A Potential Function for Describing Intermolecular Interactions in the Hydroxylamine Dimer

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A potential function that describes the interaction between two hydroxylamine molecules has been developed from ab initio determined molecular properties and IMPT calculations for various dimer configurations using the 6-311G** basis set. The function comprises an electrostatic term in the form of a series of multipoles distributed over the atoms and an exponential repulsive term determined by fitting the results for the dimer. The dispersive term is expressed according to a London formula as a function of distributed spherical polarizabilities, and the contribution of induction is a function of the polarizabilities, distributed over the atoms. The proposed function reproduces the properties of the different minima for the hydroxylamine dimer with an accuracy similar to that of MP2 calculations. The electrostatic contribution predominates in all the configurations obtained, and the maximum possible number of X−H···N hydrogen bonds is always favored. In addition, the function was employed to determine the lowest-energy configurations for the trimer, and the results were compared to those from ab initio calculations employing several methods.

1. Introduction

The study of aggregates consisting of several molecules is dramatically facilitated by the use of an analytical function to characterize the interactions involved without the need to use ab initio calculations, a technique that is frequently unfeasible. In addition, simulations[1] based on molecular dynamics or the Monte Carlo technique entail the use of analytical functions of variable complexity to accurately describe the interactions between particles in the system. One must thus obtain functions that provide the interaction energy for as many configurations as possible—particularly those of special interest such as minima and transition states. The functions can initially be developed for dimers and then applied to more complex systems with a variable degree of approximation.

Perturbation methods[2−5] determine the interaction energy as a series of terms that can be related to different physical phenomena. The symmetry-adapted perturbation theory of Jeziorski et al.[3] provides accurate results for several components of the interaction energy, allowing for intramonomer correlation effects to be taken into account. However, this kind of method is very costly in computational terms; in the present case, the potential energy surface of the hydroxylamine dimer needs to be explored, which means that over 400 calculations need to be performed and the computation time increases dramatically. The IMPT method of Hayes and Stone[4,5] is a reasonably fast and quite accurate alternative that uses SCF unperturbed wave functions. The method was employed successfully to construct potential functions for several dimers with accurate results (see, for example, refs 6 and 7), and it will be used in the present work. It is possible to simplify the construction of the potential function by expressing[8] some components of the long-range interaction energy in terms of functions dependent on the properties of the individual molecules. This type of approximation loses accuracy as distances shorten and the need arises to consider overlap between the charge clouds of the monomers in each term of the interaction energy.

The system studied in this work, the hydroxylamine dimer, exhibits a behavior midway between those of water and ammonia and has a small size that makes it amenable to ab initio calculations; however, it has scarcely been studied in this context to date.[9−15] Also, there are not many experimental studies on hydroxylamine clusters, and those that have been reported are focused on determining the infrared spectra of the dimer.[10−15] The hydroxylamine dimer presents a somewhat complex potential surface in that it can form various types of hydrogen bonds that lead to several minima with substantial interaction energies. In this respect, an analytical potential function may help to improve the knowledge of the characteristics of the hydrogen bonds that are present in the aggregates and also facilitate the study of larger clusters, allowing the characterization of the minima of the potential surface at lower computational cost.

During the course of this work, we developed a potential function that describes the interaction between two hydroxylamine molecules based on properties of the individual molecules determined from ab initio calculations and IMPT computations for the dimer. The interaction energy is resolved into electrostatic, repulsion, dispersion, and induction terms, each being represented by an appropriate analytical function. Thus, the electrostatic term is described by MP2-calculated multipoles distributed over the atoms; dispersion is described as a London expression depending on spherical polarizabilities, the induction term consists of a series of polarizabilities distributed over the atoms, and the repulsive term is an exponential function obtained by fitting to over 400 IMPT calculations for different configurations of the dimer.

To save computation time, it is customary in exploring the potential surface of clusters to assume that the monomers retain the geometries they have in isolation. In hydroxylamine, this approximation ignores the possibility that the O−H bond may rotate about the N−O bond. Calculations showed that the deviations are small, so we decided to keep the molecule in its experimentally determined geometry.[16] We will return to this point in section 3.

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TABLE 1: Distributed Multipole Moments (au) at the MP2/6-311G Level[a]**

O	Q_0	−0.3528								
	Q_1	0.2837	0.2177	0.0000						
	Q_2	0.6278	−0.2640	0.0000	0.5561	0.0000				
	Q_3	0.1424	0.0599	0.0000	0.1843	0.0000	−0.0921	0.0000		
	Q_4	0.6872	0.0541	0.0000	0.2986	0.0000	0.0847	0.0000	−0.0484	0.0000
N	Q_0	−0.0702								
	Q_1	−0.3836	−0.4341	0.0000						
	Q_2	0.6894	−0.3950	0.0000	−0.6846	0.0000				
	Q_3	0.4732	−0.2296	0.0000	0.2935	0.0000	−0.3311	0.0000		
	Q_4	−0.4230	−0.3471	0.0000	−0.1791	0.0000	−0.7294	0.0000	0.1612	0.0000
H_0	Q_0	0.2619								
	Q_1	0.0093	0.0370	0.0000						
	Q_2	−0.0027	−0.0330	0.0000	0.1498	0.0000				
	Q_3	0.0618	0.0927	0.0000	0.0397	0.0000	−0.2026	0.0000		
	Q_4	0.2234	−0.0256	0.0000	−0.1675	0.0000	−0.0476	0.0000	0.2122	0.0000
H_1	Q_0	0.0806								
	Q_1	0.0566	−0.0789	0.1377						
	Q_2	−0.0077	0.0035	−0.0199	−0.0040	−0.0178				
	Q_3	0.0133	−0.0247	0.0385	−0.0006	0.0212	−0.0720	−0.0154		
	Q_4	0.0302	0.0271	−0.0326	0.0220	0.0475	0.0415	0.0162	−0.0667	0.0675
H_2	Q_0	0.0806								
	Q_1	0.0566	−0.0789	−0.1377						
	Q_2	−0.0077	0.0035	0.0199	−0.0040	0.0178				
	Q_3	0.0133	−0.0247	−0.0385	−0.0006	−0.0212	−0.0720	0.0154		
	Q_4	0.0302	0.0271	0.0326	0.0220	−0.0475	0.0415	−0.0162	−0.0667	−0.0675

Total Multipole Moments Relative to the Center of Mass

$Q_{10} = 0.2491$	$Q_{11c} = -0.0405$			
$Q_{20} = -0.3096$	$Q_{21c} = -5.0486$	$Q_{22c} = 0.2200$		
$Q_{30} = -3.4984$	$Q_{31c} = -20.7722$	$Q_{32c} = -9.2386$	$Q_{33c} = 5.0065$	
$Q_{40} = -22.9665$	$Q_{41c} = -70.8306$	$Q_{42c} = -43.4687$	$Q_{43c} = 24.9423$	$Q_{44c} = -1.18564$

[a] The origin is in the center of mass; the nitrogen atom is in the positive branch of axis *z*, and the oxygen atom is in its negative branch. Atom H_0 is in plane *xz*, with positive *x*. H_1 and H_2 are above and below the plane *zx*, respectively. [b] Experimental dipole moment: 0.23 au.[16]

All calculations were performed by using the 6-311G** basis set employing CADPAC.[17] Potential functions were analyzed by using the program ORIENT.[18] This basis set was successfully employed[6,19] to develop potential functions using a method similar to that used for other hydrogen-bonded systems with good results.

The structure of this paper is as follows: the procedure followed in the construction of the new potential function is described in section 2, and some results are briefly commented on; in section 3, results for gas-phase complexes of two, three, and four molecules are presented and compared to results obtained employing ab initio calculations at different levels.

2. Method

As stated above, the aim of this work was to construct an analytical function to describe interactions between two hydroxylamine molecules by using a perturbation methodology[4,5,18] that resolves the interaction energy into various terms[20]

$$E_{\mathrm{int}} = E_{\mathrm{rep}} + E_{\mathrm{ele}} + E_{\mathrm{disp}} + E_{\mathrm{ind}} + ... \tag{1}$$

each being expressed as an appropriate analytical function that depends on the properties of the individual molecules, with the exception of the repulsion energy, which is obtained from calculations for the dimer.

2.1. Multipolar Electrostatic Energy. The effect of electrostatic energy, which is the result of the Coulombic interaction between the charge clouds of the two molecules, can be expressed accurately at long range by means of a multipole expansion. To facilitate convergence of the series, multipoles can be distributed over several sites so that the multipolar electrostatic energy can be expressed as a combination of interactions between individual multipoles that depends on the geometry according to

$$E_{\mathrm{ele}} = \sum_{ab,lm,l'm'} Q^{a}_{lm}\, Q^{b}_{l'm'} T_{lm,l'm'}(\Omega_{ab}) R_{ab}^{\;-(l+l'+1)} \tag{2}$$

where R_{ab} is the distance between site *a* in molecule *A* and site *b* in molecule *B*, Q_{lm} are the multipoles associated with each site, and $T_{lm,l'm'}$ are interaction tensors that depend on the orientation and have been tabulated by Price et al.[21] The DMA method of Stone and Alderton[22] was used to distribute multipoles, of order up to 4, over the atoms at the MP2 level using the 6-311G** basis set; the values employed are shown in Table 1. The calculated dipole moment (0.25 au) reproduces fairly well the experimental value (0.23 au).[16] In this respect, it should be noted that employing basis sets that include diffuse functions (i.e. 6-311++G**) leads to an overestimation of the dipole moment of about 18%. Representing the electrostatic term accurately is crucial in terms of ensuring an effective representation of the interaction, since this term is usually the one that contributes to the greatest extent to the interaction energy in complexes involving hydrogen bonding. In addition, it is largely responsible for anisotropy in the interaction. For these reasons, we opted to employ a quite complex multipolar distribution, although it is possible that a distribution employing multipoles of lower rank on hydrogen atoms could lead to similar results.

As noted earlier, multipole expansion is only accurate at long distances because, near the minimum, overlap between charge clouds can be significant and so can the contribution of the electrostatic penetration energy, which cannot be described by a mere multipole expansion. The electrostatic energy provided by the IMPT method includes the effect of overlap between charge clouds, so the penetration term can be estimated as the difference between the electrostatic energy calculated by the IMPT method and that provided by the expansion. Because the former method uses SCF wave functions, the operation entails using the distributed multipoles calculated from such wave functions:

$$E_{\text{pen}} = E_{\text{ele}}(\text{IMPT}) - E_{\text{ele}}(\text{SCF expansion}) \qquad (3)$$

Since the contribution of the penetration energy decays in a roughly exponential manner with increases in the distance, we chose to represent this and the repulsive term in combination rather than use an individual function for each.[6,7]

2.2. Repulsion Energy. The repulsion energy cannot be expressed in simple terms as a function of monomer properties, though there have been some attempts at describing it in terms of the overlap integrals of the monomer wave functions.[23,24] We chose to use the IMPT method to calculate the repulsion energy for over 400 dimer configurations and fit the results to an appropriate analytical function.

As stated in the previous section, this term also included the contribution of electrostatic penetration. We have also included the charge transfer term, which can readily be derived as part of second-order contributions by using the IMPT method and is usually a minor contribution. With the basis set used, we found the contribution of charge transfer at the minimum for the hydroxylamine dimer to be -4 mE$_h$, so we decided that it was necessary to include this in the potential function. We opted to include this contribution in the repulsion term, as we found that using an individual function for the charge transfer led to similar results.

The fitting function used was a combination of exponential terms for each pair of atoms

$$E_{\text{rep}}/\text{mE}_{\text{h}} = \sum_{ij} \exp(-\alpha_{ij}(r_{ij} - \rho_{ij})) \qquad (4)$$

where r_{ij} is the distance between the atoms considered and α_{ij} and ρ_{ij} are fitting parameters. The fitting was performed by using a nonlinear fitting program based on the Levenberg–Marquardt algorithm.[25] Also, to facilitate fitting of the less repulsive potential zones, we introduced an exponential weighting factor of the Boltzmann type, namely[26]

$$w(E) = \exp(-E_{\text{first}}/C) \quad (C = 2.5\ \text{mE}_{\text{h}}) \qquad (5)$$

It is usual to employ the repulsion energy in this type of weighting function,[26] favoring the fit for the regions of the potential surface with small repulsion energies. In the case of the hydroxylamine dimer, the repulsion energy is rather large for the configurations of the minima, and the resulting fit is very poor for these important regions of the potential. For this reason, we opted to employ first-order energy in the weighting function. The effect of the two weighting functions can be viewed in Figure 1, where the sum of electrostatic + repulsion + charge-transfer IMPT energy is compared to the results obtained with the function for three different configurations. It is clear from Figure 1 that the weighting function that employs repulsion energy underestimates the repulsion for two configurations, resulting in intermolecular distances that are too short and interaction energies that are too negative; the results are much better when the first-order energy is employed in the weighting. Figure 2 compares the IMPT results and those obtained from the best fit with the exponential function described above. As can be seen, fitting was quite good throughout the energy range considered except in the least attractive regions due to the effect of the weighting involved. The final parameters are shown in Table 2; the rms was found to be 0.11 mE$_h$, a value that can be considered sufficiently small taking into account that the interaction energy for the global minima of the dimer is about -16 millihartrees.

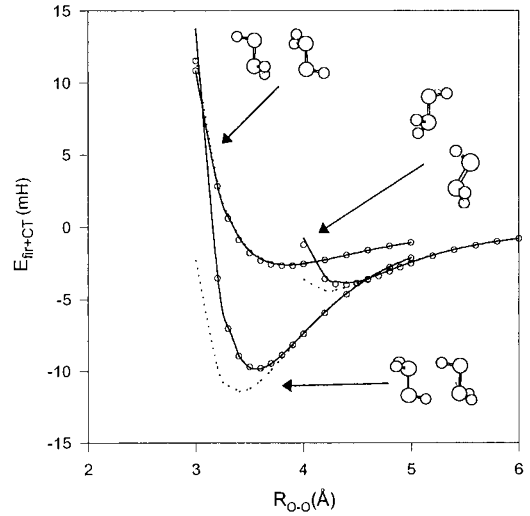


Figure 1. Comparison of IMPT ($E_{\text{ele}} + E_{\text{rep}} + E_{\text{CT}}$) energy with the sum of electrostatic and repulsion models for three different configurations at several distances between oxygen atoms. Symbols correspond to IMPT values, the dotted line corresponds to the weighting function $w = \exp(-E_{\text{rep}}/2.5)$, and the solid line refers to the weighting function $w = \exp(-E_{\text{first}}/2.5)$.

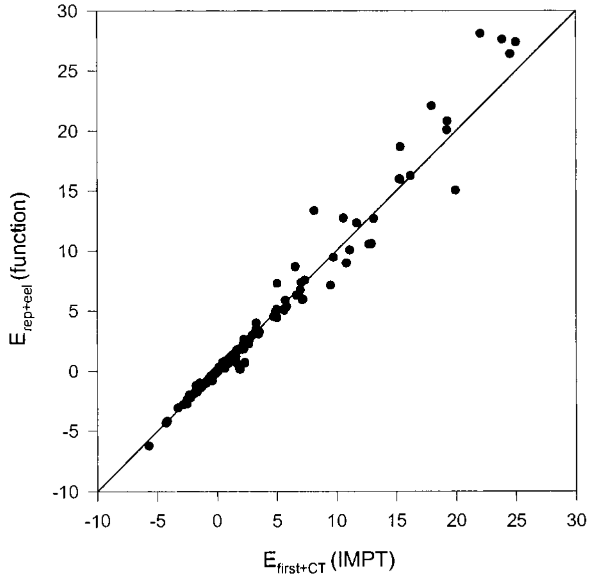


Figure 2. Fitting of the repulsive term. Comparison with the results of IMPT calculations. Energies are in millihartrees.

TABLE 2: Parameters Used To Describe the Contributions of Repulsion and Dispersion[a]

atom pair	α	ρ	C	atom pair	α	ρ	C
OO	2.931	5.807	12.243	NH$_O$	2.099	4.657	4.473
ON	1.997	5.526	16.556	NH$_N$	2.086	4.782	5.307
OH$_O$	1.785	4.071	3.308	H$_O$H$_O$	1.681	3.073	0.894
OH$_N$	2.242	4.509	3.925	H$_O$H$_N$	4.168	3.078	1.060
NN	2.285	5.896	22.388	H$_N$H$_N$	3.630	3.047	1.258

[a] α is expressed in bohr^{-1}, ρ in bohr, and C in hartrees bohr^6.

2.3. Dispersion and Induction Energies. Calculating the dispersion energy by the IMPT method involves computations that are too lengthy to allow the potential surface to be explored and the results to be fitted to an appropriate function such as

TABLE 3: Distributed Polarizabilities (au) Calculated at the MP2/6-311G Level[a]**

	zz	*xx*	*yy*	*zx*	*zy*	*xy*
O	5.89	3.54	2.45	−0.74		
N	6.73	4.31	5.05	−0.74		
H_0	1.00	1.83	0.51	−0.51		
H_1	0.98	1.21	1.77	−0.33	0.47	−0.74
H_2	0.98	1.21	1.77	−0.33	−0.47	0.74

[a] The origin is in the center of mass; the nitrogen atom is in the positive branch of axis *z*, and the oxygen atom is in its negative branch. Atom H_0 is in plane *xz*, with positive *x*. H_1 and H_2 are above and below the plane *zx*, respectively.

that obtained for the repulsive energy. We therefore expressed the contribution of dispersion in terms of the properties of individual molecules that were subsequently refined by comparison with a small number of IMPT calculations for selected configurations.

Taking into account that, broadly speaking, the dispersion term depends on R^{-6}, we used an expression of the type

$$E_{\mathrm{dis}} = -\sum_{ij} f_6(r_{ij})\, C_{ij} r_{ij}^{\ -6} \tag{6}$$

where C_{ij} is a parameter for each atom pair and f_6 is a damping function that introduces the effect of the overlap and avoids singularities at a zero distance. The specific damping function used was that described by Tang and Toennies,[27] which is of the form

$$f_6(r_{ij}) = 1 - \exp(-ar_{ij}) \sum_{k=0}^{6} \frac{(ar_{ij})^k}{k!} \tag{7}$$

This expression depends on a single parameter, which, for the sake of simplicity, we assumed to be identical for every atom pair. Since the damping function is intended to account for overlap and this is related to repulsion, we estimated parameter *a* to be 2.5 bohr^{-1} as the average of the α_{ij} values obtained by fitting the repulsion energy.[6,7]

C_{ij} values were estimated using a London expression[8,20,28] dependent on the spherical polarizabilities distributed over the atoms

$$C_{ij} = 1.5 C_0 \alpha_i \alpha_j \omega_A \omega_{B'} / (\omega_A + \omega_B) \tag{8}$$

where ω is the ionization potential estimated as the energy of the highest occupied orbital and C_0, as in previous work,[6] was assumed to be 2.3 in order to approximate the dispersion energies provided by this expression to their calculated counterparts. The C_{ij} values used in the potential function are given in Table 2.

The induction energy describes the energy change associated with changes in the charge distribution of the molecules by the effect of an external electric field. Such a contribution can be expressed by means of a series of polarizabilities, distributed over the atoms, that provide the dipole moment induced by the electric field produced by the multipole expansion associated with other molecules. We thus used a numerical integration procedure included in CADPAC[17] to distribute dipole−dipole polarizabilities over each atom from MP2 calculations in order to maintain consistency with the electrostatic model used. The results obtained in this way are given in Table 3. No effects of higher rank polarizabilities or hyperpolarizabilities were considered. As with dispersion, the expression for the induction energy exhibits singularity at a distance of zero, so it requires the inclusion of a damping function. Finally, comparison with IMPT results led us to use the same function as in the dispersion term. In addition, we chose not to use an iterative method in calculating induced moments since it did not seem to improve on the results of the model at long range to any significant extent.

TABLE 4: Characteristics of the Four Minima for the Hydroxylamine Dimer[a]

		$R_{\mathrm{O-O}}$	θ_{OON}	$R_{\mathrm{N\cdots H}}$	$R_{\mathrm{O\cdots H}}$	ΔE^b	μ (D)
M1	HF	3.421	60.1	2.070		−31.981	0.0
	DFT	3.291	59.5	1.937		−44.144	0.0
	MP2	3.274	59.7	1.923		−39.889	0.0
	function	3.339	60.0	1.990		−42.651	0.0
M2	HF	2.931	90.0 (102.3)	2.360	1.998	−23.149	1.60
	DFT	2.830	90.1 (100.0)	2.185	1.896	−29.578	1.33
	MP2	2.819	90.5 (99.9)	2.180	1.883	−27.200	1.31
	function	2.917	91.7 (99.4)	2.290	1.975	−28.856	1.31
M3	HF	2.985	117.2 (73.1)	2.147	2.188	−18.412	1.17
	DFT	2.848	110.6 (72.4)	1.975	2.064	−25.971	0.98
	MP2	2.851	105.0 (72.0)	1.850	2.075	−22.566	0.96
	function	3.211	124.9 (61.5)	1.956	2.549	−25.622	0.94
M4	HF	3.348	70.3		2.233	−18.100	0.19
	DFT	3.285	68.1		2.108	−20.820	0.13
	MP2	3.297	67.8		2.108	−19.925	0.16
	function	3.402	69.3		2.247	−19.888	0.17

[a] Distances are given in Å, angles in deg, and energies in kJ/mol. [b] Interaction energies corrected from BSSE employing the counterpoise method.

3. Results

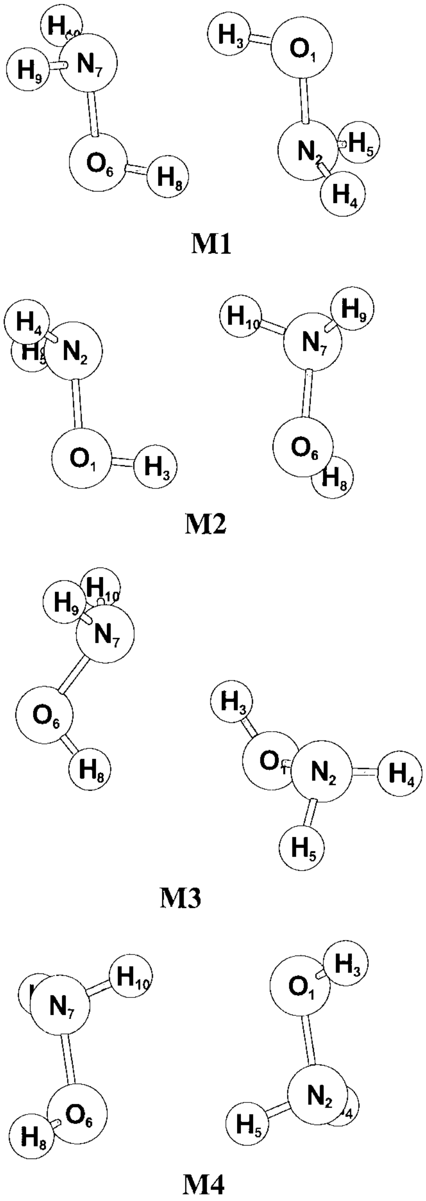
The results obtained by using the potential function described above to characterize the properties of the hydroxylamine dimer, trimer, and tetramer are presented in this section. For comparison, geometry optimizations based on ab initio calculations at the HF, MP2, and DFT/B3LYP levels, all using the 6-311G** basis set, were also performed for the dimer and trimer.

3.1. The Hydroxylamine Dimer.

As noted in the Introduction, the hydroxylamine dimer has been the subject of relatively few theoretical studies.[9−15] In previous work,[15] the global minimum for its potential surface was found to correspond to a geometry of C_{2h} symmetry, where the molecules lie in an antiparallel arrangement forming two O−H···N hydrogen bonds. The interaction energy for this structure at the CEPA level was determined to be 46.9 kJ/mol using a fairly large basis set. Other studies[10−14] based on MP2/6-31G** calculations have confirmed that this structure corresponds to the most attractive minimum in the potential surface. Two other minima corresponding to situations involving hydrogen bonding have also been identified.[14]

We used the potential function described in the previous section to locate minima in the potential surface with the aid of the program ORIENT,[18] which ensured that the stationary point reached by the optimization had positive Hessian eigenvalues and was therefore a minimum. In addition, we used the HF, MP2, and DFT/B3LYP methods in conjunction with the 6-311G** basis set to obtain reference values facilitating direct comparison with the potential. The results obtained in this way are shown in Table 4 and Figure 3.

The global minima provided by all the ab initio methods possesses a geometry similar to that obtained in previous work, which showed that molecules lie in an antiparallel arrangement forming two O−H···N hydrogen bonds. The geometries obtained at different computational levels were similar with little differences, except with the HF method, which provided slightly



M1

M2

M3

M4

Figure 3. Minima for the hydroxylamine dimer.

longer distances. The interaction energies provided by the ab initio methods, once corrected for the basis set superposition error using the counterpoise (CP) method,[29,30] were quite similar for the MP2 and DFT/B3LYP calculations and compare well to previously reported values.[14,15] On the other hand, the HF method provided significantly less negative values, thus reflecting the significant role of correlation in the interaction.

As regards the results provided by the potential function, they reproduced the ab initio calculations with a high accuracy. The geometries were very similar to those calculated using the MP2 and DFT/B3LYP methods, but intermolecular distances were slightly longer. The interaction energy was also reproduced accurately and lies between the MP2 and DFT/B3LYP values. In this respect, one should bear in mind that the ab initio geometries obtained were not corrected for BSSE and only the interaction energy of the final geometry was obtained by employing the CP method. This process may lead to some errors, particularly if the bases used are not large enough. We calculated the interaction energy at the MP2 level for the configuration of the C_{2h} minimum but used a variable distance between oxygen atoms. We found the interaction energy at a distance of 3.4 Å to be about −41.5 kJ/mol and hence about 1.6 kJ/mol more attractive that the optimized structure shown in Table 4. This result is in better agreement with the results provided by the analytical function. The interaction energy predicted by the potential function was slightly lower than reported values;[14,15] however, it was consistent with the calculations involving the same basis set used in constructing the potential surface.

TABLE 5: Decomposition of the Interaction Energy (kJ/mol) for the Minima of the Hydroxylamine Dimer

	M1	M2	M3	M4
E_{ele}	−63.121	−35.819	−37.211	−22.500
E_{rep}	44.504	22.196	26.591	13.306
E_{ind}	−9.299	−4.579	−5.503	−2.541
E_{disp}	−14.737	−10.654	−9.499	−8.152
E_{total}	−42.651	−28.856	−25.622	−19.888

In addition to the global minimum, our function identified three other minima that also arose from the ab initio calculations. These structures, once again, correspond to situations involving hydrogen bonding, and also, the two most attractive structures are very similar to others reported elsewhere.[14] To the best of our knowledge, structure **M4** has never previously been reported. Once again, the results provided by the function and those calculated at the MP2 and DFT/B3LYP levels were highly consistent and much better than those obtained at the HF level as regards both geometries and interaction energies; the largest deviations are shown for structure **M3**, although the molecular orientation was very similar to that derived from the ab initio calculations. On the basis of the relative stability of the minima, the strongest interaction appears to be favored by the formation of X−H···N hydrogen bonds. As can be seen, the global minimum is compatible with two hydrogen bonds of this type and minima **M2** and **M3** are compatible with a single hydrogen bond. In contrast, in the least stable minimum, **M4**, the hydrogen bonds are of the type X−H···O.

Table 5 shows the contribution of each potential term to the interaction energy at the four minima identified. As is usually the case with complexes involving hydrogen bonding, the electrostatic term predominates despite the relatively small dipole moment for hydroxylamine (0.23 au).[16] Following electrostatic interaction, the most important contribution to the interaction energy is repulsion, which is fairly high at all the minima. We should note that the real repulsion term is even larger and that the results shown in Table 5 are lower than would be expected due to the charge transfer and penetration contributions, which are absorbed into repulsion. Finally, dispersion and induction exhibit smaller, though significant, contributions.

Also shown in Table 4 are the values of the dipole moment for the minima obtained with the different methods employed. The function provides essentially correct values for the dipole moment, compared to those obtained from MP2 calculations (remembering that we employ MP2 multipole moments in the description of the electrostatic interaction), while the HF results are, as usual, overestimated. The results obtained with the B3LYP functional are similar to the MP2 values.

As noted in the Introduction, a question remains about the flexibility of the molecule; it is possible that the O−H bond rotates about the N−O bond. However, full optimizations carried out for the minima of the dimer at the HF/6-311G** level (with the exception of **M1**) revealed that the deviations are quite small, so it can be expected that the approach of considering a rigid molecule does not introduce any serious error into the results. The largest deviation, of about 5°, occurs for structure **M3**; for the other two minima, the deviations from the structure of the isolated molecule are even smaller, about 1−2°.

TABLE 6: Minima of the Hydroxylamine Trimer for Structures 3a and 3b (Figure 4)$^{a-d}$

	structure **3a**				structure **3b**			
	function	MP2	HF	DFT	function	MP2	HF	DFT
R_{OO}(AB)	3.322	3.241	3.401	3.207	3.854	3.865	4.075	3.914
R_{OO}(AC)	2.898	2.789	2.943	2.813	2.843	2.685	2.846	2.721
R_{OO}(BC)	5.365	5.172	5.605	5.213	3.556	3.487	3.690	3.585
$R_{\mathrm{X\cdots H}}$(AB)	1.960, 1.985	1.882, 1.841	2.069, 2.033	1.899, 1.934	1.916	1.892	2.080	1.937
$R_{\mathrm{X\cdots H}}$(AC)	2.263, *1.956*	2.126, *1.845*	2.323, *1.980*	2.139, *1.880*	*2.545*	*1.738*	*1.920*	*1.792*
$R_{\mathrm{X\cdots H}}$(BC)					1.867	1.769	1.980	1.847
ΔE	−74.93	−74.87	−57.55	−78.32	−74.87	−68.96	−51.75	−70.48
$\Delta E - E_{\mathrm{pair}}$	−1.11	−2.96	−1.05	−2.66	−5.05	−10.04	−5.32	−8.62
μ (D)	0.67	0.67	0.81	0.68	0.95	0.91	1.12	0.90

[a] Distances are given in Å, angles in deg, and energies in kJ/mol. [b] $E_{\mathrm{pair}} = E_{\mathrm{AB}} + E_{\mathrm{AC}} + E_{\mathrm{BC}}$. AB, AC, and BC refer to the pair of molecules considered as shown in Figure 4. [c] Results for hydrogen-bonded atoms only. Values in italics: X = oxygen. [d] Interaction energies corrected from BSSE employing the counterpoise method.

3.2. Trimer and Tetramer. The potential function was also employed to characterize the minima of the hydroxylamine trimer. As the potential surface for the trimer is rather complex, we employed a Monte Carlo procedure to select a wide variety of starting points for geometry optimizations. Several minima were found, the four most attractive of which are shown in Figure 4 and Tables 6 and 7. These structures were also employed as starting points for ab initio geometry optimizations employing HF, DFT/B3LYP, and MP2 methods, always with the 6-311G** basis set. The four structures are stationary points for all methods, and frequency calculations carried out at the HF level confirm them as minima. The results from ab initio calculations are also shown in Tables 6 and 7.

All ab initio methods provide similar structures, which show the same tendencies as those observed for the dimer, i.e., somewhat larger intermolecular distances for the HF method and almost equal results for MP2 and DFT/B3LYP methods. In general, a shortening of intermolecular distances with respect to the values obtained for the dimer could be understood as a consequence of stronger interactions. The distance between oxygen atoms decreases and, in addition, the intermolecular distance between the atoms that participate in hydrogen bonds also decreases. For the structures shown in Figure 4, the molecules tend to adopt configurations similar to those of the minima of the dimer: for instance, structure **3a** could be viewed as a combination of structures **M1** and **M2** shown in Figure 3. As regards the interaction energies, the values obtained for the structures in Figure 4 are rather similar, and the maximum difference is less than 10 kJ/mol. The HF-calculated binding energies are greatly underestimated, with differences of about 15−20 kJ/mol with respect to the MP2 results, and this again provides evidence for the need to take correlations into account for a proper description of these systems. As for the dimer, DFT/B3LYP and MP2 results are essentially coincident, though DFT always gives larger binding energies. The tendency to form the maximum possible number of hydrogen bonds, especially of the X−H···N type, can also be appreciated for the minima of the trimer, and all structures presented in Figure 4 form at least two X−H···N hydrogen bonds.

The results obtained with the potential function described above for the interaction energies and structures are rather similar to ab initio results obtained with the MP2 and DFT/B3LYP methods and are much better than HF values. However, the order of stability of complexes **3c** and **3d** is reversed (as also happens for HF between **3b** and **3d**). The differences are especially apparent for configuration **3b**, whose binding energy is overestimated by the function. A closer inspection suggests that the problem arises from a slightly underestimated repulsion energy. This is a result of the conditions under which the fitting was carried out: a good fit for the regions of the potential surface close to the minima of the dimer is ensured, but larger errors have to be assumed for other regions of the potential. Despite this problem, we believe that the proposed potential function gives a reasonable description of hydroxylamine trimer (the errors in the interaction energies are always less than 10%). We must take into account the facts that ab initio results are

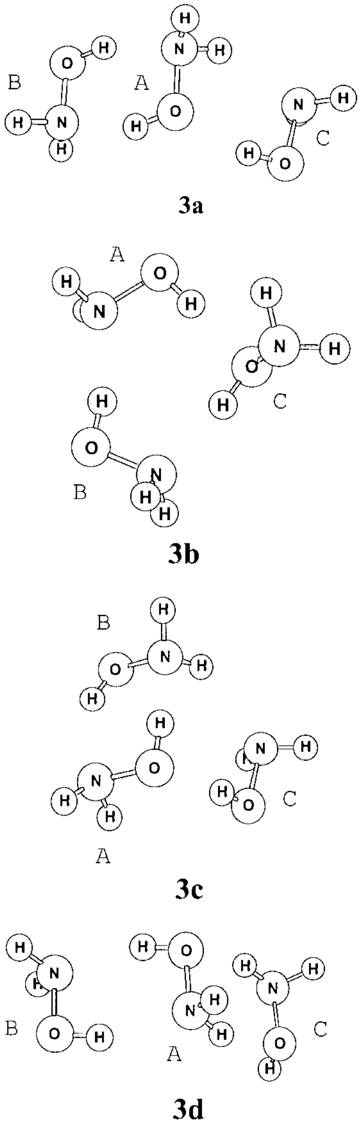


Figure 4. Several minima for the hydroxylamine trimer.

TABLE 7: Minima of the Hydroxylamine Trimer for Structures 3c and 3d (Figure 4)[a–d]

	structure **3c**				structure **3d**			
	function	MP2	HF	DFT	function	MP2	HF	DFT
R_{OO}(AB)	3.307	3.213	3.362	3.230	3.326	3.249	3.403	3.276
R_{OO}(AC)	2.916	2.818	2.930	2.820	3.386	3.275	3.998	3.267
R_{OO}(BC)	4.254	3.673	3.920	3.674	5.357	5.050	5.372	5.093
$R_{X\cdots H}$(AB)	1.893, 2.126	1.830, 1.924	2.019, 2.130	1.883, 1.949	1.979, 1.976	1.877, 1.864	2.055, 2.053	1.928, 1.916
$R_{X\cdots H}$(AC)	*1.960*	*1.969*	*2.099*	*1.976*	*2.224, 2.219*	*2.087, 2.015*	*2.219, 2.188*	*2.094, 2.070*
ΔE	−68.50	−65.58	−46.77	−65.77	−64.99	−65.65	−52.07	−68.55
$\Delta E - E_{pair}$	−1.30	−1.70	−0.42	−1.74	−0.63	−1.66	−0.62	−1.67
μ (D)	0.55	0.68	0.73	0.61	0.64	0.64	0.79	0.65

[a] Distances are given in Å, angles in deg, and energies in kJ/mol. [b] $E_{pair} = E_{AB} + E_{AC} + E_{BC}$. AB, AC, and BC refer to the pair of molecules considered as shown in Figure 4. [c] Results for hydrogen-bonded atoms only. Values in italics: X = oxygen. [d] Interaction energies corrected from BSSE employing the counterpoise method.

also subject to error and that for the C_{2h} minima of the dimer this error is 2 kJ/mol for MP2. For this reason, we can expect that even larger errors occur for the trimer, and thus the results of the function can be viewed with less criticism.

We assessed the magnitude of interactions between more than two bodies by applying the proposed potential function, with the different ab initio methods employed in this work, to the trimer minima. By keeping the molecules in the structures of the trimer minima, we calculated the energy per molecule pair, combined the contributions of all pairs, and finally obtained the difference from the interaction energy for the minimum (Tables 6 and 7). As before, the results obtained at the MP2 and DFT/B3LYP levels are essentially similar, while HF calculations result in a much smaller contribution of nonadditive effects. It can be seen from Tables 6 and 7 that the contribution of nonadditive effects to the total interaction energy calculated at the MP2 level is relatively small, contributing only 1−3 kJ/mol for most structures, and that only for structure **3b** are nonadditive effects much larger, reaching 10 kJ/mol. The results obtained with the proposed potential function show a similar behavior as seen with the HF calculations, i.e., underestimation of the contribution of cooperative effects. A reason for this behavior is that the only term in the function that is not additive by pairs is the induction term, so we neglect all possible nonadditive effects arising from other contributions to the interaction energy. We should also note that the intermolecular distances found with the function are slightly larger than the corresponding ones obtained with correlated methods. Therefore the induction energy will be smaller, leading to a smaller three-body term (three-body effects evaluated at the MP2 level for geometry **3a** obtained with the function amount only to 1.7 kJ/mol, which is in better agreement with the results provided by the potential function).

Once we had checked that the function provided results similar to those ab initio calculations for the dimer and the trimer, we attempted to localize the minima for the hydroxylamine tetramer (Figure 5). A very wide variety of different structural arrangements with similar interaction energies were found, some of which are shown in Figure 5. These minima correspond to quite compact structures and exhibit a considerable number of hydrogen bonds. The energy difference for these structures is less than 4 kJ/mol, and more accurate calculations could change the order of stability of the minima. For the tetramer, the contributions of nonadditive effects obtained with the function amount to 4, 2, 4, 2, and 2 kJ/mol for structures **4a**−**e**, respectively. For both the trimer and tetramer, the contributions are small and only account for a low proportion of the total energy; however, they increase as the number of molecules increases, and so they might eventually become substantial for a system comprising a sufficiently large number of units (e.g., in the simulation of a liquid by molecular dynamics or the Monte Carlo method).

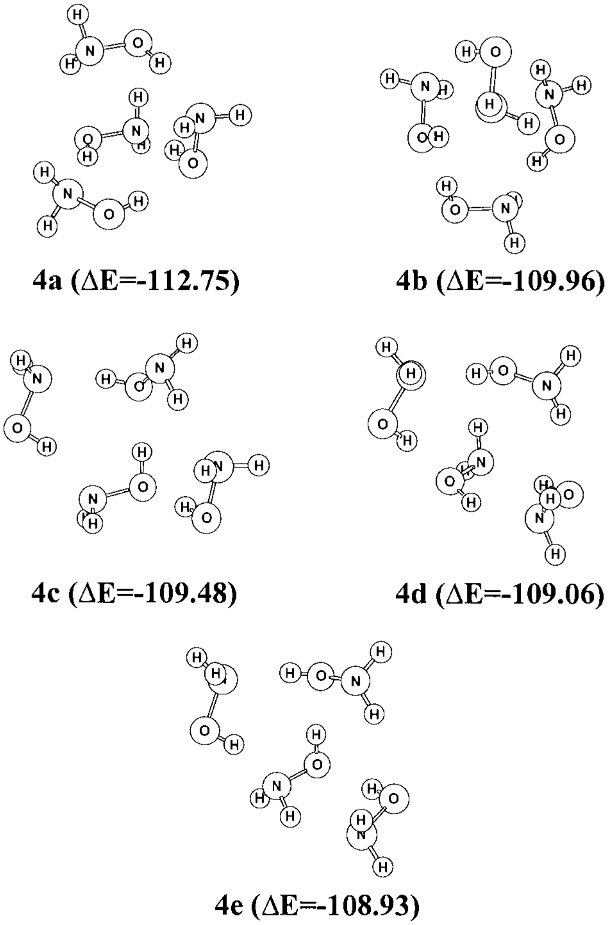

4a (ΔE=-112.75) **4b (ΔE=-109.96)**
4c (ΔE=-109.48) **4d (ΔE=-109.06)**
4e (ΔE=-108.93)

Figure 5. Most attractive minima for the hydroxylamine tetramer. Energies are in kJ/mol.

4. Conclusions

We have developed an analytical function that accurately reproduces some properties of the hydroxylamine dimer and trimer. The function is based on ab initio determined properties of the monomer and IMPT calculations for more than 400 dimer configurations.

We have identified four possible minima for the dimer corresponding to situations that allow for hydrogen bonding. The properties of these minima predicted by the proposed potential function are consistent with those obtained using the same basis set at the MP2 and DFT/B3LYP levels. HF methods cannot be used to describe the interaction between two hydroxylamine molecules because they provide grossly underestimated binding energies. On the other hand, the structures and interaction energies corresponding to the dimer and trimer of hydroxylamine are predicted by the DFT/B3LYP method with a quality similar to that of MP2 calculations. The interaction is largely governed by the electrostatic component, followed by the repulsive component and, to a much lesser extent, the dispersion and induction contributions. On the basis of the results, the most favorable geometries are those with the largest possible number of X−H···N hydrogen bonds.

The function allowed the identification of at least four minima for the trimer, with results similar to those of DFT/B3LYP and MP2 calculations, though the results are not as accurate as those for the dimer and larger differences appear with respect to the MP2 results. Once again, HF computations failed to quantitatively describe the characteristics of the interaction. The potential function predicts a variety of minima for the hydroxylamine tetramer with close interaction energies, and these correspond to structures where the formation of a large number of hydrogen bonds is favored.

In summary, the proposed potential function describes, in a sufficiently accurate manner, the properties of the interaction between hydroxylamine molecules, with results similar to those of ab initio calculations.

Clearly, the function could be improved in some of its terms—with a higher computational investment. Specifically, some problems were detected in the repulsion term, but the attempts carried out to overcome this problem did not lead to significant improvements. Also, a more appropriate function for the dispersive term and a more accurate treatment of the inductive term might lead to significantly improved results. In any case, the results show that the strategy used in developing the potential function was successful. Indeed, the function describes accurately the interaction between hydroxylamine molecules and could be implemented, either as in this work or after some simplifications, in studies of larger clusters or in molecular dynamics or Monte Carlo simulations in order to improve existing knowledge on the properties of liquid hydroxylamine.

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