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LETTERS

A Model for the Intermolecular Interactions of the Hydrogen Bond That Incorporates Its Spectroscopic Properties

Weili Qian and Samuel Krimm*

Biophysics Research Division and Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

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We have developed a new form of the intermolecular potential of the hydrogen bond that is consistent with ab initio structures, interaction energies, interaction forces, intermolecular force constants, and dipole derivatives. The model incorporates charges, charge fluxes, atomic dipoles, and van der Waals interactions, and it has been successfully applied to the formic acid dimer.

Ab initio studies have led to significant progress in understanding the structure, energetics, and, in some cases, vibrational spectra of simple hydrogen-bonded systems.[1] However, such approaches are of limited application to large systems such as macromolecules, and, as a result, methodologies based on potential energy functions are being widely implemented. The accuracy of the predictions in these molecular mechanics (MM) and molecular dynamics simulations of course depends on the reliability of the description of the intramolecular and intermolecular interactions in the energy function. This is particularly true if we wish to satisfactorily reproduce vibrational spectroscopic properties of hydrogen-bonded structures. While such accuracy is now achievable for the intramolecular force field, by direct transformation of ab initio results into the MM format to produce what we call a spectroscopically determined force field (SDFF)[2], a comparable formulation has not been available for the intermolecular hydrogen-bond interaction (especially near its equilibrium configuration, which we are mostly interested in obtaining). We present an MM model that provides a description of this interaction capable of reproducing its spectroscopic features.

In the commonly used representation of the hydrogen-bond interaction, the potential energy between atoms i and j a distance r apart, $u(r)$, is given by the Coulomb interaction between fixed charges plus a fixed van der Waals interaction of the Lennard-Jones type.[3] Such a distance-dependent form results in Cartesian interaction force constants that have the form $F_{i\alpha,j\beta} = F_{i\beta,j\alpha}$, where α and β are Cartesian components. (This follows from $F_{i\alpha,j\beta} = -(u'/r)\delta_{\alpha\beta} + (u'' - (u'/r))(\partial r/\partial x_{i\alpha})(\partial r/\partial x_{j\beta})$, where $u' = (\partial u/\partial r)$ and $u'' = (\partial^2 u/\partial r^2)$,[4] since $(\partial r/\partial x_{i\alpha}) = -(\partial r/\partial x_{j\alpha})$.) But ab initio calculations of hydrogen-bonded systems clearly show that this relation is not true (this equality is relaxed to some extent if an angular dependence is introduced in the hydrogen-bond potential,[3a,b] but this still does not assure reproduction of intermolecular force constants). Therefore, if we wish to reliably reproduce the intermolecular interaction force field, a more comprehensive model must be employed.

The clue to the direction that such an extension should take is provided by the evidence that transition dipole coupling is an important intermolecular interaction mechanism in explaining hydrogen-bond coupling in polypeptides[5] and that such coupling can be represented by charge and charge flux interactions,[6] which are also basic to reproducing infrared intensities.[7] Since our goal is to develop a description that self-consistently explains a large range of ab initio molecular properties,[2a,6b] viz., structures, interaction energies, interaction forces, intermolecular interaction force constants, and dipole derivatives, we have explored a model that incorporates charge fluxes and atomic dipoles together with charges and that has been initially

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successful in reproducing the above properties in the formic acid dimer (FAD).[6b]

The FAD is an advantageous system to examine because it provides the possibility of an independent calculation of many of the quantities in the model. This is important since otherwise we may be faced with the arbitrary determination of too many parameters. However, for planar systems, it has been shown[8] that, with a few simple assumptions, the terms in the atomic multipole expansion of the molecular charge distribution, viz. atomic charges, atomic dipoles, etc., can be uniquely calculated from (ab initio) first molecular dipole derivatives, first molecular quadrupole derivatives, etc. In this way, it was possible to account for the C═O stretch mode splitting due to the intermolecular quadratic force field while at the same time providing a consistent explanation of the intermolecular energy.[6b] In this study we use the dipole-derivative derived charges,[6b] since they are obtained naturally from the out-of-plane first molecular dipole derivatives.[8] However, we do not restrict ourselves to the second molecular dipole-derivative derived charge fluxes[8] since these[6b] do not reproduce the intermolecular force field; rather, we allow the flexibility of optimizing to these values. Also, since charge fluxes for out-of-plane displacements are zero for planar molecules, only in-plane force constants can be determined by this approach and are considered here.

Our general approach to judging the quality of a model for the intermolecular interactions of the hydrogen bond involved the following considerations. We, of course, expect such a potential function to describe the properties for different dimer geometries (in this case, for example, for different monomer separations). However, it is also desirable that the parameters in the function not depend on geometry, i.e., that the changes in properties due to variations in the hydrogen-bond conformation arise entirely from geometrical factors. (This is undoubtedly not exactly true, but if the changes are small, as we have found,[9] it is a good approximation.) In this connection, it is clear that changes in hydrogen-bond geometry are accompanied by changes in intramolecular geometry and therefore force field. We do not at this stage incorporate such features in the model, which would be complex and might mask the intermolecular interaction characteristics that we seek. Rather, we have used the intramolecular part of the ab initio force field for any given geometry. This poses no major problem in an MM application, since these ab initio variations can be incorporated as functional forms in the SDFF.[2]

Specific aspects of the calculations (full details are given elsewhere[9]) were as follows. Three nonbonded distances (two H···O and one O···O) were chosen as intermolecular in-plane coordinates, which together with the 14 intramolecular internal coordinates[6b] make a complete set for the dimer. In addition to the ab initio calculation of the equilibrium structure,[6b] which we designate as D_0, we calculated three other structures by fixing the O···H or H···H distances and relaxing all the other geometric parameters (all calculations at the HF/6-311++G** level). In one of these, D_{-1}, the O···H distance was shorter than in D_0, while in the other two, D_1 and D_2, this distance was longer. The ab initio "data" for these structures were intermolecular interaction energies, calculated for D_0, $E(D_0)$, by the counterpoise method to correct for basis set superposition error, and for the other structures as $E(D) = E(D_0) + E'(D) - E'(D_0)$, where E' is the HF energy of the dimer; forces for D_{-1}, D_1, and D_2 (obviously zero for D_0), obtained by transforming all forces from Cartesian to internal coordinates and selecting those associated with the intermolecular coordinates; force constants, with scale factors taken from the D_0 calculation[6b] and intermolecular interaction force constants obtained in Cartesian coordinates by transformation from the internal coordinate representation; dipole derivatives, taken from the D_0 structure.

TABLE 1: Comparison of ab Initio and Model Properties for Four Hydrogen-Bonded Formic Acid Dimer Structures[a]

	structure			
property	D_{-1}	D_0	D_1	D_2
r(O···H)	1.677	1.864	1.970	2.275
E(D)	−12.2	−13.4	−12.6	−9.2
	−12.4	−13.8	−12.6	−8.8
f(O···H)	−0.047	0.000	0.021	0.037
	−0.113	−0.003	0.021	0.031
f(O···O)	0.000	0.000	−0.034	−0.050
	−0.008	0.000	−0.046	−0.044
$\Delta F_{i\alpha,j\beta}$	0.13	0.07	0.05	0.03
$\Delta\nu$	15.3	5.9	4.6	10.2
ν(O···H) B_u		245		
		244		
ν(O···H) A_g		196		
		204		
ν(O···O) A_g		138		
		141		

[a] r(O···H), hydrogen-bond length, in Å; E(D), energy of dimer, in kcal/mol; f, intermolecular internal coordinate forces, in mdyn; $\Delta F_{i\alpha,j\beta}$, rms error in intermolecular force constants, in mdyn/Å; $\Delta\nu$, rms error in all normal mode frequencies, in cm^{-1}; ν, intermolecular mode frequencies, in cm^{-1}. Top line, from ab initio; bottom line, from model.

The van der Waals parameters, in the form $E_{ij} = 4\epsilon_{ij}((r^*_{ij}/r_{ij})^{12} - (r^*_{ij}/r_{ij})^6)$, where $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$ and $r^*_{ij} = (r^*_{ii} + r^*_{jj})/2$, were initially taken from recent work[3g] in which they, plus static charges, were optimized to fit the ab initio potential surface of the dimer around seven minima. (We have tried other potentials, with similar kinds of results, but this one seemed to be a reasonable starting point since it satisfactorily reproduces experimental thermodynamic and structural properties of the liquid.) We then allowed r^*_{ij} of the hydrogen-bonded O and H atoms to optimize.

The initial values of the charges, internal coordinate charge fluxes, and atomic dipoles were those of the D_0 structure.[6b] We kept all the charges fixed at these values, since we found[9] that they change no more than a few percent over the present range of structures. The C−H bond charge flux was fixed at its D_0 value, and the others were allowed to optimize. All the atomic dipoles other than those of the hydrogen-bonded O and H atoms were fixed at the D_0 values, the latter two being allowed to optimize. The above variable quantities were then least-squares optimized to the "data" of the four dimer structures. A comparison of some of the predicted properties of this optimized model with the ab initio results is given in Table 1.

We have compared the results from our model with those from optimized models in which charge fluxes and/or atomic dipoles are excluded,[9] and in all cases the more inclusive model gives significantly better results. As already seen,[6b] atomic dipoles are needed to obtain correct energies (without atomic dipoles in the present case, D_1 has a lower energy than D_0), and charge fluxes are needed to obtain C═O stretch mode splittings (without charge fluxes in the present case, this splitting is 17 cm^{-1} compared to 53 cm^{-1} for the complete model and 51 cm^{-1} from ab initio). From Table 1 we see that the energies of all structures are well reproduced, as are the forces associated with the intermolecular coordinates. There are 55 independent intermolecular force constants, and these are well reproduced and give good reproduction of the normal mode frequencies. What is particularly important, the complete model gives excellent reproduction of intermolecular mode frequencies whereas standard models do very poorly: for example, with only the otherwise acceptable charge and van der Waals parameters,[3g] we find that $\nu(\text{O}\cdots\text{H}) = 296$ (error from ab initio $\Delta\nu = 51$) and 218 ($\Delta\nu = 22$) cm^{-1} and $\nu(\text{O}\cdots\text{O}) = 75$ ($\Delta\nu = -63$) cm^{-1}.

In conclusion, we have developed a new form of the intermolecular potential of the hydrogen bond that is consistent with ab initio vibrational spectroscopic properties, such as intramolecular mode splittings and intermolecular mode frequencies, as well as interaction properties, such as structures, energies, forces, and force constants. The model incorporates charge fluxes and atomic dipoles (and perhaps dipole fluxes in the general case) and is also consistent with ab initio dipole derivatives and thus infrared intensities. Such a model has been effective for the FAD,[9] is being developed for the peptide group,[10] and will be incorporated in the SDFF.[2]

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