J. Phys. Chem. A **2002,** *106,* 363−370

The Hydration of Formic Acid

Simone Aloisio, Paul E. Hintze, and Veronica Vaida*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80307

Received: June 8, 2001; In Final Form: August 27, 2001

We examine organic acids as precursors to aerosol formation. We do this by examining the hydration of formic acid with up to three water molecules. This approach starts at the molecular level, providing insight to the first steps of the processes that result in nucleation. Our methodology involves high-level molecular calculations. We present structures and energetics for these species. Using these methods, we predict a cooperative bonding effect that may be present in other aerosol precursors. This methodology also may provide some insight into the hygroscopic growth of these particles. We discuss some possible atmospheric implications of this work.

Introduction

Atmospheric aerosols play a large part in both atmospheric chemistry and radiative transfer processes. The study of their formation, physical and chemical properties, composition, and their effects on human health is the subject of intense study in a wide range of fields. Organic species have long been known to be a large constituent of many aerosols, as well as of cloudwater and precipitation.[1] A number of recent field measurements have observed[2,3] an unusually large amount of organic species in aerosols, the source of which is thought to be biogenic in remote environments, and of anthropogenic nature in polluted areas. Urban aerosols in particular have been observed[4] to contain up to 40% carbonaceous material, of which two-thirds has been identified as being organic. Over 80 organic compounds have been identified[4] in these aerosols, with about one-half of the total organic mass remaining unidentified.

Formic acid is a major organic constituent in cloud and fogwater, as well as in precipitation.[5] Formic acid is an oxidation product of organics both naturally and anthropogenicly present, as well as being directly emitted anthropogenicly.[6] A significant amount of formic acid in the atmosphere is present in the aqueous phase. Previous studies[7−9] have examined complexes of water and formic acid using both theoretical and experimental methods. Recently, there have been some theoretical studies of hydrated strong acid complexes of sulfuric,[10] nitric,[11] and perchloric[12] acids. One of the main points of those works was to determine how many water molecules were required to “solvate” these strong acids. In these cases, both the molecular and ionized potentials were examined. Ion chemistry has previously been suggested[13,14] as a prenucleation embryo toward the formation of atmospheric aerosols. These theories have arisen due to the discrepancy in the predicted and observed binary homogeneous nucleation rate of sulfuric acid aerosols.[15] The observed rate of nucleation is faster than that predicted by classical theories. Innovative and elegant ideas have contributed to a better understanding of this discrepancy. Researchers have suggested[16] that a species other than H_2SO_4 or H_2O participates in particle production. There has also been work showing[17] that oxidized organics correlate well, in some cases, with particle production. In some cases, organic aerosols can dominate cloud condensation nuclei formation.[18] Recent theories[14,15] have been proposed to account for this type of aerosol formation involving ion complexes.

In this work, we investigate the possibility of organic acid−water complexes acting as prenucleation embryos to aerosol formation. Inspired by the theories involving ion-complexes, we propose a possible neutral-complex species that may be a precursor to aerosol formation. We use formic acid as our test molecule for this examination. We chose formic acid because of its ubiquity[19] in the atmosphere and the lower computational cost of using the simplest organic acid. Our methodology is similar to that employed to examine the hydrated small acid complexes mentioned above. We calculate the structures and energetics of different conformations of $HCOOH-(H_2O)_n$, where $n = 1-3$. The structures and energies of the complexes of formic acid with one water have been well characterized in an excellent work by Rablen et al.[8] Microwave spectroscopic studies[9] of the most stable conformations of formic acid with one and two waters have also been recently carried out. Furthermore, there are infrared frequencies for formic acid complexes with one water reported from matrix isolation experiments.[7] All of these previous studies will provide us with a means for comparing our methodology to what is known. We then compare the properties of these species to analogous complexes composed of only water. Using this approach, we examine the first steps of aerosol formation and hygroscopic growth from the molecular level. We then discuss the possible atmospheric implications of this work.

Computational Methods

All calculations were performed using the GAUSSIAN 98[20] suite of programs. Geometries were optimized using the Becke three-parameter hybrid functional combined with Lee, Yang, and Parr correlation [B3LYP][21] density functional theory method. The largest basis sets for which geometry optimizations were performed is the 6-311++G (d,p). Frequency calculations were also performed at this level of theory. Zero-point energies were computed using the harmonic vibrational frequencies at this level of theory. Zero-point energies taken from these frequency calculations can be assumed to be an upper limit due to the anharmonic nature of the potential energy surface.[22] Single-point energy calculations were performed using these geometries using the 6-311++G(2d,2p) basis set. At this level of theory, the basis-set superposition error is smaller than the intrinsic error in the calculated binding energy. Furthermore, the ordering of energies will be consistent. In their examination

10.1021/jp012190l CCC: $22.00

of over 50 hydrogen bound organic complexes with water, Rablen et al.[8] show that this computational method is at least as reliable as the second-order Møller−Plesset method (MP2) when larger basis sets are used, while being computationally less expensive. Aloisio and Francisco[23] also found this to be the case with other hydrogen-bonded species. In a fine work by Estrin et al.[24] examining water complexes of up to eight water molecules using density functional methods, the researchers found excellent agreement with previous studies for geometries and frequencies and reasonable agreement for relative energies. These earlier studies of water trimer using density functional methods overestimated the binding energies compared to Møller−Plesset and coupled-cluster methods. In a comprehensive, excellent work by Fowler and Schaefer,[25] they calculate the classic binding energy (D_e) of water trimer to be 14.8 kcal mol^{-1} at their best level of theory. As we will show, our calculated value at the highest level of theory is within 0.5 kcal mol^{-1} of this value. Many have pointed to the difficulty in determining the absolute accuracy of these calculations because of the immense task of obtaining reliable experimental data on the thermodynamics of these complexes. The basis set superposition errors were calculated for FAZ1, FAZ11, FAZ111, and all the water-only complexes using the full counterpoise correction.[26] These are listed in parentheses in the tables of the calculated energies. For a good brief summary of this method, the reader can refer to Donaldson.[27] The errors were not included in the calculated binding energy because they are small with respect to the intrinsic errors of the calculations. We have also calculated the single-point energies of the larger complexes using MP2 methods with the 6-311++G(2d,2p) basis set, with the geometries obtained using the density functional theory method. We found that this produced relative energies similar to those calculated at the B3LYP/6-311++G(d,p) level of theory. These provided a reasonable estimate of the intrinsic error in the binding energies. We will provide comparison to experimental data, where available, to validate this method—or at least provide a reference for errors to be assessed accurately. Henceforth, we will discuss only the highest level of theory we calculated for that particular parameter unless otherwise stated. For example, when presenting geometries, we will discuss the calculations done using the B3LYP/6-311++(d,p) method.

Results and Discussion

Our approach to presenting this work is as follows. We will first present the results of the calculations of the monomers, followed by the conformations of formic acid as each water molecule is added. Within each discussion, we will compare some key features of the structure and energetics of these complexes to their analogous species composed of only water. Hence, we will compare a 1:1 formic acid−water complex to the water dimer (denoted W2) and so forth. We will also compare our results to what is already known about formic acid−water complexes from previous works. Then there will be a discussion of how we interpret these results with respect to aerosol formation and hygroscopic growth in the atmosphere.

The structures for the monomers are given in Table 1. We calculate two conformations of formic acid, denoted *Z* and *E*. Both conformations are planer. (*Z*)-Formic acid has the acidic hydrogen aligned toward the oxygen atom of the carbonyl group, while (*E*)-formic acid has the hydrogen atom away from it. (*Z*)-Formic acid is more stable than (*E*)-formic acid[28] by about 4 kcal mol^{-1}. Our calculation of this value is in excellent agreement with this experimental number, with an energy difference between the two conformations of 4.0 kcal mol^{-1} at the B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(d,p) level of theory. This corresponds to a Boltzman population ratio of about 1000 to 1 in favor of the *Z* conformation at room temperature.[29] The calculated harmonic vibrational frequencies for both conformations of formic acid are listed in Table 2. These nonadjusted calculated harmonic frequencies agree within 10% of the experimental data,[29] with most of the frequencies within 5%.

TABLE 1: Geometry Optimization for the Monomers[a]

		B3LYP		
molecule	coordinate	6-31G(d)	6-31++G(d,p)	6-311++G(d,p)
H_2O	O−H	0.969	0.965	0.962
	H−O−H	103.6	105.7	105.0
formic acid (*Z*)	O−H	0.977	0.974	0.971
	C=O	1.205	1.207	1.199
	C−H	1.100	1.098	1.098
	C−O	1.347	1.348	1.346
	H−O−C	106.6	107.8	108.0
	O−C=O	125.2	125.0	125.2
	H−C=O	125.4	125.1	125.2
formic acid (*E*)	O−H	0.972	0.969	0.966
	C=O	1.198	1.200	1.192
	C−H	1.108	1.106	1.105
	C−O	1.353	1.354	1.353
	H−O−C	109.5	110.3	110.0
	O−C=O	122.7	122.4	122.6
	H−C=O	123.9	123.8	123.9

[a] All bond lengths are reported in Ångstroms, all angles are in deg.

TABLE 2: Calculated versus Observed[a] Formic Acid Vibrational Frequencies[b]

		formic acid (*Z*)		formic acid (*E*)	
mode	assignments	calculated	observed	calculated	observed
1	O−H stretch	3738	3550.5	3801	3618
2	C−H stretch	3056	2952.9	2962	2899
3	C=O stretch	1817	1767.2	1861	1808
4	CH rock	1404	1381.0	1419	1396
5	CO−COH def	1293	1215.8	1269	1244
6	COH−CO def	1126	1103.4	1099	1108
7	OCO scissors	678	629.2	660	661
8	CH out-of-plane wag	1052	1037.4	1034	980
9	COH torsion	630	635.2	524	503

[a] Observed frequencies taken from Pettersson et al.[24] [b] All frequencies are reported in cm^{-1}.

HCO_2H-H_2O. We have calculated six conformations of the complex between formic acid and one water molecule. Three of these are with (*Z*)-formic acid and three are with (*E*)-formic acid. Five of these conformations have been previously investigated using theoretical methods,[7,8] and all are shown in Figure 1. The structures reported here agree well with those calculated in these studies. Water can attach to (*Z*)-formic acid in three positions. All of these structures were found to have nonnegative vibrational frequencies. All the calculated vibrational frequencies for the complexes with one water can be found in Table S1 (Supporting Information). The most stable conformation is a cyclic complex (FAZ1), with both the water and the formic acid acting as hydrogen donor and acceptor, resulting in two relatively strong hydrogen bonds. Of the six complexes of formic acid with one water, this is the only one that has been observed experimentally.[7,9] The study by Priem et al.[9] observed this complex using microwave spectroscopy. They also performed ab initio calculations at the MP2/6-311++G(3df,2p) level of theory. Both theoretical structures obtained were similarly nonplaner minima. We compare our calculations to their data in Table 3. Our calculated data are within 2% of the observed rotational constants for this species. This difference may be due to a rapid flipping of the nonplaner hydrogen atom, making the

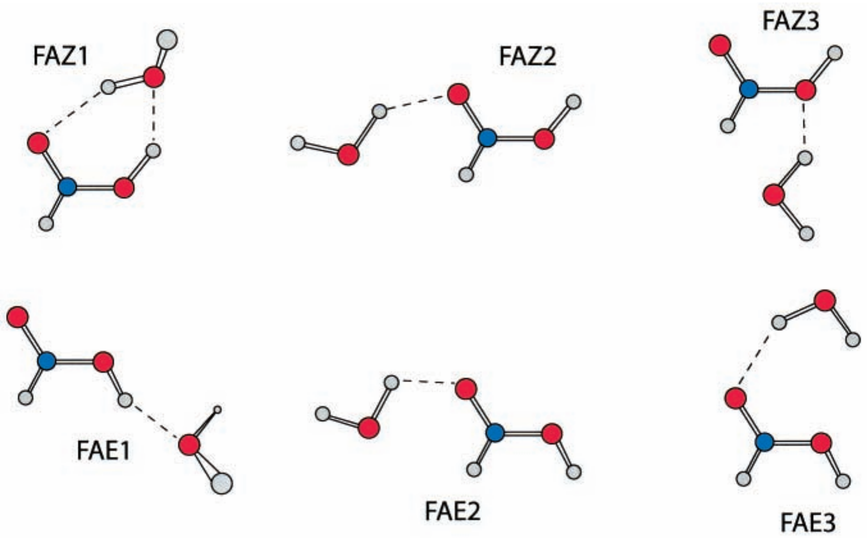

Figure 1. Formic acid complexes with one water molecule. Red atoms are oxygen, blue atoms are carbon, and white atoms are hydrogen. Dashed lines indicate hydrogen bonding.

TABLE 3: Rotational Constants for FAZ1 and FAZ11[a]

	FAZ1			FAZ11		
	Priem et al.[9]			Priem et al.[9]		
	observed	calculated	this work	observed	calculated	this work
A	11848	11853	11792	4698	4775	4716
B	4860	4995	4955	2765	2752	2805
C	3452	3536	3509	1748	1756	1769

[a] Constants are given in MHz.

experimental structure appear to be planer. Åstrand et al.[7] report the only experimentally determined vibrational frequencies for a formic acid−water complex, using matrix isolation spectroscopy. They report fundamental intermolecular modes at 322.8, 274, 202.2, and 167.0 cm^{-1}. These may correspond to our calculated modes at 375, 266, 222, and 168 cm^{-1}. Except the first one mentioned, the calculated frequencies are within 10% of the experimental ones. There is a second conformation (FAZ2) with the water acting as hydrogen donor to the carbonyl oxygen of the formic acid. In FAZ2, the water is situated on the opposite side of the carbonyl group relative to the O−H group. In a third conformation of (*Z*)-formic acid and water (FAZ3), the water acts as a hydrogen donor again, only this time to the oxygen bound to the acidic hydrogen on the formic acid. This is the most weakly bound of the three conformations involving (*Z*)-formic acid. There are another three structures of complexes with (*E*)-formic acid. Of these, FAE1 has no negative vibrational frequencies at all levels of theory. The other two, FAE2 and FAE3, have one calculated negative vibrational frequency at one of the two levels of theory we calculated. For the former, it is using the smaller 6-31G(d) basis set, while for the latter it appears only in the larger 6-311++G(d.p) basis set. This indicates that these structures may not be bound in one coordinate, and hence not a true local minima. In FAE1, formic acid acts as a hydrogen donor to the water in a nearly linear hydrogen bond. In that structure, the hydrogen atoms of water are out-of-plane with respect to the rest of the molecule. In FAE2 and FAE3, the water molecule is a hydrogen donor to the carbonyl group of formic acid. The former has the water in the proximity of the acyl hydrogen, while in the latter it is closer to the hydroxyl group. While FAE2 has been previously reported in the literature,[8] FAE3 has not.

TABLE 4: Formic Acid Bond Distances (in Ångstroms) of HCO_2H-H_2O and $(H_2O)_2$

	B3LYP/6-311++G(d,p)							
	C═O	O−H	H−C	C−O	*R*(1)	*R*(2)	*R*(3)	*R*(w)
FAZ1	1.211	0.989	1.098	1.328	1.790	2.056		
FAZ2	1.206	0.971	1.096	1.338		2.008		
FAZ3	1.198	0.970	1.096	1.358			2.189	
FAE1	1.197	0.978	1.106	1.341	1.813			
FAE2	1.199	0.966	1.103	1.346		2.027		
FAE3	1.196	0.966	1.103	1.348		2.051		
W2								1.932

The optimized geometries of the formic acid complexes with one water are in good agreement with what has been previously calculated.[8,9] As mentioned above, FAZ1 is the only structure that has been studied experimentally,[9] and we have excellent agreement with those results as well. Table 4 lists the bond distances of formic acid,as well as the hydrogen bond distance for the five conformations of formic acid complexed with one water that we present here. It also lists the hydrogen bond distance for the water dimer (W2) for the purpose of comparison and so that we can define the terminology we are using. In FAZ1, there are two hydrogen bonds, *R*(1) and *R*(2). In this work, we will designate hydrogen bonds in which the formic acid is acting as a hydrogen donor to the water as *R*(1) and hydrogen bonds where the water is donating a hydrogen atom to the carbonyl oxygen atom as *R*(2). For FAZ1, these bond distances are 1.790 and 2.056 Å respectively. These are in fairly good agreement with the structure determined by observed moments of inertia by Priem et al.[9] (1.810 and 2.210 Å) and in excellent agreement with the calculations presented both in that work (1.779 and 2.025 Å) and in the work by Rablen et al.[8] (1.775 and 2.016 Å). As one might expect, the *R*(1)-type hydrogen bond is shorter than the *R*(2)-type. Compared to the water dimer, these hydrogen bonds are calculated to be about 7% shorter and 6% longer than that hydrogen bond, *R*(w). These hydrogen bonds perturb the geometry of the formic acid with respect to an isolated formic acid to some extent. In our calculations, the O−H bond in formic acid is elongated by about 2%, and the C═O bond is elongated by about 1% in FAZ1 because of the proximity of the hydrogen bonds to these coordinates. As a result of these bonds being elongated, there is a predicted shortening of the single bond C−O, by a little over 1%. In FAZ2, there is one hydrogen bond of the type *R*(2). This is calculated to be slightly shorter than *R*(2) in FAZ1, with a distance of 2.008 Å. Again, this causes an elongation of the

TABLE 5: Relative Energies[a] (in kcal mol^{-1}) of HCO_2H-H_2O and $(H_2O)_2$ Complexes

complex	B3LYP 6-31G(d)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(2d,2p)	D_0[b]	per H-bond[c]
FAZ1	15.3	10.8	10.3	9.5 (0.3)	7.0	3.5
FAZ2	7.0	5.1	4.9	4.6	3.0	3.0
FAZ3	4.8	3.3	3.2	2.6	1.3	1.3
FAE1	11.0	9.3	9.1	7.9	6.9	6.9
FAE2	7.0	5.7	5.4	5.1	3.4	3.4
FAE3	5.7	4.4	4.2	3.9	2.5	2.5
W2	7.7	6.0	5.8	4.9 (0.2)	2.6	2.6

[a] Basis set superposition error in kcal mol^{-1}. [b] Using energies obtained at B3LYP/6-311++G(2d,2p) level of theory and zero-point-energy calculated at B3LYP/6-311++G(d,p) level. [c] Energy per hydrogen bond, including ZPE.

double bond in formic acid (C═O), this time by almost 1%. In FAZ3, the oxygen atom on the C−O−H group of formic acid acts as a hydrogen acceptor for water. As one might expect, this interaction, $R(3)$, is not terribly strong, with a calculated hydrogen bond length of 2.189 Å. Still, this causes an elongation of singly bonded C−O length of close to 1%. We have also calculated structures for H_2O complexes with $HCO_2H(E)$. The most strongly bound of these complexes, FAE1, has an $R(1)$-type hydrogen bond with a calculated length of 1.813 Å, similar to the analogous bond in FAZ1. As in that structure, the O−H bond of the formic acid is elongated. In FAE1, the carbonyl C═O bond is not hydrogen bonded to the water so that coordinate is not directly effected by the water. In FAE2, there an $R(2)$-type hydrogen bond with a calculated length of 2.008 Å, of a magnitude similar to that of the other $R(2)$-type hydrogen bonds previously discussed. FAE3 has an $R(2)$-type hydrogen bond with a calculated length of 2.051 Å. It is the highest energy structure of all the complexes of formic acid with one water molecule.

In Table 5, we present the relative energies of the complexes between formic acid and one water molecule, as well as of the water dimer. The smallest basis set overestimates the binding energies of these complexes by a large amount. As observed by Rablen et al.[8] however, the ordering of these energies remains consistent. The highest level of theory, B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(d,p) does a fairly good job predicting relative energies. Our calculation of the well depth of water dimer is in agreement with the best estimates[30] to date, about 4.8 kcal mol^{-1}, and are within the error of the experimentally determined value.[31] The most strongly bound complex, FAZ1, has a calculated well depth (D_e) of 9.5 kcal mol^{-1} at the highest level of theory. This is in excellent agreement with the calculations performed previously[8,9] and is consistent with what is seen experimentally. When we add the difference in zero-point-energies, we obtain a binding energy (D_0) of 7.0 kcal mol^{-1}. Table 5 also lists the average energy per hydrogen bond. This is obtained by dividing the binding energy by the number of author-defined hydrogen bonds, which can be seen in the figures of the complexes. For example, FAZ1 has two hydrogen bonds, FAZ2 has one, and so on. The authors are cautious that this value be taken lightly, since the binding energies involve more than just hydrogen bonding interactions. As can be seen in Table 5, FAZ2 has a binding energy similar to that of the water dimer. The well depth of water dimer is calculated to be slightly deeper, but this reverses when the zero-point-energy is taken into account. For FAZ2, D_e is 4.6 kcal mol^{-1}, and D_0 is 3.0 kcal mol^{-1} at the highest level of theory, while for water dimer (W2), D_e is 4.9 kcal mol^{-1}, while D_0 is 2.6 kcal mol^{-1}. In this case, the carbonyl oxygen is shown to be almost as good a hydrogen acceptor as water itself. As one might expect, FAZ3 is the most weakly bound of the complexes with formic acid in the Z configuration. The calculated well depth is 2.6 kcal mol^{-1}, while the binding energy is a mere 1.3 kcal mol^{-1}. This reflects that the hydroxyl group on formic acid is a poor hydrogen acceptor. Of the complexes with the formic acid in the E configuration, FAE1, with the formic acid acting as a hydrogen donor is by far the most strongly bound. The calculated D_e is 7.9 kcal mol^{-1}, while D_0 is 6.9 kcal mol^{-1}. This is relative to (E)-formic acid which is 4.0 kcal mol^{-1} higher in energy than (Z)-formic acid, so FAE1 is about 3.9 kcal mol^{-1} lower in energy than isolated (Z)-formic acid and one water molecule. This large stabilization is probably due to more than just the one hydrogen bond. After all, that hydrogen bond is slightly longer than the calculated $R(1)$-type hydrogen bond in FAZ1. The FAE2 and FAE3 complexes have calculated well depths (D_e) of 4.5 and 3.9 kcal mol^{-1}, similar in magnitude to FAZ2. This puts their energies very close to the energies of the isolated monomers with formic acid in the Z configuration. As mentioned earlier, (Z)-formic acid is about 1000 times more abundant than (E)-formic acid at room temperature. We will focus on the Z configuration of formic acid when calculating structures with more than one water molecule.

$HCO_2H-(H_2O)_2$. We have calculated six complexes of formic acid with two water molecules. All of these have formic acid in the Z configuration and are shown in Figure 2. Of these, FAZ11 has been observed in laboratory experiments using microwave spectroscopy.[9] We list the observed and calculated rotational constants from that work in Table 3. Our calculations of these values for FAZ11 are within 1.5% of experiment.[9] To the best of our knowledge, the other structures have not been investigated. FAZ11 is the most stable of these complexes, forming a cyclic structure. The other structures investigated are formed either by adding a water molecule to a different site on formic acid or by adding to the water molecule already bound to the formic acid. All six resulting complexes have nonnegative frequencies, indicating that they are true local minima. These frequencies are listed in Table S2. Selected geometrical parameters of these complexes are reported in Table 6. From these data, there are two observations we would like to point out. The first is that the trends exhibited in the complexes of formic acid with one water molecule are typically strengthened when another water molecule is added. In FAZ12, for instance, there is an elongation of the carbonyl double bond in the formic acid molecule due to the two hydrogen bonds formed by the water with this oxygen of the formic acid. The FAZ11 structure shows a further elongation of the O−H bond in formic acid, as a result of a much stronger $R(1)$-type hydrogen bond. In fact, the $R(1)$-type hydrogen bond is stronger in all three structures that have it with two waters (FAZ11, FAZ12, and FAZ13) than it is in FAZ1. In FAZ11, this hydrogen bond is exceptionally short, with a bond distance 1.662 Å.

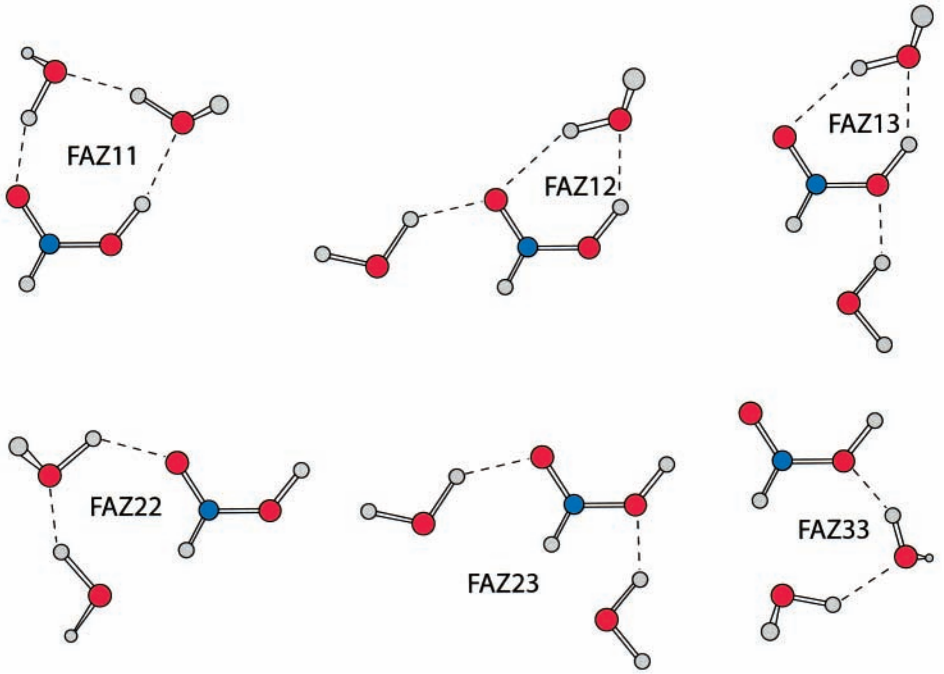

Figure 2. Formic acid complexes with two water molecules. Red atoms are oxygen, blue atoms are carbon, and white atoms are hydrogen. Dashed lines indicate hydrogen bonding.

TABLE 6: Formic Acid Bond Distances (in Ångstroms) of $HCO_2H-(H_2O)_2$ and $(H_2O)_3$

	B3LYP/6-311++G(d,p)								
	C═O	O−H	H−C	C−O	R(1)	R(2)	R(2)′	R(3)	R(w)
FAZ11	1.216	1.003	1.098	1.316	1.662	1.841			1.758
FAZ12	1.218	0.991	1.096	1.320	1.762	2.033	1.958		
FAZ13	1.209	0.991	1.096	1.338	1.764	2.040		2.073	
FAZ22	1.211	0.971	1.097	1.337		1.897			1.860
FAZ23	1.205	0.971	1.094	1.347		1.973		2.460	
FAZ33	1.197	0.971	1.097	1.368				2.001	1.865
W3									1.894
									1.897
									1.919

The second observation is that the formic acid molecule makes water bind more strongly to itself. There are three complexes that have a water−water hydrogen bond, R(w): FAZ11, FAZ22, and FAZ33. These species are similar in structure to the water trimer (W3). If we substitute a water molecule in the trimer with a formic acid molecule, three possible results are the complexes aforementioned. For $(H_2O)_3$, there are three R(w)-type hydrogen bonds with lengths of 1.894, 1.897, and 1.919 Å. The water−water hydrogen bond distances for FAZ11, FAZ22, and FAZ33 are all shorter, 1.758, 1.860, and 1.865 Å, respectively. For FAZ11, this bond distance is about 7% shorter than the shortest R(w)-type hydrogen bond in the water trimer. Even for the more weakly bound FAZ22 and FAZ33, this bond distance is over 2% shorter than the mean hydrogen bond distance in the water trimer. This is somewhat surprising since some of these complexes are of similar binding energy.

The relative energies of complexes $HCO_2H-(H_2O)_2$ and of $(H_2O)_3$ are shown in Table 7. As mentioned earlier, FAZ11 is the structure of formic acid and two water molecules with the lowest energy, with a well depth, D_e, of 25.1 kcal mol^{-1} and a binding energy of 19.8 kcal mol^{-1} at the highest level of theory, B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(d,p). There is an overall strengthening of all the hydrogen bonds in this structure. The average per-hydrogen-bond energy of FAZ11 is 6.6 kcal mol^{-1}, compared to 3.5 kcal mol^{-1} in FAZ1. The FAZ11 structure has an added hydrogen bond of type R(w). A more appropriate comparison would be adding the calculated binding energy of water dimer to that of FAZ1, which would only be about 9.6 kcal mol^{-1}. This, combined with the geometric evidence, infers strongly that adding an additional water molecule stabilizes the complex in FAZ11. This holds true for the other structures as well. FAZ13 has a D_0 of 12.7 kcal mol^{-1}, but the sum of the same values for FAZ1 and FAZ3 is 8.3 kcal mol^{-1}. Of the complexes of formic acid with two water molecules, only FAZ23 has a smaller binding energy than the water trimer.

$HCO_2H-(H_2O)_3$. We have calculated eight structures of complexes of formic acid with three water molecules. These are shown in Figure 3. While there may be more possible structures, we limited our search to ones that are more likely to form, ones that will provide insight into hydrogen bonding, and ones that we can compare to analogous complexes composed of only water molecules. All the structures presented have nonnegative calculated harmonic vibrational frequencies, indicating that they are all true minima. These frequencies are listed in Table S3. To the best of our knowledge, none of these structures have been previously studied either experimentally or using theoretical methods. Selected geometric parameters for these structures are given in Tables 8 and 9. Three of the structures—FAZ111, FAZ222, and FAZ333—are ring-like structures similar to the water tetramer, W4, with a formic acid molecule substituted for a water molecule. Another four structures—FAZ112, FAZ113, FAZ122, and FAZ133—are ring-like species similar to water trimer, with an added water molecule bonded to another formic acid site. The FAZ123 structure has a water molecule on each of the three bonding sites on the formic acid molecule.

In comparing the four-membered ring structures of FAZ111, FAZ222, FAZ333, and W4, it is seen that the ability to make water bond more strongly to itself is somewhat diminished than in the case with the three-membered ring structures. In fact, of these three structures, only FAZ111 has water−water hydrogen bonds that are shorter than those of the tetramer, about 3% shorter. Energetically, this is the most stable structure. The

TABLE 7: Relative Energies[a] (in kcal mol^{-1}) of HCO_2H-$(H_2O)_2$ and $(H_2O)_3$ Complexes

	B3LYP				MP2[b]		
complex	6-31G(d)	6-31++G(d,p)	6-311++G(d,p)	6-311++G(2d,2p)	6-311++G(2d,2p)	D_0[c]	per H-bond[d]
FAZ11	31.1	23.7	22.8	25.1 (0.5)	22.0	19.8	6.6
FAZ12	22.2	16.0	15.3	18.4	15.8	14.0	4.7
FAZ13	20.5	14.5	14.0	16.8	14.5	12.7	4.2
FAZ22	20.5	15.5	14.9	17.6	15.0	13.0	6.5
FAZ23	11.4	8.0	7.7	10.9	8.4	8.1	4.0
FAZ33	17.0	12.5	12.2	14.5	12.3	10.3	5.1
W3	25.5	18.0	17.3	15.2 (0.3)	16.4	9.5	3.2

[a] Basis set superposition error in kcal mol^{-1}. [b] Using geometries calculated at the B3LYP/6-311++G(d,p) level of theory. [c] Using energies obtained at B3LYP/6-311++G(2d,2p) level of theory and zero-point-energy calculated at B3LYP/6-311++G(d,p) level. [d] Energy per hydrogen bond, including ZPE.

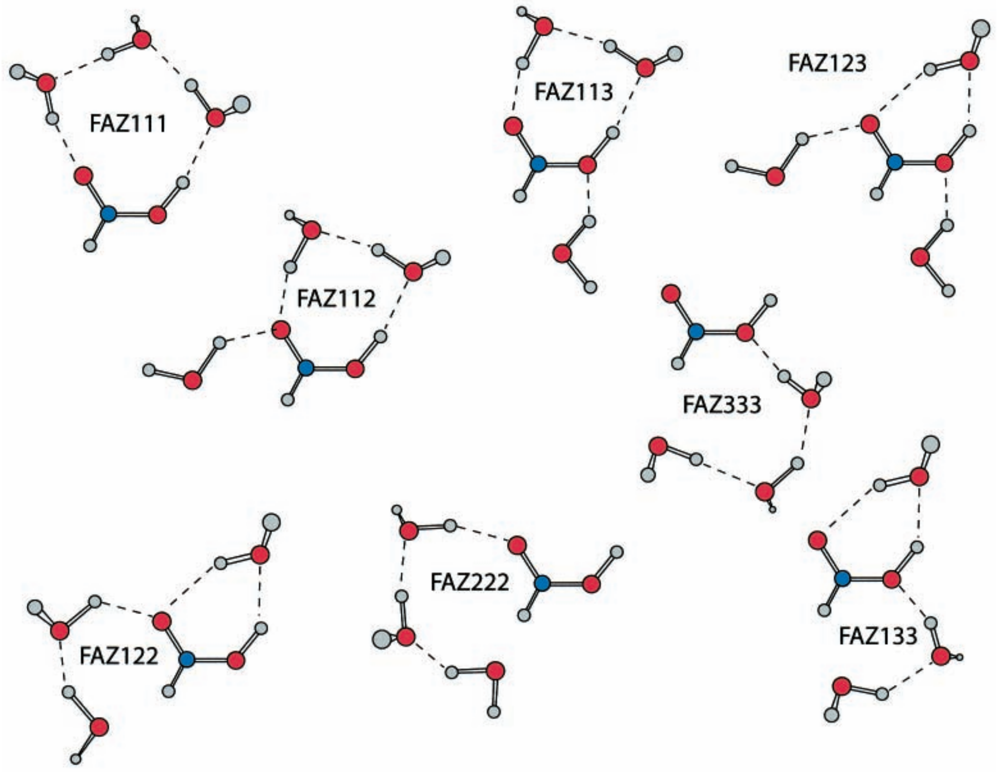

Figure 3. Formic acid complexes with three water molecules. Red atoms are oxygen, blue atoms are carbon, and white atoms are hydrogen. Dashed lines indicate hydrogen bonding.

cooperative bonding that is seen in the other formic acid water complexes continues to be exhibited in these structures. The structures of FAZ111, FAZ112, and FAZ113 have essentially equal $R(1)$-type hydrogen bonds that are the shortest intermolecular bonds in this study. FAZ112, which has a calculated distance of 1.635 Å in this coordinate, is essentially FAZ11 with an additional water molecule attached to the carbonyl oxygen of formic acid. Yet the $R(1)$-type hydrogen bond in this coordinate is significantly shorter in FAZ112 than in FAZ11. Even the hydrogen bonds between the water molecules within these structures is shorter than those in FAZ11, and all four of these formic acid water complexes have shorter water−water hydrogen bonds than those in the water tetramer. The increased cooperative bonding significantly alters the geometry of the formic acid molecule with respect to the isolated monomer. In FAZ112 and FAZ122, the C═O bond length is increased by over 2%, while in FAZ111, FAZ112, and FAZ113, the O−H bond length is increased by nearly 4%. The relatively far-removed C−O bond length can be shortened by nearly 3%, as predicted for the structure of FAZ112. All of these are extensions of trends that are seen in the formic acid complexes with one and two water molecules. Perhaps this effect is most obvious in the FAZ123 structure. This structure has one water molecule at each bonding site, similar to the three complexes of (Z)-formic acid with one water molecule. Every intermolecular bond in

TABLE 8: Formic Acid Bond Distances (in Ångstroms) of HCO_2H−$(H_2O)_3$ and $(H_2O)_4$

	B3LYP/6-311++G(d,p)								
	C═O	O−H	H−C	C−O	$R(1)$	$R(2)$	$R(2)'$	$R(3)$	$R(\mathrm{w})$
FAZ111	1.215	1.006	1.099	1.313	1.637	1.808			1.738 1.714
FAZ112	1.223	1.007	1.097	1.307	1.635	1.861	1.953		1.754
FAZ113	1.213	1.007	1.097	1.325	1.636	1.857		2.028	
FAZ122	1.224	0.99	1.097	1.319	1.774	2.089	1.872		1.864
FAZ123	1.215	0.993	1.095	1.329	1.744	2.045	1.962	2.185	
FAZ133	1.209	0.991	1.097	1.348	1.767	2.057		1.960	1.879
FAZ222	1.213	0.971	1.098	1.337			1.841		1.780 1.802
FAZ333	1.197	0.971	1.098	1.372				1.937	1.809 1.814
W4									1.775 1.777 1.778 1.779

TABLE 9: Relative Energies[a] (in kcal mol^{-1}) of $HCO_2H-(H_2O)_3$ and $(H_2O)_4$ Complexes

complex	B3LYP 6-31G(d)	B3LYP 6-31++G(d,p)	B3LYP 6-311++G(d,p)	B3LYP 6-311++G(2d,2p)	MP2[b] 6-311++G(2d,2p)	D_0[c]	per H-bond[d]
FAZ111	43.1	34.1	32.9	33.8 (1.5)	31.1	26.3	6.6
FAZ112	38.0	28.8	27.6	29.5	27.3	22.7	5.7
FAZ113	36.7	27.7	26.6	28.3	26.3	21.6	5.4
FAZ122	35.4	26.0	25.1	26.9	25.1	19.8	5.0
FAZ123	27.0	19.3	18.6	20.9	19.3	15.4	3.9
FAZ133	32.9	23.9	23.1	24.6	23.2	17.8	4.5
FAZ222	33.0	26.1	25.2	26.5	24.2	19.4	4.9
FAZ333	28.9	22.5	21.8	22.9	21.1	16.2	4.1
W4	42.5	32.1	30.8	27.3 (0.2)	28.7	18.6	4.7

[a] Basis set superposition error in kcal mol^{-1}. [b] Using geometries calculated at the B3LYP/6-311++G(d,p) level of theory. [c] Using energies obtained at B3LYP/6-311++G(2d,2p) level of theory and zero-point-energy calculated at B3LYP/6-311++G(d,p) level. [d] Energy per hydrogen bond, including ZPE.

FAZ123 is shorter than the analogous bond in FAZ1, FAZ2, and FAZ3. To accommodate this, the geometry of the formic acid molecule is altered. This is true even though the FAZ123 structure is one of the more weakly bound of the $HCO_2H-(H_2O)_3$ complexes.

The most stable structure of $HCO_2H-(H_2O)_3$ is FAZ111, with a D_e of 33.8 kcal mol^{-1} and a D_0 of 26.3 kcal mol^{-1}. This amounts to an average hydrogen-bond energy of 6.6 kcal mol^{-1}, which is about the same as FAZ11. The binding energy for FAZ111 is considerably larger than that of FAZ1 added to the water trimer binding energy, 16.5 kcal mol^{-1}. It is also larger than the binding energy of FAZ11 added to that of W2, which is 20.4 kcal mol^{-1}. This shows the continued effect of cooperative bonding. Many of these structures have similar binding energies. FAZ111, FAZ112, and FAZ113 are all within 5 kcal mol^{-1} of each other.

Atmospheric Implications

In this work, we are examining clustering of water around formic acid to understand the first steps of aerosol formation induced by organics. By starting at the molecular level, we hope to provide new insight into the process by which gas phase molecules form condensed phase material in the atmosphere, as well as provide insight into hygroscopic growth. This model can be extended to other species, including other organic acids and possibly even strong acids, such as H_2SO_4. By using formic acid as a model, we are also examining under what conditions formic acid may act as a precursor to aerosol formation. Earlier models[13,14] of atmospheric aerosol formation have examined the role of ion complexes in the process. Neutral complexes were disregarded because they are generally less stable than their ionic counterparts. Homogeneous nucleation is not thought to be the major mechanism for aerosol formation in the atmosphere.[33] For pure water, it is only important at very low temperatures, whereas binary homogeneous nucleation can be important for nonvolatile species, such as sulfuric acid. Photochemical smog formation may result in the formation of low vapor pressure species that lead to aerosols via homogeneous nucleation as well.[34] In presenting our work, we will start by discussing two aspects of the complexes studied critical to their growing while still on the molecular scale: their stability and their stickiness.

We have shown that formic acid−water complexes can be very stable compared to complexes containing only water molecules. The most stable complex of formic acid with three water molecules, FAZ111, is lower in energy (D_0) by 26.3 kcal mol^{-1} compared to the isolated monomers. This compares to the water tetramer, which is lower in energy than isolated water by 18.6 kcal mol^{-1}. The relatively large binding energies of these neutral complexes will lead to longer lifetimes, perhaps approaching those of ion complexes. Recent calculations and experiments[35] show that the $K^+(H_2O)_3$ ion has a binding energy (D_e) around 50 kcal mol^{-1}, less than factor of 2 larger than that of FAZ111. Sulfuric acid forms even stronger complexes with water than formic acid, even on the nonionic potential.[10] It seems that the stability of these molecular complexes is approaching that of the ionic hydrates and so cannot be neglected.

The next consideration we will examine is the stickiness of these complexes. It was stated earlier that the presence of formic acid causes water to bond more tightly to itself than otherwise. This is due to cooperative bonding in these complexes. It seems reasonable to expect that the formic acid water complex is stickier to hydrogen bonding species than a complex composed of just water. This is exemplified in the R(w)-type bonds in FAZ11 and FAZ111, which are shorter than in the water trimer and tetramer. One can imagine a formic acid molecule that is nearly surrounded by water molecules, similar in size to its analogous complex formed only of water molecules. The calculated diameter of an $HCO_2H-(H_2O)_3$ complex is about 0.0005 μm. A potential collision partner with the ability to hydrogen bond will do so more favorably with a formic acid−water complex than the complex containing only water molecules. Upon examination of a recent work on sulfuric acid water complexes,[10] the same seems to hold true. This same effect on hygroscopic growth seems to hold true for the second solvating shell as well as the first. The three cyclic structures, FAZ111, FAZ222, and FAZ333, are essentially the water trimer attached to a formic acid molecule. In each case, the intermolecular bond distances are much shorter than those in the water trimer. This is not just the shorter formic acid−water bonds, but also the water−water bonds. This is strong evidence that formic acid makes water stick more readily to itself.

Because of their increased stickiness, these hydrated acid complexes are more likely to grow, on a molecular level, than their counterparts composed of only water. This may occur through collisions with other species that can hydrogen bond, including each other. They may also be scavenged by other aerosols. Formic acid is present in large amount in the polluted urban atmosphere,[6] so it is most likely that these hydrates are formed under those conditions. Some of the hydrates may become large enough to become stable nuclei. The presence of a soluble material (i.e., the acid) in the microdroplet will permit particle growth at relatively low super-saturation.[34] This point has been made in a recent article concerning the reshaping of cloud formation theories.[36]

Conclusions

We have calculated the structures and energetics of several conformations of formic acid complexes with up to three water molecules. Formic acid was used as a model species, but many of the conclusions drawn from these calculations are applicable to other organic acids. Three water molecules seem to constitute the minimum number to form a first solvating shell around the formic acid. We also provide calculated rotational and vibrational frequencies to assist laboratory measurements in identifying these complexes. This is especially important for the complexes with more than one water molecule, as they are similar in binding energy and hence more likely to coexist. When possible, we compare our results with experimental data to give the reader a better understanding of the uncertainty in the calculated values. There are clear signs of cooperative bonding so that as each water molecule is added the hydrogen bonds of the complex get stronger. This, in turn, causes the water molecules to become stickier to other hydrogen bonding species, and may propagate hygroscopic growth on the molecular scale.

It seems reasonable to think that organic acids may play a role in nucleation under some conditions in the atmosphere. While the largest amounts of these species are found in polluted environments, they seem to be ubiquitous in the atmosphere. More long-chain acids are being identified in field measurements under different conditions.[2,3] On a molecular scale, they propagate growth by causing the water molecules to bind more easily to themselves. This, in itself, may be an important consideration to the formation of pre-nucleic embryos in the atmosphere. A similar mechanism has been proposed[13,14] involving ionic complexes. It could be that these embryos promote condensation of low vapor pressure species, such as sulfuric acid or longer chain organic acids. Since these embryos are sticky themselves, other aerosols may scavenge them quite easily. This would provide a faster mechanism for growth than the scavenging of isolated molecules, since it would require less collisions to obtain the same amount of material. For these reasons, we feel continued study is appropriate of these organic acids as aerosol precursors.

Acknowledgment. The authors would like to thank the National Science Foundation for funding this research. Simone Aloisio would also like to thank the Camille and Henry Dreyfus Foundation for financial support. We would also like to thank Prof. Jamie Donaldson, Dr. Roberto Bianco, Jill Headrick, Teresa Eliason, and Shane Murphy for creative discussion of this work, which led to its improvement.

Supporting Information Available: Tables listing the vibrational frequencies of all the complexes calculated in this work, including calculated harmonic vibrational frequencies at the B3LYP/6-311++G(d,p) level of theory, along with their shifts relative to the isolated monomers, and intermolecular modes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Facchini, M. C.; Fuzzi, S.; Lind, J. A.; Fierlingeroberlinninger, H.; Kalina, M.; Puxbaum, H.; Winiwarter, W.; Arends, B. G.; Wobrock, W.; Jaeschke, W.; Berner, A.; Kruisz, C. *Tellus, Ser. B* **1992**, *44*, 533−544.

(2) Lelieveld, J.; Crutzen, P. J.; Ramanathan, V.; Andreae, M. O.; Brenninkmeijer, C. A. M.; Campos, T.; Cass, G. R.; Dickerson, R. R.; Fischer, H.; de Gouw, J. A.; Hansel, A.; Jefferson, A.; Kley, D.; de Laat, A. T. J.; Lal, S.; Lawrence, M. G.; Lobert, J. M.; Mayol-Bracero, O. L.; Mitra, A. P.; Novakov, T.; Oltmans, S. J.; Prather, K. A.; Reiner, T.; Rodhe, H.; Scheeren, H. A.; Sikka, D.; Williams, J. *Science* **2001**, *291*, 1031−1036.

(3) Murphy, D. M.; Thompson, D. S.; Mahoney, M. J. *Science* **1998**, *282*, 1664−1669.

(4) Rogge, W. F.; Mazurek, M. A.; Hildemann, L. M.; Cass, G. R.; Simoneit, B. R. T. *Atmos. Environ., A* **1993**, *27*, 1309−1330.

(5) Graedel, T. E.; Weschler, C. J. *Rev. Geophys. Space Phys.* **1981**, *19*, 505−539.

(6) Chebbi, A.; Carlier, P. *Atmos. Environ.t* **1996**, *30*, 4233−4249.

(7) Åstrand, P. O.; Karlstrom, G.; Engdahl, A.; Nelander, B. *J. Chem. Phys.* **1995**, *102*, 3534−3554.

(8) Rablen, P. R.; Lockman, J. W.; Jorgensen, W. L. *J. Phys. Chem. A* **1998**, *102*, 3782−3797.

(9) Priem, D.; Ha, T. K.; Bauder, A. *J. Chem. Phys.* **2000**, *113*, 169−175.

(10) Re, S.; Osamura, Y.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 3535−3547.

(11) Staikova, M.; Donaldson, D. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1999−2006.

(12) Weber, K. H.; Tao, F.-M. *J. Phys. Chem. A* **2001**, *105*, 1208−1213.

(13) Hoppel, W. A.; Frick, G. M.; Fitzgerald, J.; Larson, R. E. *J. Geophys. Res., [Atmos.]* **1994**, *99*, 14443−14459.

(14) Turco, R. P.; Zhao, J. X.; Yu, F. Q. *Geophys. Res. Lett.* **1998**, *25*, 635−638.

(15) Kulmala, M.; Laaksonen, A.; Pirjola, L. *J. Geophys. Res., [Atmos.]* **1998**, *103*, 8301−8307.

(16) Weber, R. J.; Marti, J. J.; McMurry, P. H.; Eisele, F. L.; Tanner, D. J.; Jefferson, A. *J. Geophys. Res., [Atmos.]* **1997**, *102*, 4375−4385.

(17) Marti, J. J.; Weber, R. J.; McMurry, P. H.; Eisele, F.; Tanner, D.; Jefferson, A. *J. Geophys. Res., [Atmos.]* **1997**, *102*, 6331−6339.

(18) RiveraCarpio, C. A.; Corrigan, C. E.; Novakov, T.; Penner, J. E.; Rogers, C. F.; Chow, J. C. *J. Geophys. Res., [Atmos.]* **1996**, *101*, 19483−19493.

(19) Bonsang, B.; Boissard, C. *Reactive Hydrocarbons in the Atmosphere*; Academic Press: New York, 1998.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 98*; GAUSSIAN Inc.: Pittsburgh, PA, 1998.

(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.

(22) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822−2827.

(23) Aloisio, S.; Francisco, J. S. *J. Phys. Chem. A* **2000**, *104*, 3211−3224.

(24) Estrin, D. A.; Paglieri, L.; Corongiu, G.; Clementi, E. *J. Phys. Chem.* **1996**, *100*, 8701−8711.

(25) Fowler, J. E.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 446−452.

(26) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *17*, 553.

(27) Donaldson, D. J. *J. Phys. Chem. A* **1999**, *103*, 62−70.

(28) Hurtmans, D.; Herregodts, F.; Herman, M.; Lievin, J.; Campargue, A.; Garnache, A.; Kachanov, A. A. *J. Chem. Phys.* **2000**, *113*, 1535−1545.

(29) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Rasanen, M. *J. Am. Chem. Soc.* **1997**, *119*, 11715−11716.

(30) van Duijneveldt-van de Rijdt, J.; van Duijneveldt, F. B. *J. Chem. Phys.* **1999**, *111*, 3812−3819.

(31) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703−2711.

(32) Paul, J. B.; Provencal, R. A.; Chapo, C.; Roth, K.; Casaes, R.; Saykally, R. J. *J. Phys. Chem. A* **1999**, *103*, 2972−2974.

(33) Seinfeld, J. H.; Pandis, S. N. *Atmospheric and Chemical Physics*; Wiley and Sons: New York, 1998.

(34) Hinds, W. C. *Aerosol Technology*; John Wiley and Sons: New York, 1999.

(35) Saiful Islam, M.; Pethrick, R. A.; Pugh, D. *J. Phys. Chem. A* **1998**, *102*, 2201−2208.

(36) Charlson, R. J.; Seinfeld, J. H.; Nenes, A.; Kulmala, M.; Laaksonen, A.; Facchini, M. C. *Science* **2001**, *292*, 2025−2026.