

# Nitrogen and Sulfur Compounds in Atmospheric Aerosols: A New Parametrization of Polarized Molecular Orbital Model Chemistry and Its Validation against Converged CCSD(T) Calculations for Large Clusters

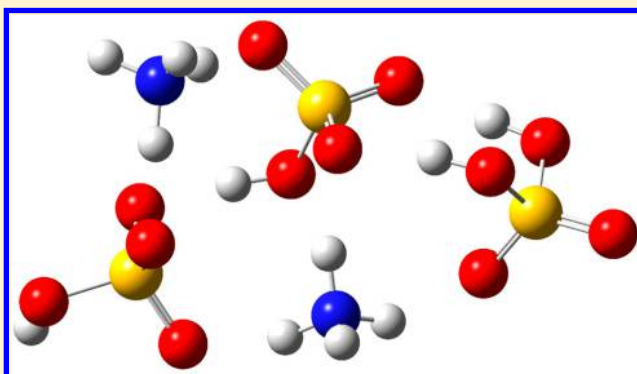
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## S Supporting Information

**ABSTRACT:** The parametrization of the polarized molecular orbital (PMO) method, which is a neglect-of-diatomic-differential-overlap (NDDO) semiempirical method that includes polarization functions on hydrogens, is extended to include the constituents that dominate the nucleation of atmospheric aerosols, including ammonia, sulfuric acid, and water. The parametrization and validation are based mainly on CCSD(T)/CBS results for atmospheric clusters composed of sulfuric acid, dimethylamine, and ammonia and on M06-2X exchange-correlation functional calculations for other constituents of the atmospheric aerosols. The resulting model, called PMO2a, is parametrized for molecules containing any type of H, C, or O, amino or ammonium N, and S atoms bonded to O. The new method gives greatly improved electric polarization compared to any other member of the family of NDDO methods. In addition, PMO2a is shown to outperform previous NDDO methods for atomization energies and atmospheric aerosol reaction energies; therefore, its use can be recommended for realistic simulations.



## 1. INTRODUCTION

Atmospheric nucleation is of current interest in atmospheric chemistry, because of the importance of the role of aerosol particles in understanding global climate regulation. Aerosols in the atmospheric boundary layer play a role in climate through dispersion of solar energy and cloud formation via nucleation. The conversion from gas clusters to particles is believed to be strongly promoted by the presence of sulfuric acid molecules.<sup>1–3</sup> In addition, it is thought that organic amines, such as dimethylamine,<sup>4</sup> also contribute to atmospheric aerosol formation. To understand these issues better, it is desirable to have a model that may accurately predict the chemical energetics of the constituents of atmospheric aerosols.

Molecular simulations of the clusters that constitute atmospheric aerosols require a potential energy function. Potential energy functions for some problems may be represented by molecular mechanics methods, but these methods (or at least standard molecular mechanics) do not include polarization and do not handle chemical reactivity; therefore, we will consider obtaining the potential energy function by electronic structure methods. The most reliable electronic structure methods are limited in applicability, because of the cost of the computations steeply increasing

with system size, scaling unfavorably as the size of the gas cluster grows. Even density functional calculations, despite their favorable accuracy-to-cost ratio, can be prohibitively expensive for full direct dynamics simulations. Semiempirical methods employing neglect of diatomic differential overlap (NDDO),<sup>5,6</sup> such as AM1<sup>7</sup> and PM6,<sup>8</sup> whose computational effort scales approximately as  $N^3$  ( $N$  being the number of basis functions used in the model, where, for a given stoichiometry, the number of basis functions is proportional to the number of atoms) with a relatively low prefactor, offer a possible compromise. With general parameters, they are less accurate than density functional calculations, but they offer orders-of-magnitude-faster computational speed, and with parameters optimized for a specific range of systems, their accuracy can be improved.

As mentioned above, one of the major reasons to use quantum mechanical electronic structure methods rather than molecular mechanics is the ability of quantum methods to treat systems along the pathway of a chemical reaction. Another reason to prefer quantum mechanical methods is that they

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**Table 1.** CCSD(T)/CBS Binding Energies, Compared to Results Obtained by Less-Accurate Methods and the Mean Unsigned Error (MUE) of Each Method

	Binding Energies (kcal/mol)						
method	1A1D	2A1N	2A2D	3A2N	3A3D	4A3N	mean unsigned error, MUE (kcal/mol)
Wave Function Theory with Explicit Correlation Functions							
CCSD(T)/CBS <sup>a</sup>	−24	−46	−84	−93	−145	−144	
iCC/DZ-F12 <sup>b</sup>	−23	−45	−83	−92	−144	−142	0.9
MP2/DZ-F12 <sup>b</sup>	−25	−46	−86	−94	−147	−146	1.1
MP2/TZ-F12 <sup>c</sup>	−25	−46	−86	−95	−147	−147	1.7
Density Functional Theory without Molecular Mechanics Terms							
M06-2X <sup>d</sup>	−22.8	−46.0	−79.7	−92.4	−139.5	−143.2	2.1
PW91 <sup>e</sup>	−23.7	−44.1	−77.3	−89.7	−132.3	−137.6	5.1
Density Functional Theory with Molecular Mechanics Terms							
PW6B95-D3 <sup>e</sup>	−24.1	−45.8	−84.7	−93.5	−146.4	−146.6	0.9
PBE-D3 <sup>e</sup>	−26.2	−47.3	−87.3	−97.8	−151.3	−151.5	4.3
BLYP-D3 <sup>e</sup>	−26.5	−45.8	−91.3	−95.7	−157.6	−148.2	4.9

<sup>a</sup>iCC/TZ-F12 with cc-pVTZ-F12 basis. <sup>b</sup>Basis: cc-pVDZ-F12. <sup>c</sup>Basis: cc-pVTZ-F12. <sup>d</sup>Basis: may-cc-pV(T+d)Z. <sup>e</sup>Basis: MG3S.

<sup>a</sup>iCC/TZ-F12 with cc-pVTZ-F12 basis. <sup>b</sup>Basis: cc-pVDZ-F12. <sup>c</sup>Basis: cc-pVTZ-F12. <sup>d</sup>Basis: may-cc-pV(T+d)Z. <sup>e</sup>Basis: MG3S.

allow for electronic polarization necessary to treat inductive forces, which are very important in condensed-phase systems and clusters. However, conventional NDDO methods have the disadvantage that they systematically underestimate molecular electric polarization. This underestimate was the primary motivation for the development of the polarized molecular orbital (PMO) method,<sup>9</sup> which has solved this problem. The PMO method is distinguished from previous NDDO methods in that it includes polarization basis functions on H atoms, and this has been shown to greatly improve the accuracy of calculated molecular polarizabilities.<sup>10</sup> The PMO method has previously been parametrized for all compounds containing only H and O (PMOv1),<sup>9</sup> reparametrized more specifically for water simulations (PMOw),<sup>11</sup> and extended for all compounds containing only H, C, and O (PMO2).<sup>12</sup>

The purpose of the present work is to develop a new semiempirical method specifically tailored to treating gas-phase clusters of importance for atmospheric aerosol formation, as exemplified by clusters composed of sulfuric acid, dimethylamine, and water molecules, as required to simulate atmospheric aerosols or chemically similar systems. The new method will be called PMO2a, denoting the extension of PMO2 to new functionalities. The chemistry has been expanded from hydrogen, oxygen, and carbon in PMO2 to also include amino nitrogen groups and molecules containing sulfur–oxygen bonds (and so the model, although motivated by the goal of treating atmospheric aerosols, is actually much more general). An accurate treatment of sulfuric acid would ordinarily require d-basis functions on sulfur, but by limiting the present parametrization to the type of sulfur functionality sulfuric acid, bisulfate ion, and SO<sub>3</sub>, we hope to obtain good results without d-functions. Similarly, it is well-known that obtaining accurate semiempirical parameters for nitrogen is very challenging, because of the many different types of functional groups in which it appears (amines, amides, and nitro groups, for example, may require quite different parameters), but by restricting the present parametrization to amines and ammonium functionalities, we hope to obtain acceptable results at reasonable cost. The nitrogen parameters were specifically optimized for ammonia and organic amino groups, and the sulfur parameters were optimized for sulfuric acid, SO<sub>3</sub>, and similar systems.

The data used to parametrize and test the PMO2a method comes mainly from two sources. First, for the important binding energies of clusters composed of sulfuric acid, dimethylamine, and ammonia, the benchmark data comes from coupled cluster theory with a quasi-perturbative treatment of connected triple excitations<sup>13</sup> at the complete basis set limit, as obtained by the incremental method.<sup>14–17</sup> Most of the other data comes from density functional calculations with the M06-2X density functional,<sup>18</sup> which has been well-validated elsewhere.<sup>19–21</sup>

## 2. NEW VALIDATION DATA

A key set of data used for training and validation is a set of clusters made of sulfuric acid, ammonia, and dimethylamine; these clusters are of the type implicated in the formation of atmospheric aerosol particles through clustering of condensable vapors. Six clusters were selected for new benchmark calculations. The clusters are called *x*AyD and *x*AyN, where A denotes H<sub>2</sub>SO<sub>4</sub> (A is for “acid”), D denotes dimethylamine (DMA), and N denotes ammonia (NH<sub>3</sub>); thus, *x*AyD denotes a cluster composed of *x* acid molecules and *y* dimethylamine molecules, and *x*AyN denotes a cluster composed of *x* acid molecules and *y* ammonia molecules; although each cluster has no net charge, in some of them, a proton transfer has occurred, so that often the clusters are actually composed partly of bisulfate ions and ammonium or dimethylammonium ions. Pictures of the clusters are given in a previous paper.<sup>3</sup>

In the previous work, we performed calculations at various levels of ab initio and parametrized wave function theory to obtain more accurate data for the cluster binding energies than was previously available. However, for the largest clusters, we were unable to obtain CCSD(T) results that completely converged, with respect to the basis set. In the present work, we first return to the problem of obtaining accurate data for these clusters. We use a fully automated implementation<sup>16</sup> of the incremental scheme proposed by Stoll<sup>22–24</sup> to obtain CCSD(T) results that are essentially at the complete basis set (CBS) limit; this is a method that has dramatically extended the size of system that can be treated at the CCSD(T) level.<sup>17</sup>

We define the binding energy as the cluster electronic energy (including nuclear repulsion) relative to the energy of separated monomers. The binding energy of each cluster was calculated by the incremental CCSD(T)(F12) method<sup>16,25</sup> with the cc-

pVTZ-F12 basis set.<sup>26</sup> This method essentially yields the complete basis set limit of CCSD(T), and so we denote it as CCSD(T)/CBS. The explicitly correlated<sup>27</sup> CCSD(T)(F12) calculations were performed using ansatz 2, approximation B<sup>28</sup> and the fixed amplitude approach.<sup>29</sup> The Hartree–Fock energies were corrected with the CABS singles method.<sup>30</sup> The results are given in Table 1. The table shows results by the incremental CCSD(T)(F12) method with the cc-pVTZ-F12 basis set and less-accurate results by the MP2-F12 method with the cc-pVTZ-F12 and cc-pVDZ-F12 basis sets. In addition, we make comparisons to some of the density functional results that we reported previously, because these methods can now be tested against more-accurate benchmark data. The functionals employed are M06-2X,<sup>18</sup> PW91,<sup>31</sup> PW6B95-D3,<sup>32,33</sup> PBE-D3,<sup>33,34</sup> and B3LYP-D3.<sup>33,35</sup> The table shows that the M06-2X and PW6B95-D3 methods are best in their respective classes.

### 3. PMO METHODS

The equations describing the new PMO2a are identical to those of the previous PMO2 method<sup>12</sup> for carbon, hydrogen, and oxygen; PMO2a differs from PMO2 only in the parameters. PMO2 (and, hence, PMO2a) includes (by definition) a post-SCF damped dispersion term, as described previously.<sup>36,37</sup> Thus, there are two types of parameters: electronic structure parameters and damped dispersion parameters. Some of these parameters were taken from previous work, and some were optimized here. The present section discusses the optimization of the new parameters.

In order to create the PMO2a method from the existing PMO2 method (which was parametrized only for the elements hydrogen, carbon, and oxygen), it was necessary to extend the parametrization based on a training set of selected molecules containing the elements nitrogen and sulfur. In particular, the new method was required to accurately calculate several properties, namely, vertical ionization potentials, dipole moments, electric polarizabilities, geometries, atomization energies, and reaction energies, for the molecules such as sulfuric acid, ammonia, and dimethylamine. We include only N atoms with sp<sup>3</sup> hybridization and only S atoms that are only bonded to O. In testing methods for geometries, we do not directly use the bond distances, bond angles, and torsion angles, but rather we minimize the gradient per coordinate for each set of input geometries that provide reasonable approximations to the equilibrium geometries of selected molecules. In considering atomization energies, we always work with them as atomization energy per bond (AEPB). In addition to neutral system geometries, we consider the gradients per coordinate for ammonium ion, dimethylammonium, and the bisulfate ion. Finally we consider reaction energies of several complexes containing these molecules and ions and five other amines in protonated and unprotonated form plus water and hydronium.

The parametrization of the PMO2a method was mainly carried out using a genetic algorithm (GA) with an embedded version of the semiempirical program MOPAC-5.020mn.<sup>38</sup> The genetic algorithm program is a locally modified and parallelized version of Carroll's code,<sup>39</sup> which was originally a single-processor program, but that has here been parallelized for faster calculations. The parallelization enables great gains in the speed of execution of the genetic algorithm by dedicating a single processor to each of the individuals in the genetic algorithm population. The aim of the parametrization was to improve over existing semiempirical methods for calculations on the types of clusters that occur in atmospheric aerosols (for

example, clusters of water, sulfuric acid, ammonia, dimethylamine, bisulfate, and ammonium), but the resulting model should be useful for any compound containing H, C, N, O, and/or S, provided the nitrogens are all sp<sup>3</sup> and the sulfurs are only bonded to O. To compare against the existing semiempirical methods, calculations for the dataset considered here were also done by MNDO,<sup>40</sup> AM1,<sup>7,41</sup> PM3,<sup>42</sup> RM1,<sup>43</sup> PM6,<sup>8</sup> PM7,<sup>44</sup> as well as the two explicit-dispersion methods AM1-D and PM3-D (using McNamara and Hillier's parameters<sup>36</sup> for the damped dispersion terms) and the Pairwise Distance Directed Gaussian semiempirical method PDDG/PM3.<sup>45</sup> We note that all of these methods are based on s orbitals on H and s and p orbitals on C, N, O, and S, except PM6 and PM7, which also have a d subshell on S. PMO2a has no d orbitals, but it has a p subshell on H. All calculations for eight of these methods were carried out with MOPAC-5.020mn; the calculations with the ninth method, PM6, were carried out with a combination of MOPAC-5.020mn and Gaussian 09.<sup>46</sup> The calculations with the tenth method, PM7, were performed with MOPAC2012.<sup>47,48</sup>

In order to efficiently optimize the parameters, it is usually necessary to work temporarily with subsets of the entire set of 121 available parameters available. Sensitivity analyses, whereby numerical derivatives were taken of the group property mean unsigned errors (MUEs) and root-mean-square errors (RMSEs), with respect to the variation of individual parameters, were used in order to identify small but influential subsets of parameters to receive special attention. To give more importance to specific properties and reactions during the GA optimization, inverse weights were assigned to them in the calculation of the GA fitness function; this had the desirable effect of allowing a more balanced parametrization. The final choice of parameters was not based on any one number or weighted error or fitness function, but rather on trying to achieve good across-the-board accuracy on the full dataset; ultimately, we had to make a subjective judgment regarding which set of parameters to use as the final parameter set by choosing from among the final parameter sets of a myriad of runs with different parameter seeds, parameter ranges, and data weights.

The structures used for the atmospheric clusters of water, sulfuric acid, dimethylamine, and ammonia come from the work of Leverenz et al.<sup>3</sup> and are labeled according to the number of sulfuric acid molecules (the number preceding A), the number of dimethylamine molecules (the number preceding D), and the number of ammonia molecules (the number preceding N). The water clusters (dimer up through octamer) come from Bryantsev et al.<sup>49</sup> A complete set of geometric information and sources for the structures used during the optimization is given in Tables S4–S7 of the Supporting Information. The target property values in Tables 2–6 came from calculations with the M06-2X density functional<sup>50</sup> and the MG3S basis set,<sup>51</sup> except in the case of water's polarizability and reference structure (both of which came from ref 52).

### 4. RESULTS

**4.1. Parameters for PMO2a.** The monatomic parameters for H and C and the pairwise HH, HC, CC, CO, and OO parameters were fixed from the PMO2 method.<sup>12</sup> Therefore, the new parametrization inherits the performance of PMO2 for hydrocarbons. However, the monatomic O parameters and the pairwise OH parameters were modified, since they play an

Table 2. Vertical Ionization Potentials and Signed Errors

	notes	target ionization potential (eV)	Signed Errors (eV)										rank
			MNDO	AM1	PM3	AM1-D	PM3-D	PDDG/PM3	RM1	PM6	PM7	PMO2a	
H <sub>2</sub> O	<i>a, b</i>	12.78	−1.01	−0.77	−0.70	−0.59	−0.67	−0.45	−0.93	−1.19	−0.85	−0.79	6
NH <sub>3</sub>	<i>a, b</i>	10.96	−0.33	−0.77	−1.33	−0.69	−1.31	−1.23	−1.22	−0.92	−0.64	−0.08	1
H <sub>3</sub> CNH <sub>2</sub>	<i>a, b</i>	9.64	0.24	−0.31	−0.57	−0.29	−0.56	−0.57	−0.75	−0.66	−0.40	0.09	1
(CH <sub>3</sub> ) <sub>2</sub> NH	<i>a, b</i>	9.58	0.54	−0.10	−0.23	−0.10	−0.22	−0.32	−0.55	−0.68	−0.93	−0.02	1
(CH <sub>3</sub> ) <sub>3</sub> N	<i>a, c</i>	8.45	0.77	0.12	0.17	0.10	0.18	0.03	−0.29	−0.59	−0.28	−0.06	2
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	<i>a, c</i>	9.64	0.27	−0.33	−0.59	−0.31	−0.58	−0.61	−0.76	−0.70	−0.44	−0.12	1
<i>t</i> -BuNH <sub>2</sub>	<i>a, c</i>	9.35	0.35	−0.20	−0.38	−0.18	−0.36	−0.40	−0.05	−0.48	−0.27	−0.34	5
HC(O)NH <sub>2</sub>	<i>a, c</i>	10.91	−0.75	−0.86	−1.39	−0.66	−1.36	−1.27	−0.94	−0.73	−0.83	−0.99	7
CH <sub>3</sub> C(O)NH <sub>2</sub>	<i>a, c</i>	10.50	−0.52	−0.68	−1.19	−0.50	−1.16	−1.08	−0.79	−0.54	−0.66	−0.90	7
H <sub>2</sub> SO <sub>4</sub>	<i>a, b</i>	12.12	−0.58	0.02	−0.90	0.44	−0.95	−0.94	0.00	0.53	−0.30	0.75	7
SO <sub>3</sub>	<i>a, b</i>	12.81	−0.51	−0.15	−1.08	0.18	−1.05	−0.99	−0.22	−0.82	−0.87	1.07	9
RMSE			0.58	0.49	0.88	0.42	0.86	0.82	0.70	0.74	0.64	0.62	4
MUE			0.53	0.39	0.78	0.37	0.76	0.72	0.59	0.71	0.59	0.47	3

<sup>a</sup>Target value calculated by M06-2X/MG3S. <sup>b</sup>Used in parametrization (training and validation). <sup>c</sup>Not used in parametrization (validation only).

Table 3. Dipole Moments and Signed Errors<sup>a</sup>

	notes	target dipole moment (debye)	Signed Errors (debye)										rank
			MNDO	AM1	PM3	AM1-D	PM3-D	PDDG/PM3	RM1	PM6	PM7	PMO2a	
H <sub>2</sub> O	<i>b, c</i>	1.85	−0.06	0.00	−0.09	0.17	−0.06	0.00	0.02	0.27	0.29	0.00	1
NH <sub>3</sub>	<i>b, c</i>	1.47	0.27	0.46	0.11	0.57	0.13	0.29	0.52	0.84	0.94	−0.19	3
H <sub>3</sub> CNH <sub>2</sub>	<i>b, c</i>	1.31	0.16	0.34	0.11	0.44	0.13	0.30	0.38	0.81	0.92	0.07	1
(CH <sub>3</sub> ) <sub>2</sub> NH	<i>b, c</i>	1.06	0.19	0.30	0.20	0.41	0.22	0.35	0.31	0.73	0.84	0.22	3
(CH <sub>3</sub> ) <sub>3</sub> N	<i>b, d</i>	0.61	0.47	0.60	0.56	0.71	0.58	0.74	0.61	1.10	1.22	0.48	2
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	<i>b, d</i>	1.30	0.12	0.23	0.06	0.34	0.08	0.21	0.26	0.62	0.72	0.05	1
<i>t</i> -BuNH <sub>2</sub>	<i>b, d</i>	1.23	0.14	0.24	0.10	0.34	0.12	0.23	0.28	0.59	0.70	0.35	8
HC(O)NH <sub>2</sub>	<i>b, d</i>	3.73	−0.32	−0.18	−0.13	0.08	−0.10	−0.12	−0.16	0.42	0.35	−0.50	10
CH <sub>3</sub> C(O)NH <sub>2</sub>	<i>b, d</i>	3.68	−0.30	−0.18	−0.07	0.10	−0.04	−0.05	−0.11	0.46	0.39	−0.38	8
H <sub>2</sub> SO <sub>4</sub>	<i>b, c</i>	3.10	−0.20	−0.58	−0.20	−0.48	−0.19	0.16	−0.32	−0.10	−0.12	−0.17	4
RMSE			0.25	0.36	0.21	0.41	0.22	0.31	0.34	0.66	0.73	0.29	4
MUE			0.22	0.31	0.16	0.36	0.17	0.25	0.30	0.59	0.65	0.24	4

<sup>a</sup>SO<sub>3</sub> is not included in this table, because its dipole moment is zero by symmetry. <sup>b</sup>Target value calculated by M06-2X/MG3S. <sup>c</sup>Used in parametrization (training and validation). <sup>d</sup>Not used in parametrization (validation only).

important role in sulfuric acid and in hydrogen bonding and proton transfer in the atmospheric clusters.

The notation used for parameters is the same as in previous work.<sup>12</sup> The monatomic parameters for N, O, and S are given in Table S1 in the Supporting Information. The new pairwise resonance term parameters are given in Table S2 in the Supporting Information, and the core–core interaction parameters are given in Table S3 in the Supporting Information. As in the previous PMO2 method, the damped dispersion parameters that are used for all elements employ the same functional form as used by McNamara and Hillier<sup>36</sup> and use the parameters given by Grimme.<sup>37</sup>

**4.2. Performance of PMO2a.** The molecules in the dataset were selected to represent the type of molecules relevant to the atmospheric clusters of interest, in particular clusters containing sulfuric acid, dimethylamine, ammonia, and water. Because sulfuric acid may be considered to be a complex of SO<sub>3</sub> and water, we also included SO<sub>3</sub> in order to obtain the best set of S–O bonding parameters, while leaving out SO<sub>2</sub> and compounds containing H–H, C–S, or N–S bonds.

Tables 2–6 show the target property values and signed errors for the various semiempirical methods for the ionization potentials, dipole moments, polarizabilities, atomization energies per bond, and gradients per Cartesian coordinate, respectively; Table 7 shows the target values and signed errors for the same methods for various chemical reactions involving the compounds included in Tables 2–6. Note that all energetic properties (bond energies and reaction energies) in this paper are internal energies (not enthalpy changes); neither the reference value nor the calculated values contain zero point energy. All of the calculations in Tables 2–6 are based on the same set of geometries as specified at the end of section 3, with full sets of coordinates given in the Supporting Information. The ionization potentials in Table 2 come from energy differences between the ground state and the first excited state of each molecule (i.e., the vertical ionization potential).

The rank of the new PMO2a method among the 10 methods considered is given in the rank column of each table. In other words, a “1” in the last column indicates that PMO2a has the smallest absolute magnitude of the error (called “unsigned error” for brevity) among the 10 NDDO methods considered,



Table 4. Polarizabilities and Signed Errors

	notes	target polarizability (Å <sup>3</sup> )	Signed Errors (Å <sup>3</sup> )										rank
			MNDO	AM1	PM3	AM1-D	PM3-D	PDDG/PM3	RM1	PM6	PM7 <sup>a</sup>	PMO2a	
H <sub>2</sub> O	ref 52, c	1.45	−0.99	−0.95	−0.93	−0.98	−0.93	−0.96	−0.94	−1.04	−0.92	−0.12	1
NH <sub>3</sub>	b, c	2.81	−1.99	−1.96	−1.89	−1.99	−1.90	−1.92	−1.99	−2.10	−1.87	−0.62	1
H <sub>3</sub> CNH <sub>2</sub>	b, c	4.01	−1.97	−1.89	−1.99	−1.93	−2.00	−2.06	−1.92	−2.26	−1.16	0.08	1
(CH <sub>3</sub> ) <sub>2</sub> NH	b, c	5.36	−2.10	−1.96	−2.24	−2.01	−2.25	−2.33	−1.99	−2.52	−0.58	0.75	2
(CH <sub>3</sub> ) <sub>3</sub> N	b, d	8.15	−3.78	−3.59	−4.04	−3.64	−4.05	−4.13	−3.64	−4.28	−1.47	0.75	1
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	b, d	7.10	−3.98	−3.83	−4.06	−3.87	−4.07	−4.14	−3.92	−4.38	−2.28	−1.26	1
<i>t</i> -BuNH <sub>2</sub>	b, d	8.86	−3.66	−3.41	−3.89	−3.43	−3.90	−3.94	−3.59	−4.23	−0.17	0.51	2
HC(O)NH <sub>2</sub>	b, d	4.08	−1.62	−1.52	−1.32	−1.60	−1.33	−1.38	−1.52	−1.43	−0.56	−0.14	1
CH <sub>3</sub> C(O)NH <sub>2</sub>	b, d	5.67	−2.07	−1.92	−1.87	−1.98	−1.88	−1.93	−1.98	−2.02	−0.03	0.07	2
H <sub>2</sub> SO <sub>4</sub>	b, c	5.05	−1.11	−1.44	−1.49	−1.57	−1.53	−2.43	−1.82	−1.34	0.30	0.07	1
SO <sub>3</sub>	b, c	3.84	−0.69	−1.08	−1.06	−1.15	−1.10	−1.76	−1.34	−0.79	0.66	−0.26	1
RMSE			2.44	2.35	2.52	2.39	2.53	2.67	2.44	2.71	1.14	0.56	1
MUE			2.18	2.14	2.25	2.20	2.27	2.45	2.24	2.40	0.91	0.42	1

<sup>a</sup>PM7 polarizabilities were calculated with MOPAC2012, which automatically includes empirical corrections to the reported values of the polarizability. In order to calculate the polarizability without such corrections, the polarizabilities were evaluated using the numerical second derivative of the total SCF energy of each molecule, with respect to an electric field that is created by positioning two opposing point charges,  $\pm e$ , at 100 Å on opposite sides of the molecule on each coordinate axis in turn. This follows from the following formula for the polarizability matrix components (in atomic units):  $\alpha_{ij} = -(\partial^2 U / \partial E_i \partial E_j)$  as  $|E| \rightarrow 0$ , where  $U$  is the SCF energy, and  $E_i, E_j$  are the components of the electric field along the various axes. (In this way, an almost-homogeneous electric field over the space occupied by the molecule is generated, and when repeating this calculation for ever-greater origin-to-point-charge distances, one can verify the convergence to the asymptotic average polarizability value, where the average polarizability is defined as one-third of the trace of the diagonal polarizability matrix elements:  $\alpha_{\text{average}} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ .) <sup>b</sup>Target value calculated by M06-2X/MG3S. <sup>c</sup>Used in parametrization (training and validation). <sup>d</sup>Not used in parametrization (validation only).

Table 5. Atomization Energies Per Bond and Signed Errors

	notes	target atomization energy (kcal/mol per bond)	Signed Errors (kcal/mol per bond)										rank
			MNDO	AM1	PM3	AM1-D	PM3-D	PDDG/PM3	RM1	PM6	PM7	PMO2a	
H <sub>2</sub> O	a, b	116.1	−3.96	−4.61	−7.62	50.51	6.45	−7.80	−5.31	−7.12	−5.33	−0.03	1
NH <sub>3</sub>	a, b	98.43	−6.60	−6.36	−7.74	32.41	8.13	−5.19	−6.56	−7.64	−7.43	0.40	1
H <sub>3</sub> CNH <sub>2</sub>	a, b	96.41	−4.77	−5.01	−5.08	19.12	5.18	−4.81	−5.33	−5.58	−5.41	−1.77	1
(CH <sub>3</sub> ) <sub>2</sub> NH	a, b	96.54	−4.92	−5.10	−4.66	14.31	3.97	−4.87	−5.16	−5.29	−5.11	−2.94	1
(CH <sub>3</sub> ) <sub>3</sub> N	a, c	96.58	−5.75	−5.50	−4.71	11.48	3.11	−5.03	−5.36	−5.46	−5.18	−3.56	2
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	a, c	97.34	−4.99	−5.08	−5.14	15.65	2.91	−5.00	−5.30	−5.50	−5.44	−0.43	1
<i>t</i> -BuNH <sub>2</sub>	a, c	97.99	−5.93	−5.52	−5.08	12.26	1.09	−4.66	−4.89	−5.04	−5.19	−0.04	1
HC(O)NH <sub>2</sub>	a, c	113.31	−6.09	−5.03	−5.94	15.70	11.08	−5.46	−4.36	−5.64	−4.98	−3.33	1
CH <sub>3</sub> C(O)NH <sub>2</sub>	a, c	107.93	−5.76	−5.28	−5.51	12.01	6.05	−4.88	−4.25	−4.62	−4.44	−0.58	1
H <sub>2</sub> SO <sub>4</sub>	a, b	98.38	−31.18	−0.73	0.01	−6.30	4.88	−3.24	−1.74	−3.23	−1.37	−1.34	3
SO <sub>3</sub>	a, b	111.28	−54.64	0.83	5.00	−42.10	5.72	−4.18	1.49	1.54	4.05	−1.75	4
RMSE			19.60	4.80	5.48	25.05	5.92	5.12	4.76	5.39	5.09	1.93	1
MUE			12.24	4.46	5.14	21.08	5.32	5.01	4.52	5.15	4.90	1.47	1

<sup>a</sup>Target value calculated by M06-2X/MG3S. <sup>b</sup>Used in parametrization (training and validation). <sup>c</sup>Not used in parametrization (validation only).

and a “10” would imply that it has the largest unsigned error—however, there is only one “10”. The datasets contain a total of 83 data; MNDO has the largest error in 27 cases, AM1-D in 22, PM6 in 10, PM7 in 8, PM3 in 5, PDDG/PM3 in 4, RM1 in 3, and PM3-D in 2; AM1 and PMO2a each have the largest error only once.

The last two rows of the tables are the root-mean-square error (RMSE) and the mean unsigned error (MUE). Tables 2–7 have 12 mean errors (six RMSEs and six MUEs); PMO2a has the smallest mean error (rank 1) in 5 of these 12 cases, the second smallest (rank 2) in 1 case, rank 3 in 1 case, and rank 4 in 5 cases; it never has a rank of worse than 4 out of the 10 methods. [The training set of molecules used for para-

metrization did not contain trimethylamine, ethylamine, *t*-butylamine, formamide, and acetamide, two of which are amides, a class of compounds not included in the training; when these molecules are removed from the tables, the number of cases in which PMO2a ranks first increases from 5 to 7. Although we include amides in the test set, they are believed to play a more minor role than amines in atmospheric nucleation. Thus, the rankings for the smaller set are relevant.] Next, we consider the individual tables in order.

PMO2a performs well for the nitrogen compounds, in terms of ionization potential, but not as well for the other compounds; we included ionization potential because it is an important fundamental property, but of the properties

Table 6. Gradients Per Cartesian Coordinate and Signed Errors

	notes	target gradient (kcal/mol/Å per coordinate)	Signed Errors (kcal/mol/Å per coordinate)										rank
			MNDO	AM1	PM3	AM1-D	PM3-D	PDDG/PM3	RM1	PM6	PM7	PMO2a	
H <sub>2</sub> O	ref 52, <i>b</i>	0.00	4.80	0.62	2.69	27.84	8.34	1.31	0.80	1.11	0.57	0.40	1
NH <sub>3</sub>	<i>a</i> , <i>b</i>	0.00	1.24	2.24	2.30	18.27	6.74	3.88	1.44	0.79	2.09	3.65	7
H <sub>3</sub> CNH <sub>2</sub>	<i>a</i> , <i>b</i>	0.00	2.53	3.61	1.88	9.33	4.26	2.45	1.59	1.88	1.57	2.86	7
NH <sub>4</sub> <sup>+</sup>	<i>a</i> , <i>b</i>	0.00	0.01	0.25	3.62	12.40	7.01	4.61	0.61	0.49	0.49	0.34	3
(CH <sub>3</sub> ) <sub>2</sub> NH	<i>a</i> , <i>b</i>	0.00	1.46	2.40	1.21	5.61	2.33	1.41	0.96	1.78	1.24	1.53	6
(CH <sub>3</sub> ) <sub>3</sub> N	<i>a</i> , <i>c</i>	0.00	1.50	1.89	1.16	3.45	1.50	1.11	1.51	2.06	1.53	0.78	1
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	<i>a</i> , <i>c</i>	0.00	1.78	2.38	1.45	7.21	2.50	1.76	1.14	1.53	1.33	1.55	5
<i>t</i> -BuNH <sub>2</sub>	<i>a</i> , <i>c</i>	0.00	1.38	1.71	1.13	5.19	1.57	1.24	0.63	0.81	0.66	0.97	4
HC(O)NH <sub>2</sub>	<i>a</i> , <i>c</i>	0.00	5.37	6.94	5.10	13.73	6.16	5.40	3.79	3.22	2.86	4.53	4
CH <sub>3</sub> C(O)NH <sub>2</sub>	<i>a</i> , <i>c</i>	0.00	3.36	4.50	3.39	9.48	4.13	3.37	2.38	2.30	2.04	3.26	4
H <sub>2</sub> SO <sub>4</sub>	<i>a</i> , <i>b</i>	0.00	12.53	6.18	5.50	16.11	7.50	6.91	4.80	4.11	2.86	6.78	6
HSO <sub>4</sub> <sup>−</sup>	<i>a</i> , <i>b</i>	0.00	14.83	5.88	4.93	14.73	5.83	3.11	4.34	5.26	4.90	3.65	2
SO <sub>3</sub>	<i>a</i> , <i>b</i>	0.00	22.35	8.30	3.04	4.54	5.99	6.13	3.54	0.58	1.74	0.56	1
RMSE			8.28	4.26	3.14	12.76	5.27	3.67	2.47	2.35	2.11	3.01	4
MUE			5.33	3.55	2.76	10.96	4.77	3.13	2.02	1.92	1.78	2.40	4

<sup>a</sup>Target value calculated by M06-2X/MG3S. <sup>b</sup>Used in parametrization (training and validation). <sup>c</sup>Not used in parametrization (validation only).

considered, it is probably the least relevant for simulations of atmospheric aerosols.

Because the PMO method is designed to give more-accurate induction forces than previous NDDO methods (because of the improved polarizabilities), we believe it is also important to have accurate permanent electric moments, since they are the properties that induce the induced moments. Furthermore, getting the right distribution of charge demonstrates the physicality of the model. Table 3 shows that the PMO2a dipole moments never have absolute errors more than 0.50 debye and rank among the top three for the most relevant aerosol molecules (sulfuric acid, small amines, and water), with the fourth-best MUE and RMSE.

Table 4 shows that, as expected, PMO2a stands out by its excellent polarizabilities, with an error 5.1 times smaller than that of the second-best method, when excluding PM7. The polarizability MUE for PMO2a is 2.2 times better than that for the second-closest method, PM7, although PM7 does rank first on three of the test set molecules. (The new PM7 method has much better polarizabilities than any previous NDDO method except PMO.) For the two important atmospheric cluster molecules, ammonia and dimethylamine, the errors are larger than for the other molecules; however, PMO2a surpasses all of the other NDDO methods (except PM7 in the case of dimethylamine) by a large margin, even for these two compounds.

Table 5 shows that PMO2a is, on average, the best method for atomization energies. Just as for polarizabilities, the margin of superiority is large, with the MUE being 3.0 times smaller than for the second-best method.

The gradient per Cartesian coordinate ( $G$ ) for a given database molecule with coordinates  $(x_i, y_i, z_i)$  ( $i$  runs over all atoms in the molecule) is defined by eq 1, where  $E$  is the self-consistent field energy and  $N$  is the number of atoms in the molecule:

$$G = \frac{\sqrt{\sum_{i=1}^N \left[ \left( \frac{\partial E}{\partial x_i} \right)^2 + \left( \frac{\partial E}{\partial y_i} \right)^2 + \left( \frac{\partial E}{\partial z_i} \right)^2 \right]}}{3N} \quad (1)$$

If the geometries were close to the reference geometries, the gradients would be small. Table 6 shows that PMO2a gives reasonable geometries.

The water clusters used in optimizing the original PMO method are included in Table 7. The abbreviation H<sub>5</sub>O<sub>2</sub><sup>+</sup>(MP) in Table 7 denotes H<sub>5</sub>O<sub>2</sub><sup>+</sup> with  $r_{\text{OO}} = 2.7$  Å and H<sup>+</sup> at the O–O midpoint, which is included to test if the proton transfer barrier is reasonable. Following the water clusters in Table 7 are the nitrogen planarization energy, the ammonia dimerization energy, and three proton transfer energies.<sup>3</sup> Last in Table 7 are the complexation energies of the atmospheric clusters. The atmospheric clusters include both the sulfuric acid–dimethylamine clusters, xAyD, and the sulfuric acid–ammonia clusters, xAyN. So that the influence of the larger atmospheric clusters would not dominate the influence of the small clusters, the complexation energies for the atmospheric clusters were scaled down by a factor according to the number of monomers in each complex, as can be seen in Table 7. The target reaction energy for the first six atmospheric clusters (1A1D through 4A3N) were calculated in the present work using incremental coupled-cluster CCSD(T)(F12) calculations. The binding energy of the final atmospheric cluster (4A4D) was calculated previously<sup>3</sup> using PW6B95/MG3S.

Among the water cluster binding energies, PMO2a is always in the top half of semiempirical methods and has no absolute error of >2.5 kcal/mol. For the planarization energy for ammonia, PMO2a ranks second among semiempirical methods. For the atmospheric cluster binding energies, the PMO2a method ranks first in five of seven cases (second and fourth in the others), and none of its absolute errors exceed 4.94 kcal/mol for any of the atmospheric clusters, whereas each of the other nine NDDO methods has at least one error of >9 kcal/mol.

Table 7 is probably the most important of all the tables for simulations of atmospheric aerosols. The only methods

Table 7. Reaction Energies and Conformational Energy Differences and Signed Errors

reaction	target reaction energy (kcal/mol)	Signed Errors (kcal/mol)										rank
		MNDO	AM1	PM3	AM1-D	PM3-D	PDDG/ PM3	RM1	PM6	PM7	PMO2a	
H <sub>2</sub> O → 1/2(H <sub>2</sub> O) <sub>2</sub>	-2.51	6.06	1.08	1.28	-0.02	0.34	2.08	2.07	0.62	1.19	-0.14	2
H <sub>2</sub> O → 1/3 (H <sub>2</sub> O) <sub>3</sub>	-5.27	18.89	4.59	2.27	-4.03	-1.61	2.83	4.89	1.40	2.93	1.34	1
H <sub>2</sub> O → 1/4(H <sub>2</sub> O) <sub>4</sub>	-6.85	18.10	5.40	2.40	2.42	-0.27	2.58	5.18	1.67	3.51	0.32	2
H <sub>2</sub> O → 1/5(H <sub>2</sub> O) <sub>5</sub>	-7.18	21.23	7.62	3.46	-1.57	-0.82	2.15	5.30	2.28	4.29	1.53	2
H <sub>2</sub> O → 1/6(H <sub>2</sub> O) <sub>6</sub> (book)	-7.63	20.09	5.95	3.16	2.47	0.09	3.52	5.92	2.04	4.06	-0.25	2
H <sub>2</sub> O → 1/6(H <sub>2</sub> O) <sub>6</sub> (cage)	-7.67	20.66	5.00	3.58	1.38	0.30	4.70	6.50	2.02	3.97	-1.68	3
H <sub>2</sub> O → 1/6(H <sub>2</sub> O) <sub>6</sub> (cyclic)	-7.38	18.80	6.57	2.79	3.23	-0.05	2.28	4.98	1.91	3.88	0.83	2
H <sub>2</sub> O → 1/6(H <sub>2</sub> O) <sub>6</sub> (prism)	-7.55	20.30	4.02	3.90	0.40	0.59	5.16	6.32	1.74	3.49	-2.49	4
H <sub>2</sub> O → 1/8(H <sub>2</sub> O) <sub>8</sub>	-9.08	24.26	6.26	4.14	1.82	0.26	5.30	7.52	2.34	4.72	-2.24	3
H <sub>3</sub> O <sub>2</sub> <sup>+</sup> → H <sub>3</sub> O <sub>2</sub> <sup>+</sup> (MP)	9.99	1.85	-4.64	-3.11	17.00	3.36	-6.48	-0.44	-8.82	-7.13	-2.08	3
H <sub>3</sub> O <sub>2</sub> <sup>+</sup> (r <sub>OO</sub> = 2.7 Å) → H <sub>3</sub> O <sub>2</sub> <sup>+</sup> (MP)	5.27	9.75	1.24	8.58	15.21	11.60	3.14	-2.63	-7.48	-6.25	4.08	4
H <sub>3</sub> CNH <sub>2</sub> + H <sub>3</sub> O <sup>+</sup> → H <sub>3</sub> CNH <sub>3</sub> <sup>+</sup> + H <sub>2</sub> O	-51.83	25.25	1.99	-3.34	7.80	-6.01	-1.08	-2.48	1.34	-2.79	20.93	9
NH <sub>3</sub> (pyramidal) → NH <sub>3</sub> (planar)	5.00	-17.90	-10.89	-16.09	-11.71	-15.93	5.27	-5.89	-11.88	-0.12	0.65	2
(NH <sub>3</sub> ) <sub>2</sub> → 2NH <sub>3</sub>	3.15	-6.44	-2.65	-3.34	-0.94	-1.21	-4.00	-2.23	-0.89	-0.51	-0.61	2
NH <sub>3</sub> + H <sub>3</sub> O <sup>+</sup> → NH <sub>4</sub> <sup>+</sup> + H <sub>2</sub> O	-39.09	14.76	-8.49	-17.13	3.38	-19.18	-12.15	-14.17	-5.01	-9.92	14.91	8
H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O → HSO <sub>4</sub> <sup>-</sup> + H <sub>3</sub> O <sup>+</sup>	145.38	3.08	9.12	24.91	13.69	24.59	31.26	-6.14	2.18	17.70	-18.16	7
NH <sub>3</sub> + H <sub>3</sub> CNH <sub>3</sub> <sup>+</sup> → NH <sub>4</sub> <sup>+</sup> + H <sub>3</sub> CNH <sub>2</sub>	12.74	-10.49	-10.48	-13.79	-4.42	-13.17	-11.07	-11.69	-6.35	-7.13	-6.03	2
H <sub>2</sub> SO <sub>4</sub> + NH <sub>3</sub> → HSO <sub>4</sub> <sup>-</sup> + NH <sub>4</sub> <sup>+</sup>	106.29	17.84	0.63	7.78	17.07	5.41	19.11	-20.31	-2.83	7.78	-3.26	3
H <sub>2</sub> SO <sub>4</sub> → H <sub>2</sub> O + SO <sub>3</sub>	24.24	-15.25	2.35	0.32	-12.49	-0.80	8.69	-4.25	-9.65	-9.70	-2.70	4
H <sub>2</sub> SO <sub>4</sub> + H <sub>3</sub> CNH <sub>2</sub> → HSO <sub>4</sub> <sup>-</sup> + H <sub>3</sub> CNH <sub>3</sub> <sup>+</sup>	93.55	28.33	11.11	21.57	21.49	18.58	30.18	-8.62	3.52	14.91	2.77	1
1/2[1A1D → H <sub>2</sub> SO <sub>4</sub> + (CH <sub>3</sub> ) <sub>2</sub> NH]	11.83	-34.70	-18.73	-18.03	-18.39	-13.68	-14.63	-6.47	-6.03	-4.73	-3.44	1
1/3[2A1N → 2H <sub>2</sub> SO <sub>4</sub> + NH <sub>3</sub> ]	15.22	-33.44	-15.24	-10.15	-14.18	-4.11	-2.36	-1.59	-4.80	2.99	3.74	4
1/4[2A2D → 2H <sub>2</sub> SO <sub>4</sub> + 2(CH <sub>3</sub> ) <sub>2</sub> NH]	20.97	-40.02	-19.60	-19.34	-16.40	-12.96	-16.25	-9.89	-8.98	2.25	-4.94	2
1/5[3A2N → 3H <sub>2</sub> SO <sub>4</sub> + 2NH <sub>3</sub> ]	18.64	-37.26	-14.64	-10.00	-12.90	-2.87	-4.18	-2.51	-4.56	7.19	2.26	1
1/6[3A3D → 3H <sub>2</sub> SO <sub>4</sub> + 3(CH <sub>3</sub> ) <sub>2</sub> NH]	24.18	-49.12	-22.97	-21.74	-17.95	-13.39	-15.49	-11.41	-10.51	4.82	-2.14	1
1/7[4A3N → 4H <sub>2</sub> SO <sub>4</sub> + 3NH <sub>3</sub> ]	20.59	-42.24	-14.80	-12.62	-12.65	-4.57	-6.42	-3.38	-4.74	9.15	2.40	1
1/8[4A4D → 4H <sub>2</sub> SO <sub>4</sub> + 4(CH <sub>3</sub> ) <sub>2</sub> NH]	25.44	-48.95	-22.06	-21.52	-16.28	-12.60	-16.04	-11.94	-10.41	6.93	-3.45	1
RMSE		25.86	10.94	12.29	11.57	10.00	11.95	7.81	5.75	6.95	6.58	2
MUE		22.41	8.82	9.64	9.31	6.98	8.83	6.47	4.67	5.71	4.05	1

competitive with PMO2a for the reactions in Table 7 are PM6 and PM7, but PM6 and PM7 have much larger errors than PMO2a for polarizabilities, dipole moments, and atomization energies.

One concern during parameter optimization was that the geometry around the N atoms in ammonia and dimethylamine could become overly planar during geometry optimization of these molecules. This prompted a check of the geometries around the N atoms in ammonia, methylamine, and dimethylamine, where all degrees of freedom were frozen except those surrounding the N atom. The final PMO2a geometry-optimized bond angles around nitrogen are given for several compounds in Table 8 and compared to their target values

**Table 8. Geometry Optimization of Bond Angles at Nitrogen**

molecule	bond angle	target	PMO2a	deviation
NH <sub>3</sub>	H2–N1–H3	106.7°	108.2°	1.5°
	H2–N1–H4	106.7°	108.2°	1.5°
	H3–N1–H4	106.7°	108.2°	1.5°
H <sub>3</sub> CNH <sub>2</sub>	H2–N1–H3	106.6°	103.9°	–2.7°
	H2–N1–C4	110.3°	106.4°	–3.9°
	H3–N1–C4	110.3°	106.4°	–3.9°
(CH <sub>3</sub> ) <sub>2</sub> NH	C2–N1–C3	111.8°	115.3°	3.5°
	C2–N1–H4	107.0°	103.5°	–3.5°
	C3–N1–H4	107.0°	103.5°	–3.5°

using their reference geometries, which can be found in the Supporting Information. In each case, the bond angles around the N atoms deviate no more than 4° from their target values, so no serious distortions are occurring (particularly planarization) to the geometry about the N atoms in ammonia and the two amino compounds.

The PMO2a errors of proton transfer energies of selected molecules that are of interest in atmospheric nucleation were calculated and are given in Table 9. Each molecule serves as both proton donor (D–H<sup>+</sup>) and acceptor (A) in a reaction of the type: D–H<sup>+</sup> + A → D + A–H<sup>+</sup>. The corresponding proton transfer energy MUEs are given in Table 10, wherein the MUEs of all the proton transfer reactions in Table 9 are presented for

all 10 NDDO methods, arranged by proton donor. We see that PMO2a is inaccurate for proton transfers from H<sub>3</sub>O<sup>+</sup> but otherwise has reasonable accuracy for proton transfers. Despite the inaccurate results for proton transfers from H<sub>3</sub>O<sup>+</sup>, PMO2a is significantly outperformed only by PM6 and PM7 when MUEs for the entire set of all the proton transfers are considered.

With the exception of PM6, PMO2a compares very favorably against the other semiempirical methods for estimating proton transfer energies as seen in Table 10. The PMO2a proton transfer energy MUEs rank in the top half among the set of 10 semiempirical methods (and never in last place) in Table 10 for 7 of the 9 classes of proton transfer reactions, and the overall proton transfer energy MUE for PMO2a ranks fourth (behind only PM6, PM7, and RM1).

## 5. DISCUSSION OF NEW PMO METHOD

During parametrization, several individual molecules and properties were difficult to optimize without decreasing the accuracy of other already well-optimized properties. Notably, the ionization potential of SO<sub>3</sub> often presented a problem, because there was a significant tradeoff in its improvement against deterioration in the AEPB errors. There is an anticorrelation between the gradient and the atomization energy per bond, but closing in on reasonably good gradients while simultaneously keeping AEPB errors at acceptably low levels proved a very difficult challenge. The most efficient means we found for dealing with the tradeoff in errors between different properties and/or different subsets of molecules is to perform a sensitivity analysis by varying each parameter a small amount (typically 0.1%) and taking first numerical derivatives of all group property errors, with respect to the parameter value. From this, insights into correlated and offsetting parameters were obtained, and these led to the selection of very efficient small subsets of parameters upon which to concentrate to push the overall errors down.

PMO2a demonstrates its advantages over previous NDDO methods for atmospheric calculations on several fronts. The MUEs for dipole moments, polarizabilities, and atmospheric and water cluster binding energies are better than any of the tested NDDO methods on the set of atmospheric compounds—even better than PM6 and PM7, which uses d orbitals on sulfur.

**Table 9. Proton Transfer Energy Errors between Selected Molecules for PMO2a**

proton acceptor	Proton Transfer Energy Errors <sup>a</sup> (kcal/mol)								
	H <sub>3</sub> O <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	H <sub>2</sub> SO <sub>4</sub>	MA–H <sup>+</sup>	DMA–H <sup>+</sup>	TMA–H <sup>+</sup>	TBA–H <sup>+</sup>	EA–H <sup>+</sup>	DEA–H <sup>+</sup>
H <sub>2</sub> O	0.00	–14.90	–18.16	–20.93	–25.26	–24.81	–8.16	–17.05	–16.29
NH <sub>3</sub>	14.90	0.00	–3.26	–6.03	–10.35	–9.91	6.74	–2.15	–1.39
HSO <sub>4</sub> <sup>–</sup>	18.16	3.26	0.00	–2.77	–7.10	–6.65	10.00	1.11	1.87
MMA	20.93	6.03	2.77	0.00	–4.33	–3.88	12.77	3.88	4.64
DMA	25.26	10.35	7.10	4.33	0.00	0.44	17.10	8.20	8.96
TMA	24.81	9.91	6.65	3.88	–0.44	0.00	16.65	7.76	8.52
TBA	8.16	–6.74	–10.00	–12.77	–17.10	–16.65	0.00	–8.89	–8.13
MEA	17.05	2.15	–1.11	–3.88	–8.20	–7.76	8.89	0.00	0.76
DEA	16.29	1.39	–1.87	–4.64	–8.96	–8.52	8.13	–0.76	0.00
MUE <sup>b</sup>	18.20	6.84	6.37	7.40	10.22	9.83	11.06	6.23	6.32

<sup>a</sup>Errors are shown for various proton donors. Notation: MA = H<sub>3</sub>CNH<sub>2</sub> (methylamine), DMA = H<sub>3</sub>CCH<sub>2</sub>NH (dimethylamine), TMA = (CH<sub>3</sub>)<sub>3</sub>N (trimethylamine), TBA = *t*-BuNH<sub>2</sub> (*t*-butylamine), EA = CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> (ethylamine), and DEA = (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH (diethylamine). <sup>b</sup>The mean unsigned errors (MUEs) reported in this table do not include proton transfers between identical species (e.g., it excludes H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>O → H<sub>2</sub>O + H<sub>3</sub>O<sup>+</sup> in its calculation of the MUE of all H<sub>3</sub>O<sup>+</sup> reactions).



**Table 10.** Comparison of Mean Unsigned Errors of Semiempirical Proton Transfer Energy Mean Unsigned Errors (MUEs) for All PTEs with the Associated Proton Donors

method	Proton Transfer Energy (kcal/mol)									MUE
	H <sub>2</sub> O <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	H <sub>2</sub> SO <sub>4</sub>	MA-H <sup>+</sup>	DMA-H <sup>+</sup>	TMA-H <sup>+</sup>	TBA-H <sup>+</sup>	EA-H <sup>+</sup>	DEA-H <sup>+</sup>	
PMO2a	18.20	6.84	6.37	7.40	10.22	9.83	11.06	6.23	6.32	9.2
MNDO	25.62	16.39	28.32	12.46	14.61	17.26	12.59	12.30	15.09	17.2
AM1	6.79	12.10	12.65	6.41	10.59	13.59	6.35	6.33	8.38	9.2
PM3	9.48	17.55	24.36	9.06	12.39	16.69	9.06	9.23	11.34	13.2
AM1-D	10.20	8.09	22.18	6.43	7.45	8.78	6.31	6.28	7.54	9.3
PM3-D	10.00	18.23	22.97	10.00	11.97	17.19	9.47	9.54	11.86	13.5
PDDG/PM3	8.82	14.95	31.68	8.69	12.21	14.23	8.99	8.83	10.52	13.2
RM1	6.41	16.26	7.75	6.72	7.98	11.43	7.33	7.20	6.89	8.7
PM6	2.90	6.51	3.97	2.74	4.50	4.02	3.34	3.22	2.80	3.8
PM7	5.90	8.72	15.53	5.25	8.19	7.59	5.67	5.47	5.45	7.5

A major intent of parametrizing the present method was to give good electrostatics and induction forces, relative to other semiempirical methods, and this objective was achieved by obtaining very good dipole moments and polarizabilities. In particular, the method distinguishes itself by the far greater accuracy in molecular polarizabilities (MUE of 0.42 Å<sup>3</sup>, compared to the next closest methods, PM7 and AM1, with MUEs of 0.91 Å<sup>3</sup> and 2.14 Å<sup>3</sup>, respectively), a result which is to be attributed to the presence of p orbitals as in all PMO parametrizations (the original motivation for the PMO methods was the improvement of molecular polarizabilities over classical semiempirical methods). For all properties considered in Tables 2–6 and Table 10, the PMO2a method ranks (according to MUE) in the top half of the 10 semiempirical methods considered (actually never ranking lower than fourth out of 10 methods).

Proton transfer energy MUEs for PMO2a rank among the top half of the 10 methods for 6 out of 9 categories (see Table 10). The overall MUE on all proton transfer energies is fourth-best.

The parameters for hydrogen and carbon (both monatomic and pairwise) were left intact in PMO2a, so that PMO2a inherits the good performance of PMO2 for hydrocarbon chemistry.

The optimized geometries of the nitrogen-containing molecules NH<sub>3</sub>, H<sub>3</sub>CNH<sub>2</sub>, and (H<sub>3</sub>C)<sub>2</sub>NH were inspected to ensure no distortion to a completely planar geometry about the N atoms in several compounds in the atmospheric database. The deviation from target HNH bond angles in these compounds turned out to be reasonable (Table 8) and avoids the case of a barrierless inversion from one nitrogen pyramidalized geometry to its inverted pyramidalized geometry.

The test set molecules formamide and acetamide—both amides that were not in the training set—are not representative of the amines and compounds in the training set and, accordingly, have errors that are predictably worse than the other compounds in Tables 2–6. However, their inclusion in the test sets serves to show the limitations of the PMO2a method outside of the amine-promoted nucleation chemistry realm for which the method was developed. However, amides are important in the atmosphere; for example, alkyl amides, like formamide and acetamide, have been shown to be photo-oxidation products of 2-aminoethanol<sup>53</sup> (itself an important atmospheric molecule), and amides are also found in aerosols, such as in urban aerosol samples.<sup>54–56</sup>

The applicability of the PMO2a method to atmospheric clusters and simulations is seen most clearly by examining the

results for the xAyD and xAyN atmospheric clusters included in Table 6. For this most important class of reactions, whose accurate calculation is a top priority for the new method, the PMO2a method MUE ranks first among all methods (3.20 kcal/mol versus the second-best MUE from the d-orbital-containing PM7 method of 5.44 kcal/mol). The dipole moments and polarizabilities of PMO2a on the monomers appearing in the atmospheric clusters (Tables 2 and 3) are 0.14 debye and 0.39 Å<sup>3</sup> for PMO2a versus 0.79 debye and 1.75 Å<sup>3</sup> for PM6; thus, while PMO2a is only 13% better than the second-best method for cluster binding energies, it excels in terms of electrostatic and inductive properties on these atmospheric molecules. We conclude that PMO2a should be useful for simulations of atmospheric aerosols composed of sulfuric acid, ammonia and/or amines, and water monomers.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Parameters, structures, and additional tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ NOTE ADDED AFTER ASAP PUBLICATION

This article was published ASAP on July 2, 2014. Footnote (a) in Table 4 has been modified. The correct version was published on July 3, 2014.