the contributions of the virtual orbitals yields local polarizabilities with an atom pair index, these are in turn summed up to yield atomic polarizabilities.

3. RESULTS AND DISCUSSION

A) Ethane

The properties of ethane as a function of dihedral angle are given in Tables 2 and 3. The barrier to rotation compares well with other SCF-HF calculations [14] but is overestimating the experimental value obtained from vapour at room temperature [15]. The largest part of this discrepancy arises from the lack of electron correlation. This is also reflected in the too large quadrupole moment of the equilibrium configuration [16]. However, changes of the moment should have a better precision due to error cancellation between the isomers. The lack of large diffuse basis functions contributes to the low value of the polarization compared to experiments [17].

In rotating the methyl group from a staggered to an eclipsed configuration the magnitude of the quadrupole moment increases and reaches a maximum. This rotation is associated with a decrease of the local electron density in the CC σ-bond and at the hydrogen atoms as seen in Table 3. A corresponding buildup is associated with the carbon and CH bond centers. Thus the origin of the rotational barrier lies in changes of the methyl bond which occurs during the rotation and partly to charge interactions between CH bond centers. The total molecular polarizability is not very dependent on configuration, it does however decrease slightly in the eclipsed geometry mainly due to the lowered polarizability on the hydrogens. The lowered hydrogen polarizability is a consequence of the transfer of electron density away from the hydrogen atoms. The decrease in polarizability in the eclipsed conformation indicates that solvent coupling in a polar media would slightly favour the staggered rotamer,

Table 3 Excess charge in CH_3CH_3

Center	*Staggered (0°) (e)*	*Eclipsed (60°) (e)*
C	1.289	1.258
H	0.524	0.533
CC	−0.681	−0.630
CH	−0.841	−0.847

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whereas the increase in quadrupolar moment would favour the reverse behaviour. If ethane is solvated in a non-polar media where the dispersion forces between all molecules were similar, the quadrupolar coupling to the solvent would determine the equilibrium conformation.

In a model of ethane consisting of partial charges located at the atoms one can fit the only independent quadrupole moment component with one parameter, namely the partial charge located on the hydrogen. This uniquely determines the partial charge composition for that configuration as the total charge of the molecule is zero and thus sets the carbon charge. Now as the quadrupole moment changes upon rotation of the methyl groups, the partial charge will also change. In order to model the quadrupole change one thus needs a variable charge model. An equivalent way of modelling the quadrupole moment would be to dislocate the partial charges from the atoms, retaining a fixed partial charge and varying the position as a function of dihedral angle.

The dominant attractive energy between ethane molecules are dispersion forces, with quadrupolar interactions about a magnitude less in size at distances on the order of a molecular diameter. Thus total changes in the intermolecular interaction potential upon rotation only amount to a few percent, with contributions arising about equally from changes in electrostatics and polarizability.

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B) Methanol

In Table 4 the results for different methanol configurations are given. The barrier to rotation is underestimated compared to the gas phase value obtained from microwave spectroscopy [18]. Likewise the experimental dipole moment [19] and polarizability [20,21] are not reproduced in the SCF-HF scheme.

In the case of methanol the CO bond is of σ-character and remains intact during the rotation as indicated by the absence of any change in the local charge at the CO bond, oxygen and carbon sites. It is only in the region of the hydrogen atom connected to the carbon and CH bond, and between the hydrogen atom bonded to the oxygen atom and OH bond site that there is an increase in the charges leading to the enhanced dipole moment of the eclipsed conformation. The lack of charge migration minimizes the change in orbital overlap between the methyl and hydroxy hydrogen. Thus the dominant forces operative during a rotation are electrostatic in nature. Changes in polarizabilities are minor, even for the individual atomic components. The polarization of the methyl group is lower in methanol that in ethane. Both the dipole moment and the polarizability are larger for the eclipsed conformation compared to the

Table 4 Methanol, CH_3OH

Rotation (degrees)	V_{excess} *(kcal/mole)*	μ *(D)*	α_{mol} $(Å^3)$	α_C $(Å^3)$	$\alpha_{H1(C)}$ $(Å^3)$	$\alpha_{H2(C)}$ $(Å^3)$	$\alpha_{H3(C)}$ $(Å^3)$	α_O $(Å^3)$	$\alpha_{H(O)}$ $(Å^3)$
0	0.00	1.830	2.221	0.650	0.249	0.260	0.260	0.632	0.171
20	0.21	1.838	2.223	0.644	0.252	0.261	0.263	0.635	0.169
40	0.63	1.855	2.226	0.646	0.258	0.259	0.261	0.637	0.165
60	0.84	1.862	2.228	0.658	0.257	0.257	0.256	0.638	0.162
Exp	1.07[18]	1.701[19]	3.31[20]/3.23[21]						

staggered one. Due to the relatively small barrier to rotation (1 kcal/mole), the methanol conformational equilibria may be strongly influenced in polar solvents [22].

If one wants to model the electrostatics only via partial charges assigned to atoms, as is common for intermolecular potentials used in molecular dynamics and Monte Carlo simulations, it is impossible to fit both the dipole and quadrupole moment at the same time. Instead it is necessary to use partial charge sites dislocated from the nuclei. Retaining partial charges on the hydrogen nuclei and using dislocated charges for the oxygen and carbon atoms allows for a good fit of the electrostatic moments of all rotational conformers. In fact, by allowing non-atom based partial charges the rotational energy barrier for methanol can be reproduced with only electrostatic interactions by one unique set of partial charges [23]. The barrier can thus not only be understood but also modelled by purely electrostatic terms.

C) Formamide

In Table 5 the properties of formamide are given for different rotational angles. The experimental barrier heights determined by NMR techniques vary according to the solvent media [24], making a direct comparision between the calculated value difficult. With the large variations in both dipole moment [25] and polarizability, medium effects on the conformational equilibria can be expected to be important. The decrease in dipole moment upon rotation is accompanied by intramolecular charge relocation. In Figure 1 the local charge variations for atom and bond sites are shown. When rotating the CHO fragment around the NC axis the π-bonding character is destroyed and electron density associated with the NC bond is diminished. At the same time the nitrogen and carbon atoms gain while the oxygen loses electrons. The breaking of the π-bonding system localizes orbitals on the nitrogen and carbon.

The variation in total molecular polarizability is similar to those of ethane and methanol. The individual atomic components exhibit a marked dependence on the dihedral angle. The largest variations are seen at the carbon and oxygen sites. The local charge increase at the carbon atom is reflected in a higher polarizability and vice versa for the oxygen site. Thus even if the total polarizability is not changing, locally there may be strong variations which will be reflected in dispersion interactions and the locally induced dipole moments.

Modelling of the charge migration with partial charges can only be done by allowing the magnitudes of these to vary. Without variable charges the loss of dipole moment cannot be reproduced. Using dislocated charges and variable charges in the CHO fragment was found to account for the electrostatic moments [26]. However, the electrostatic intramolecular interaction of such a model does not accurately model the

Table 5 Formamide, $HCONH_2$

Rotation (degrees)	V_{excess} *(kcal/mole)*	μ *(D)*	α_{mol} $(\AA^3)$	α_C $(\AA^3)$	α_O $(\AA^3)$	α_N $(\AA^3)$	$\alpha_{H(C)}$ $(\AA^3)$	$\alpha_{H(N)}$ $(\AA^3)$	$\alpha_{H2(N)}$ $(\AA^3)$
0	0.00	4.264	3.067	0.443	0.946	0.878	0.330	0.252	0.219
30	1.91	4.078	3.067	0.453	0.939	0.869	0.330	0.252	0.225
60	10.42	3.603	3.053	0.483	0.913	0.836	0.339	0.250	0.231
90	14.94	3.618	3.029	0.526	0.847	0.851	0.336	0.235	0.235
Exp	17–21[23]	3.29[25]							

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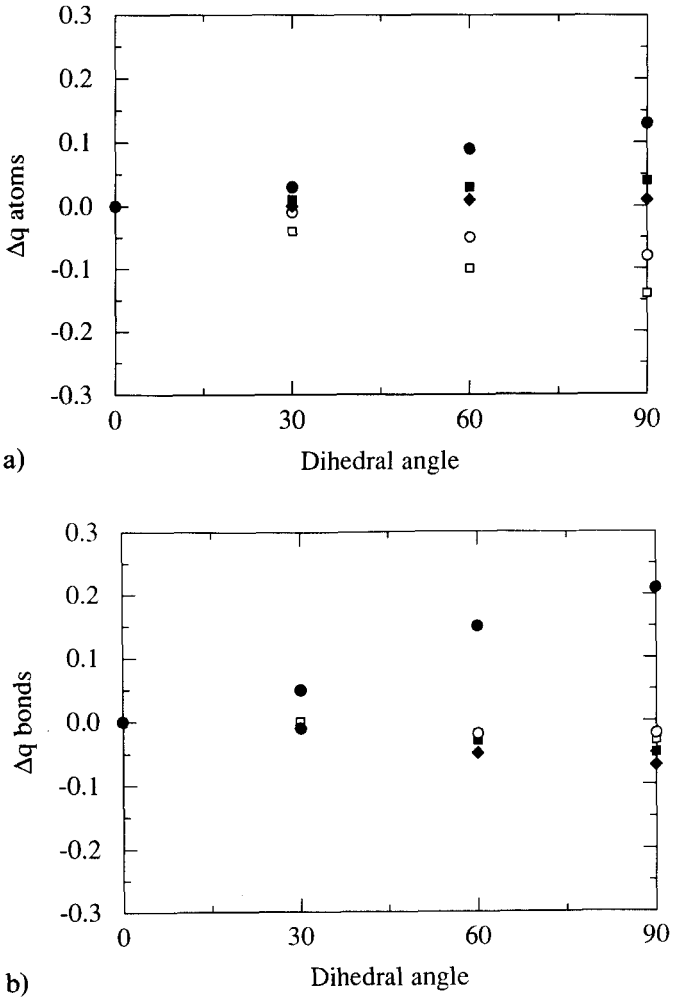

Figure 1 The local charge variation upon rotation around the NC bond in formamide: a) atom centers, ● oxygen, ■ hydrogen H(C), ◆ hydrogen H(N), ○ nitrogen, and □ carbon; b) bond centers, ● CN, ○ NH_1, □ OH, ■ CH, and ◆ NH_2. A positive Δq indicates a loss of electron density.

barrier to rotation. This is a reflection of the non-electrostatic character of the rotational barrier, the contributions of repulsive orbital overlaps cannot be modelled by a simple point charge scheme.

Given a barrier height of roughly 15 kcal/mole the variations in molecular properties may not be important in a neat liquid at room temperature. If the internal motion is in a frequency range that is commensurate with the surrounding media the energy exchange between intramolecular and intermolecular modes becomes important. Then even small variation in the intramolecular conformations causing changes in the intermolecular interaction will change the dynamical properties of the system. For proteins a normal distribution of dihedral angle in the peptide bond is around 20° to

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30° [27]. The motion of these peptide bonds are both of rapid character with a correlation time of a few picoseconds as well as a very slow motion extending over several decades of picoseconds [27]. Correctly taking into account the changes in intermolecular interactions necessitates a variable charge model. For problems with few internal dihedral angles it could be possible to simulate a set of selected rigid rotational isomers. In such a scheme equilibrium properties should be well reproduced whereas dynamical quantities will be unreliable.

D) Water vibrations

It is also of interest to investigate how molecular properties depend on vibrations of bonds and angles. Water is a molecule that is often treated as flexible in molecular dynamics simulations [28]. The dipole moment of these models is calculated using partial charges and as these are kept fixed the dipole moment will vary depending on the bond lengths and angle. The resulting dipole moment derivatives tend to overestimate the nuclear polarization compared to experimental [29] and theoretical data [30]. Accordingly a set of calculations have been carried out on a number of different water configurations to map the dependency of molecular properties on small distortions of bonds and angles. From the corresponding equilibrium water structure an intermolecular potential has been derived [9] and shown, using molecular dynamics simulations, to give good liquid water properties [31].

From a set of 22 SCF calculations it was found that the electrostatic moments could be reproduced using the partial charge position of the original model and varying the magnitude of the charge. These charge variation could in turn be fitted to a functional form,

$$\Delta q_{\text{var}}(r_1, r_2, \theta) = 0.3341(r_0 - r_1) + 0.3341(r_0 - r_2) - 0.1084(\theta_0 - \theta), \qquad (5)$$

where the equilibrium oxygen-hydrogen bondlength in Ångstöm is denoted r_0, the instantenous OH bonds r_1 and r_2, with a similar notation for the HOH angle θ. The range of validity of this functional approach is surprisingly good, the total static dipole moment is reproduced well in the interval $\mu_{nuq.eq} \pm 0.15$D. For equilibrium simulations of liquid water at 300 K this spread is adequate as the nuclear motion of a water molecule is restricted at these temperatures. The drawback with this approach is that SCF-HF results are not able to reproduce experimental dipole derivative. Sufficient accuracy is only achieved with CI methods [30]. Of course experimental values can be used in a parameterization of the charge variation. The variation of the total molecular polarizability of water was found to be reproduced using,

$$\Delta\alpha_{\text{var}}(r_1, r_2, \theta) = -5.4138(r_0 - r_1) - 5.4138(r_0 - r_2) + 0.3769(\theta_0 - \theta), \qquad (6)$$

with r_0, r_1, r_2, θ_0 and θ is in Equation (5) and the polarizability given in atomic units. It is also possible to use the variable polarizability to construct a conformationally dependent dispersion energy term from a London type expression. Simulations of polarizable water [32] using different combinations of variable charge and polarizability/dispersion indicates that *both* processes are important in such a case. The coupling between intra and intermolecular degrees of freedom influences dynamical properties as studies of flexible water using different intramolecular potential functions [28] have shown. The influence of variable charges and polarizabilities will likewise alter the mechanism of energy transfer between intra and intermolecular modes.

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4. CONCLUSION

The rotation around dihedral bonds is associated with charge redistributions in ethane and formamide. This is manifested in variations of the electrostatic moments of the molecules. In methanol there is no corresponding large charge relocation. The total molecular polarizability is rather insensitive to conformational changes, but individual atomic components can significantly alter the local polarizabilities.

The change in intermolecular interaction upon the variation in the quadrupole moment of ethane is energetically small compared to the dominant attractive dispersion energy. The breaking of the π-bonding character in formamide is associated with large changes in electron density and polarizability. The rotational barrier for such a process is about 15 kcal/mole, but peptide bonds in protein can well have amplitudes of 20 to 30 degrees causing significant redistribution of charge. The correct modelling of such processes with molecular dynamics or Monte Carlo would require variable charge models.

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[26] The partial charge set describing formamide in the equilibrium conformation consists of $q_{H(C)} = 0.0866e$, $q_C = 0.3353e$, $q_{H1(N)} = 0.4061e$, $q_{H2(N)} = 0.4763e$, $q_{Osite} = -0.2281e$, $q_{Nsite} = -04240e$. The two oxygen sites are located at $2.2680v_1 +/- 0.8715v_2 - 0.0902v_3 + r_C$ with $v_1 = (r_O-r_C)/|r_O-r_C|, v_2 = (r_{H(C)}-r_C) \times (r_O-r_C)/|(r_{H(C)}-r_C) \times (r_O-r_C)|$ and $v_3 = (r_{H(C)}-r_C)/|r_{H(C)}-r_C|$. The two nitrogen sites are located at $0.2330v_1 +/- 1.0025v_2 + 0.0702v_3 + r_N$ with $v_1 = (r_{H1(N)}-r_N)/|r_{H1(N)}-r_N|, v_2 = (r_{H1(N)}-r_N) \times (r_{H2(N)}-r_N)/|(r_{H1(N)}-r_N) \times (r_{H2(N)}-r_{(N)})|$ and $v_3 = (r_{H2(N)}-r_N)/|r_{H2(N)}-r_N|$. The charges reproducing the electrostatic moments during the rotation of 30°, 60° and 90° are respectively $q_{H(C)} = 0.0877$, 0.1018, 0.1048e, $q_C = 0.3321$, 0.2768, 0.2570, and for $q_{Osite} = 0.2204$, -0.1885, $-0.1692e$. The partial charges of the other sites remain constant on rotation.

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