

# The role of cluster energy nonaccommodation in atmospheric sulfuric acid nucleation

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(Received 23 September 2009; accepted 21 December 2009; published online 11 January 2010)

We discuss the possible role of energy nonaccommodation (monomer-cluster collisions that do not result in stable product formation due to liberated excess energy) in atmospheric nucleation processes involving sulfuric acid. Qualitative estimates of the role of nonaccommodation are computed using quantum Rice–Ramsberger–Kassel theory together with quantum chemically calculated vibrational frequencies and anharmonic coupling constants for small sulfuric acid—containing clusters. We find that energy nonaccommodation effects may, at most, decrease the net formation rate of sulfuric acid dimers by up to a factor of 10 with respect to the hard-sphere collision rate. A decrease in energy nonaccommodation due to an increasing number of internal degrees of freedom may kinetically slightly favor the participation of amines rather than ammonia as stabilizing agents in sulfuric acid nucleation, though the kinetic enhancement factor is likely to be less than three. However, hydration of the clusters (which always occurs in ambient conditions) is likely to increase the energy accommodation factor, reducing the role that energy nonaccommodation plays in atmospheric nucleation. © 2010 American Institute of Physics. [doi:10.1063/1.3291213]

## I. INTRODUCTION

Sulfuric acid is generally thought to be one of the most important molecules participating in atmospheric new-particle formation through nucleation.<sup>1</sup> In previous decades, theoretical nucleation studies have mainly been based on various versions of classical nucleation theory (CNT)<sup>2,3</sup> (CNT; see Ref. 4 for a recent review), which treats clusters as spherical droplets of bulk liquid, and assumes that the growth rates of clusters by monomer addition are given by their hard-sphere collision rates. The thermodynamics predicted by CNT are known to be incorrect for the smallest clusters, and this issue has been extensively investigated using various molecular—based modeling methods.<sup>5–8</sup> Recently, the kinetic assumptions of CNT have also been called into question, as some experimental and theoretical studies indicate that the net formation rate of small clusters may be significantly smaller than the collision rate.<sup>9–16</sup>

The net formation rate of molecular clusters can be lower than the collision rate due to three different reasons. First, the activation energy (as defined in chemical kinetics) for the cluster-forming reaction may be significantly greater than zero. The clusters of interest for atmospheric nucleation are usually held together by hydrogen bonds, and no bonds are broken in the formation of the clusters (apart from subsequent barrierless proton transfer reactions, e.g., during hy-

dration of the clusters). This alternative is therefore improbable. Second, there may be steric effects associated with the structure of the clusters and/or monomers, so that only certain collision geometries will lead to cluster formation. For the specific case of sulfuric acid clusters, this alternative is also implausible, as each acid has two hydrogen bond donor and two acceptor sites, and can be considered to be quite “sticky” in all directions with respect to hydrogen bond formation. Third, the initially formed clusters may break apart very quickly due to the excess energy liberated in the formation of the cluster. If the rate for this dissociation due to energy nonaccommodation is much faster than the average collision rate with gas molecules (which thermalize the cluster by removing excess energy) then only a small fraction of the clusters will survive long enough to be collisionally stabilized, and the net formation rate will be much lower than the cluster collision rate. It should be noted that in addition to detailed collision kinetics, the evolution of the cluster distribution (and thus the nucleation rate) also depends on evaporation rates, which are not easy to measure or calculate for small molecular clusters. For example, the difference between sulfuric acid collision rates and net particle formation rates observed in field studies<sup>15,16</sup> is caused by a combination of evaporation and possible kinetic effects such as energy nonaccommodation. The issue of obtaining accurate evaporation rates has been discussed extensively elsewhere and will not be explored further here.

The competition between cluster dissociation and stabi-

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lization can be modeled as a set of three reactions with bimolecular quantum Rice–Ramsperger–Kassel (QRRK) theory,<sup>17</sup> an extension to the unimolecular RRK theory developed by Rice and Ramsperger<sup>18</sup> and Kassel.<sup>19</sup> In the first reaction, a monomer-cluster collision yields an energetically unstable collision complex. This energized complex then either dissociates into the starting monomer and cluster, or is stabilized by collision with a third body that removes the excess energy. QRRK theory assumes that a cluster is composed of  $s$  identical oscillators, all having frequency  $\nu$  with cluster energies  $E$  expressed in vibrational quanta  $n$  ( $E = n h \nu$ ). Applying a pseudosteady-state condition to the collision complex yields an expression for the cluster energy accommodation coefficient  $P$ , the probability that a monomer-cluster collision forms a stable product

$$P = \sum_m^{\infty} \frac{\beta \omega}{\beta \omega + k_d(n)} f(n), \quad (1)$$

where  $f(n)$  is the fraction of collision complexes that are formed containing  $n$  quanta,<sup>19</sup>  $m$  is the critical quanta equivalent to the cluster-monomer binding energy  $E_{\text{crit}}$  ( $E_{\text{crit}} = m h \nu$ ), and  $\omega$  is the hard-sphere frequency of collisions of the cluster with gas molecules.  $\beta$  is a collisional stabilization efficiency, which contains details regarding collisional energy transfer between the cluster and the buffer gas.<sup>20</sup> Usually,  $f(n)$  is computed by assuming that the cluster energy distribution immediately after the cluster-forming collision corresponds to the binding energy  $E_{\text{crit}}$  (liberated in the cluster formation) plus a Boltzmann distribution of thermal energies of the original collision partners. The cluster dissociation rate  $k_d(n)$  is calculated according to the expression

$$k_d(n) = \nu \frac{n! (n - m + s - 1)!}{(n - m)! (n + s - 1)!}. \quad (2)$$

Dissociation occurs when energy that is equal to or larger than  $E_{\text{crit}}$  is localized in a single oscillator, and occurs at a rate proportional to the oscillator vibrational frequency  $\nu$  and the probability of this energy localization in a single oscillator [given by the fraction in Eq. (2)]. As the collision complex increases in size, the cluster lifetime (proportional to  $1/k_d$ ) increases, since there are a greater number of vibrational modes  $s$  over which the collision energy can be distributed, resulting in a lower probability of localizing the critical energy in a single oscillator. Full development of the cluster accommodation model is detailed in Ref. 21.

The energy accommodation coefficient and the widely used mass accommodation coefficient—sometimes called sticking probability<sup>22,23</sup>—are closely related. Energy nonaccommodation is one of the mechanisms by which the mass accommodation may differ from unity. Recently, the mass and heat accommodation coefficient has been found to be near unity for water<sup>24</sup> and for nitric acid-water mixtures<sup>25</sup> in condensation experiments using Vienna expansion chamber (see Ref. 24). It should be noted that these experiments have not focused primarily on nanoscale clusters (for example, the smallest clusters studied in Ref. 25 had radii of 500 nm), and

that the energy nonaccommodation mechanism discussed here is likely not relevant for collisions with macroscopic surfaces.

To model the dissociation of complex polyatomic systems relevant to atmospheric nucleation, certain modifications were made in modeling cluster dissociation. Cluster dissociation can potentially occur through multiple vibrational modes (each characterized by their own vibrational mode) instead of one, as is assumed in conventional QRRK theory. To account for this possibility of multiple dissociative vibrational modes, the probability of critical oscillator dissociation was extended to include the localization of the cluster binding energy in an arbitrary number of vibrational modes.<sup>21</sup> The required parameters needed for determining the cluster dissociation rate are the cluster binding energy, the number of accessible vibrational modes, the number of dissociating vibrational modes, and the appropriate vibrational frequency for each dissociating cluster. While the binding energy is readily available from quantum chemical calculations, the latter three parameters are far from trivial to determine.

In QRRK studies on single covalently bound molecules, all modes are often assumed to be accessible, though the best fit to experimental results is often obtained by taking the number of accessible modes to be roughly half the total number of modes.<sup>26</sup> It should be noted that this correction does not necessarily reflect the real degree of vibrational energy redistribution inside the molecules, but rather the qualitative nature of the QRRK approach. For clusters formed from a monatomic vapor such as argon, the number of modes is simply equal to  $3k-6$ , where  $k$  is the number of monomers in the cluster. However, for clusters consisting of polyatomic molecules, the situation is more complicated. The number of vibrational normal modes of a nonlinear polyatomic molecule is  $3N-6$ , where  $N$  is the number of atoms in the molecule. For a cluster containing  $k$  (identical, nonlinear, and polyatomic) molecules, there are thus  $3(N \times k)-6$  vibrational modes in total. However, all of these are unlikely to be “accessible” in the sense of the QRRK calculations. In other words, the energy liberated by the cluster formation can probably not be rapidly redistributed over all of the vibrational modes of the cluster, but only some subset of them (called the number of accessible modes,  $s$ , in QRRK theory). The main reason for this is that some of the original intramolecular modes are not affected much by the cluster formation and are unlikely to be coupled to the vibrations corresponding to cluster formation or dissociation. Thus, energy flow into these modes from the cluster-forming reaction (the “critical oscillator” or “dissociative mode”) is likely to be fairly inefficient. In principle, the  $3(N \times k)-6$  vibrational modes of a cluster can be divided into  $6k-6$  intermolecular and  $3(N \times k)-6k$  intramolecular modes. At the limit of very weakly bound clusters, the number of accessible modes could thus be taken to be  $6k-6$ . However, for example, sulfuric acid clusters are moderately strongly bound, and some of the intramolecular modes are likely to be strongly coupled to the intermolecular ones, the most prominent example being the O–H stretching vibrations of SOH groups involved in hydrogen bonds. (As can be seen from the computed and

experimental vibrational data presented in the supplementary material,<sup>27</sup> O–H stretching vibrations for SOH groups participating in H-bonding are typically redshifted by several hundred  $\text{cm}^{-1}$  in cluster formation, and are often very strongly coupled to intermolecular vibrational modes.) On the other hand, not all intermolecular modes are necessarily very strongly coupled together.

Determining the correct mean frequency to use is also nontrivial. In studies on single molecules, the geometric mean of all vibrational frequencies is often taken as a representative value. However, for studies on cluster dissociation, this is likely to produce systematic errors. The geometric mean of all vibrational frequencies of, say, a dimer, is almost certainly significantly higher than that of the six intermolecular vibrational modes. For the sulfuric acid dimer, the intermolecular modes typically have wavenumbers of 50–500  $\text{cm}^{-1}$ , while the most rigid intramolecular vibrations (O–H stretches) are typically found in the 3000–3600  $\text{cm}^{-1}$  range. A simple solution might be to take the geometric mean of the 6k-6 lowest frequencies, but this is likely to produce systematic errors in the opposite direction, as some of the higher-frequency intramolecular modes are likely to be coupled to the intermolecular modes and thus accessible. For loosely bound clusters, it is known that the QRRK model tends to underestimate the rate of cluster decay by 2–4 orders of magnitude when compared to measurements,<sup>28,29</sup> leading to an overestimation of the accommodation coefficient. Results from this QRRK analysis should thus be viewed as qualitative.

In any case, the use of harmonic vibrational frequencies computed at a single minimum-energy geometry does not give a very realistic description of the internal dynamics of a hydrogen-bonded cluster structure at atmospheric temperatures. For example, the sulfuric acid dimer has at least three or four different local minimum-energy structures, all of which may be significantly populated at atmospherically realistic temperatures of 200–300 K. The vibrations of real molecules and molecular clusters are known to be significantly anharmonic, and some of the harmonic vibrational modes may in reality correspond, e.g., to internal rotations or other large-amplitude motions connecting the different local minima to each other.

A quantitatively accurate study of the post-collision energy redistribution within a cluster would probably require a rather lengthy series of high-level *ab initio* molecular dynamics simulations, preferably accounting also for quantum nuclear effects such as proton tunneling. Since such a study is beyond the scope of this qualitative assessment, we have instead chosen to focus on the minimum-energy structures, but expand our analysis beyond the harmonic approximation by computing anharmonic vibrational frequencies and couplings at a qualitatively reliable level of theory.

We have proceeded as follows: first, a harmonic frequency calculation was performed on a set of cluster structures (encompassing the minimum-energy geometries found in previous studies) to determine the vibrational normal modes. These were then visualized (using the MOLEKEL program<sup>30</sup>) and the mode or modes corresponding most closely to cluster dissociation (e.g., of a dimer into two

monomers, or of a tetramer into a trimer and a monomer) were identified. Next, an anharmonic frequency calculation was performed. This yielded not only somewhat more reliable frequencies but also cubic and quartic coupling constants between the normal modes. The couplings between the dissociative mode and the other modes indicate how easily vibrational energy can be redistributed from the dissociative mode into the other modes and can thus be used to give a rough estimate of the number of accessible modes required for QRRK calculations. The simplest method to estimate the coupling between modes is to study the cubic force constants of type  $k_{211}y_2y_1y_1$ , where  $y_1$  and  $y_2$  are normal mode coordinates and  $k_{211}$  is the cubic force constant that describes how strongly the vibrational mode  $y_2$  is coupled to mode  $y_1$ . (See Ref. 31 for definitions of vibrational normal modes and descriptions on how they are derived.) Note that while the quadratic force constants  $k_{11}y_1y_1$ —the only terms present in the harmonic approximation—are by definition positive at minimum-energy geometries, the cubic force constants coupling two different modes together can be either positive or negative, and the strength of the coupling is reflected by their absolute magnitude.

In this study, only dimer and selected tetramer clusters have been studied. This is justified by the fact that the energy nonaccommodation effect decreases very rapidly as a function of cluster size. If—as it will later be seen—the energy nonaccommodation effect is relatively small already for dimer clusters, it will thus be negligible for trimers, tetramers, etc. It should further be noted that only energy transfer between vibrational modes is modeled here, leaving out vibration—rotational and vibrational—electronic energy transfer processes, which might conceivably also affect cluster lifetimes.

All of the sulfuric acid dimer configurations studied here contain two or three hydrogen bonds. In principle, the dissociation of the dimers could thus occur sequentially with one bond at a time breaking. Such behavior has been experimentally observed for formic acid dimers.<sup>32</sup> However, no singly bonded local minima for sulfuric acid dimers has, to our knowledge, ever been reported, and all initial singly bonded guess geometries rapidly collapsed into one of the doubly or triply bonded configurations in our energy minimizations. The difference between sulfuric acid and formic acid dimers is likely due to the extreme “stickiness” of sulfuric acid in all directions, as discussed earlier: both acids in the dimer have two H-bond receptors and two donors, and the two molecules can simply not be combined without at least two acceptor-donor pairs being in contact with each other. In the absence of any evidence of a singly bonded structure, sequential dissociation can therefore probably be ruled out.

However, even though the dissociation process is likely to occur in one step, there may still be more than one dissociative mode. As an upper limit (corresponding to an extreme “local mode” picture of vibrational motion), the number of dissociative modes can be taken to equal the number of hydrogen bonds to be broken.

To our knowledge, there are no previous studies on energy nonaccommodation in sulfuric acid cluster formation. For argon, the effect is known to be important.<sup>9</sup> In a recent

study on water clusters,<sup>12</sup> the role of energy nonaccommodation was found to be very large, but this result was obtained by assuming that water can be treated as a monatomic vapor with only 3k-6 accessible vibrational modes. As will be seen below, such a treatment is not justified for polyatomic molecules.

## II. COMPUTATIONAL DETAILS

Anharmonic frequency calculations were performed using the GAUSSIAN 03 program suite<sup>33</sup> and the perturbative method of Barone.<sup>34</sup> Calculations were performed at the Perdew–Burke–Ernzerhof<sup>35</sup> (PBE)/6-31+G(2d,p) level using density fitting, tight optimization criteria and the ultrafine integration grid. The level of theory was chosen as a reasonable compromise between computational cost and accuracy. The anharmonic frequencies computed here are not intended to be quantitatively accurate, but simply to give a qualitatively reliable picture of the vibrational modes and the couplings between them. The PBE functional was chosen as the density fitting procedure—which reduces the computational effort significantly—can only be used together with pure density functionals, ruling out the use of hybrid functionals such as B3LYP. Out of the available pure density functionals, we chose PBE based on recommendations from previous studies.<sup>36,37</sup> Test calculations on the sulfuric acid dimer using the same basis set but several different methods indicate that the difference between BPE, B3LYP, and MP2 frequencies and couplings is relatively small.

For the  $(\text{H}_2\text{SO}_4)_2$  cluster, the zero-point energy (ZPE) corrected RI-MP2/QZVPP binding energy from Salonen *et al.*<sup>38</sup> was used in the QRRK calculations. Binding energies for the sulfuric acid dimer given by other quantum chemistry methods including electron correlation (for example DFT or RI-CC2 with large basis sets, see Refs. 39 and 40) differ from each other by less than 2 kcal/mol with the value used here lying in the middle of the range of literature values. Thus, uncertainties in the binding energies are not a major problem for our purposes. For the  $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_2$  clusters, the ZPE-corrected RI-MP2/aug-cc-pV(T+d)Z//MPW1B95/aug-cc-pV(D+d)Z binding energy from Torpo *et al.*<sup>41</sup> was used. For the  $\text{H}_2\text{SO}_4 \cdot \text{NH}_3$  and  $\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH}$  clusters, the RI-CC2/aug-cc-pV(T+d)Z//RI-MP2/aug-cc-pV(D+d)Z enthalpies from Kurtén *et al.*<sup>40</sup> were used (the difference between enthalpies and ZPE-corrected binding energies is small). All calculations were done for  $T=298$  K and  $p=1$  atm. All clusters were assumed to have the density of bulk sulfuric acid for the cluster radius and volume calculations. A sensitivity analysis was performed in regards to various model input parameters related to collisional energy transfer, binding energy, cluster density and possible systematic errors in the vibrational frequencies. [See the supplementary information (Ref. 27), Table S10, for a list of parameters and their values.] The results indicate that the minimum energy accommodation factor for sulfuric acid dimers (assuming a single dissociative mode) changes by at most 40% as the parameters are varied over some reasonable

ranges. For the purposes of our order-of-magnitude assessment, the uncertainty in the parameter set is not a major issue.

## III. RESULTS AND DISCUSSION

### A. $(\text{H}_2\text{SO}_4)_2$ clusters

In previous studies,<sup>38–43</sup> four minima have been identified for the sulfuric acid dimer, corresponding to isomers with point group symmetries *c*1, *c*2, *cs*, and *ci*. (For definitions of point group symmetries and their application to molecular systems, see, e.g., Ref. 44). Either the *c*1 or the *ci* isomer has been claimed to be the lowest-energy configuration, depending on the level of theory used. In a recent RI-MP2/QZVPP study<sup>38</sup> (the highest-level study with data on sulfuric acid dimers published so far,) the *c*1 isomer was lowest in energy, though the *c*2 isomer was the lowest in free energy at 298 K. All four isomers were used as input structures for the optimization and frequency calculations. At the qualitative PBE/6-31+G(2d,p) level, the *ci* isomer was found to be the lowest in energy, though all except the *cs* isomers were within 0.5 kcal/mol of each other. The three most stable isomers (with *c*1, *c*2, and *ci* symmetry) are shown in Fig. S1 in the supplementary information.<sup>27</sup>

In the harmonic frequency calculations, the *cs* isomer was found to be a transition state rather than a minimum (i.e., one of the harmonic frequencies was negative). In all of the remaining three isomers, there were some vibrational modes for which the anharmonic frequency was larger than the corresponding harmonic frequency. This may at first glance seem counterintuitive, as single-mode anharmonicity should always lower the frequency of the vibrational mode, and anharmonic corrections to rigidly bound single molecules almost always act in this direction. However, in cluster structures the couplings between modes may be much more significant than the single-mode anharmonicities, and the anharmonic frequencies may thus, in principle, sometimes be higher than the harmonic ones. This effect is rather routinely encountered in anharmonic frequency calculations on clusters (see, e.g., Ref. 45 for numerous examples on hydrated sulfate ion clusters). However, for the *ci* isomer there was also one mode for which the anharmonic frequency was negative (though very close to zero; about  $-3$   $\text{cm}^{-1}$ ). This may be related to internal rotations such as those found in our recent study on sulfuric acid and hydrogensulfate ion hydrates.<sup>46</sup> Fortunately, this frequency turned out not to be coupled to the dissociative mode (it has a different symmetry), and the issue does not affect the further analysis.

Next, the normal modes corresponding to the harmonic vibrational frequencies were visualized. For the *ci* and *c*2 clusters, one of the modes (with AG and A symmetry, respectively) clearly corresponded to the dissociation of the cluster into two separate sulfuric acid molecules. For the *c*1 cluster, no single mode could be identified as a “dissociative” mode; instead, two separate modes both contained elements of dissociative motion (together with some twisting of the acid monomers with respect to each other). In all cases the dissociative mode(s) had wavenumbers around 100–150  $\text{cm}^{-1}$ .

To illustrate the nature of the mode selection process, the dissociative mode of the *ci* isomer is visualized by a series of snapshots in Fig. S2 of the supplementary information.<sup>27</sup>

The harmonic and anharmonic vibrational wavenumbers as well as the cubic anharmonic couplings reported by GAUSSIAN (all larger than  $2\text{ cm}^{-1}$ ) of all other modes to the dissociative vibrational modes are given in the supplementary information,<sup>27</sup> Tables S1–S3. Available experimental vibrational data for the sulfuric acid dimer is given in Table S4. Computed wavenumbers for the sulfuric acid monomer are also given for reference (Table S5), together with reported experimental wavenumbers and high-level (MP2/TZP with CC-VSCF anharmonics, from Ref. 47) *ab initio* data. A comparison of the results for the sulfuric acid monomer indicates that the method used here systematically underestimates the vibrational wavenumbers for modes  $>500\text{ cm}^{-1}$  by  $20\text{--}150\text{ cm}^{-1}$  compared with the experimental results (a similar pattern is observed for the few experimental values available for the dimer), and  $5\text{--}120\text{ cm}^{-1}$  compared with the higher-level *ab initio* values. For the two  $<500\text{ cm}^{-1}$  modes for which experimental data is available, our method actually performs better than that of Ref. 47 by a factor of over 3, which may be coincidental, but is nevertheless encouraging, given that the dissociative modes we are focusing on are found in this wavenumber region. The mean unsigned error of the method used in this paper for the 12 vibrational modes of the sulfuric acid monomer for which experimental data is available is  $83.1\text{ cm}^{-1}$ , compared with  $55.3\text{ cm}^{-1}$  for the high-level *ab initio* method in Ref. 47. Given that their high-level method is computationally more expensive by several orders of magnitude, this result is not unreasonable, and indicates that the vibrational data presented here is qualitatively, though not quantitatively, reliable.

For the *c2* and *ci* dimers, there were 12 and 15 vibrations, respectively, coupled to the dissociative vibrations with a cubic force constant of more than  $2\text{ cm}^{-1}$ . Since half of the 36 vibrational normal modes in the *ci* and *c2* clusters have a different symmetry than the dissociative mode (and thus zero cubic force constants for couplings between them), this means that the majority of the couplings that are symmetry-allowed actually exist. For the *c1* dimer, the two dissociative vibrations are coupled to 27 and 22 other modes.

On a qualitative level, this confirms the discussion in the Introduction that the number of accessible normal modes of a sulfuric acid dimer is likely to be greater than six (the number of “new” vibrational modes formed in the complexation), but smaller than 36 (the total number of vibrational modes in the dimer). Especially the values for the *c2* and *ci* dimers seem realistic, as they are close to the “rule-of-thumb” value of 18 (corresponding to half the total number of vibrations) typically used in kinetics studies<sup>26</sup> but slightly smaller than it, reflecting the partial separation of intra- and intermolecular vibrational modes.

QRRK calculations using the entire set of coupled vibrations (with the “mean” frequency taken as the geometric mean of the set) and one dissociative mode yield energy accommodation factors [at standard conditions, using the parameters defined earlier and given in Table S10 of the supplementary information (Ref. 27)] of 0.9674, 0.9858, and

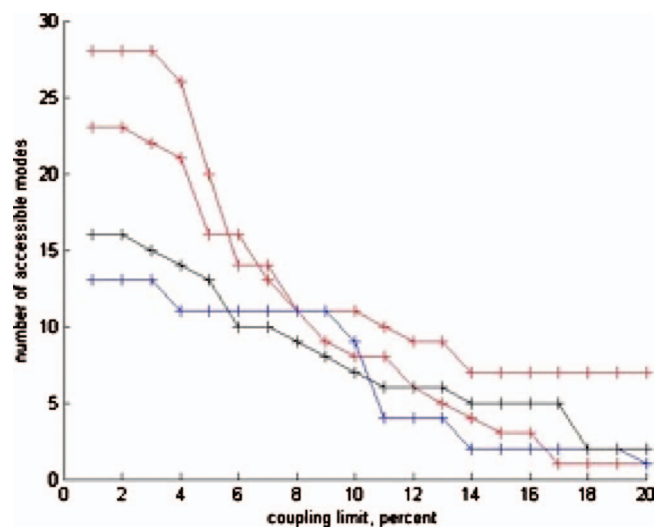


FIG. 1. The number of accessible modes for sulfuric acid dimer clusters with *c1* (red), *c2* (blue), and *ci* (black) symmetry, as a function of the coupling limit. The two lines for the *c1* cluster correspond to the two different dissociative vibrational normal modes.

0.9991 or 0.9936 for the *c2*, *ci*, and *c1* clusters, respectively (the latter choice depending on which of the dissociative modes is used).

It should be noted that the decision on which modes to include in the set of accessible modes is somewhat arbitrary. The GAUSSIAN program reports all cubic force constants with an absolute value larger than about  $2\text{ cm}^{-1}$ , but the limit for which modes to include could equally well be set higher, e.g., to  $10\text{ cm}^{-1}$  or to some fixed percentage of the vibrational wavenumber of the dissociative mode. Using a higher limit would yield a smaller number of accessible modes, and thus a lower energy accommodation factor. Figure 1 plots the number of accessible modes of the three sulfuric acid dimer clusters as a function of such a limit, expressed as a percentage of the vibrational wavenumber of the dissociative mode. (The set of accessible modes is then the dissociative mode plus the number of modes coupled to it with a cubic force constant with an absolute value greater than this coupling limit.) Figure 2 plots the geometric mean frequency of the set of accessible modes as a function of the coupling limit.

From Fig. 1, it can be seen that the number of accessible modes decreases steeply as a function of the coupling limit beyond about 5%–6% with the different cluster structures (and the two different dissociative modes in the *c1* cluster) behaving quite differently. The geometric mean frequency (see Fig. 2), on the other hand, does not decrease monotonically toward the frequency of the dissociative mode itself. In three of the four cases, it displays a maximum, reflecting the fact that the most strongly coupled modes are usually the O–H stretching modes which have high vibrational wavenumbers. For the other dissociative mode of the *c1* cluster, the mean frequency actually displays a minimum, reflecting the fact that this mode is strongly coupled to several high-frequency intramolecular O–H stretching and S–O–H bending vibrations.

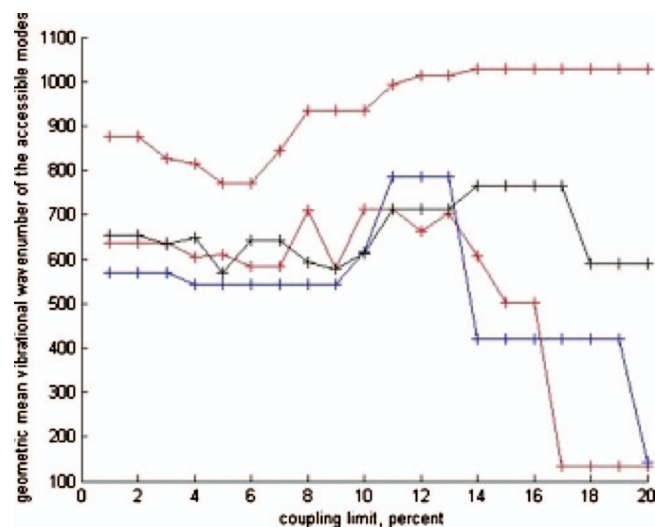


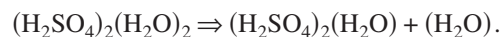
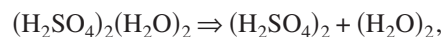
FIG. 2. The geometric mean wavenumber (in  $\text{cm}^{-1}$ ) of the accessible vibration modes for sulfuric acid dimer clusters with c1 (red), c2 (blue), and ci (black) symmetry, as a function of the coupling limit. The two lines for the c1 cluster correspond to the two different dissociative vibrational normal modes.

To estimate the maximum effect of energy nonaccommodation on the formation of sulfuric acid dimers, we have recomputed the energy accommodation factors with the assumption that only six vibrations (the dissociative vibration itself plus the five vibrations most strongly coupled to it) are accessible. This corresponds to rather large coupling limits, around 10%–25% of the wavenumber of the dissociative vibration (or 15–35  $\text{cm}^{-1}$ ) depending on the cluster, indicating that this is a somewhat extreme estimate. The energy accommodation factors computed using these sets of accessible vibrations are 0.4611, 0.2492, and 0.3252–0.1779 for the c2, ci, and c1 clusters, respectively (the latter range again reflecting the fact that the c1 cluster had 2 normal modes with dissociative character). The dissociation rates  $k_d$  (averaged over the cluster energy distribution), mean lifetimes with respect to dissociation (equal to  $1/k_d$ ) and mean frequencies used in the calculations are given in Table S11 of the supplementary information.<sup>27</sup>

If we also include the possibility of two dissociative modes (justified for the c1 cluster from the normal mode analysis, though not the c2 and ci clusters) we obtain somewhat lower energy accommodation factors of around 0.1 for all the clusters. If the c1 cluster is assumed to have three dissociative modes, the accommodation coefficient drops further to about 0.05. However, the combined assumptions of three dissociative modes but only six accessible modes in total is not very well justified from the normal mode analysis (as indicated in Fig. 1, at least one of the dissociative modes is very strongly coupled to several others), and the latter value can therefore not be considered particularly realistic. As a rough order-of-magnitude estimate, we can thus conclude that energy nonaccommodation can decrease the net formation rate of sulfuric acid dimers by maximally a factor of 10 compared with the hard-sphere collision rate.

## B. $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_2$ clusters

In atmospheric conditions, the majority of sulfuric acid molecules are bound to at least one, and often [in high RH (relative humidity) or low temperature conditions] two or three water molecules.<sup>39,46</sup> At, e.g., 298 K and RH 50%, each sulfuric acid molecule collides with a water molecule on the order of  $10^8$  times per second. The sulfuric acid-water cluster distribution can thus always be assumed to be in thermodynamic equilibrium and energy nonaccommodation effects on the hydrate distribution itself can probably be disregarded. Conclusions drawn from the study of unhydrated sulfuric acid clusters does not give a full picture of the role of energy accommodation in sulfuric acid nucleation. The presence of water molecules increases the total number of vibrational modes (presumably also the number of accessible modes), and also provides new routes for dissociation. For instance, a cluster formed from the collision of two sulfuric acid monohydrates has, in principle, four different dissociation channels



Especially the latter two channels are interesting from a nucleation point of view, as they provide a way of removing excess energy without decreasing the number of sulfuric acid molecules in the cluster.

A qualitative analysis of the role of hydration was performed here by focusing on only one dissociation pathway leading to the formation of sulfuric acid monomers. We have chosen the  $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_2$  cluster as a representative example; though sulfuric acid dimers in atmospheric conditions are typically bound to more than two water molecules, information drawn from this cluster should be sufficient to qualitatively describe the effect of hydration.

For the  $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_2$  clusters, we used as input structures the lowest-energy clusters found in previous studies by Ianni and Bandy,<sup>42</sup> Ding *et al.*,<sup>43</sup> and Torpo *et al.*<sup>41</sup> Though it is by no means certain that the global minimum at the PBE/6-31+G(2d,p) level corresponds to any of these, the resulting structures should in any case be moderately representative. All of the structures were found to be minima in the harmonic frequency calculations, but in the anharmonic frequency calculations, the structure of Ianni and Bandy<sup>42</sup> had no less than three negative anharmonic fundamental frequencies, and was therefore excluded from the further analysis. At the PBE/6-31+G(2d,p) level, the cluster optimized from the input structure of Ding *et al.*<sup>43</sup> was predicted to be 1.3 kcal/mol more stable than the one optimized from the input structure of Torpo *et al.*<sup>41</sup> It should be noted that the more stable structure actually corresponds to  $\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^- \cdot \text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ , as one proton has transferred from a sulfuric acid to a water molecule.

For the cluster without proton transfer, a normal mode (with harmonic/anharmonic wavenumber  $138\text{ cm}^{-1}/135\text{ cm}^{-1}$ ) was found that corresponded quite neatly to dissociation into  $(\text{H}_2\text{SO}_4)+(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2$ . For the cluster with proton transfer, a similar mode (with harmonic/anharmonic wavenumber  $141\text{ cm}^{-1}/134\text{ cm}^{-1}$ ) was found that corresponded to dissociation into  $(\text{H}_2\text{SO}_4)+(\text{HSO}_4^-)\times(\text{H}_3\text{O}^+)(\text{H}_2\text{O})$ . These modes were coupled to 28 and 38 other modes, respectively, thus qualitatively proving the above hypothesis that the number of accessible modes should be larger than for the unhydrated cluster. [Vibrational wavenumbers computed for the two hydrated clusters, together with their couplings to the dissociative modes, are given in the supplementary information (Ref. 27), Tables S6–S7.] In addition, both of the modes were coupled to at least one mode roughly corresponding to the dissociation of a water molecule from the cluster. Since the  $\text{H}_2\text{SO}_4-(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_2$  binding energy (before ZPE corrections) is about 21.7 kcal/mol, but the  $\text{H}_2\text{O}-(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})$  binding energy is only 13.4 kcal/mol (RI-MP2/aug-cc-pV(T+d)Z//MPW1B95/aug-cc-pV(D+d)Z data from Ref. 41), dissociation of water should happen much easier and faster than dissociation of an acid, but the remaining cluster would still be stabilized enough to make a subsequent acid dissociation very improbable at atmospherically realistic temperatures of 200–300 K.

Energy accommodation factors computed using the above set (and ignoring the presence of other dissociation routes) are, for all practical purposes, equal to 1 for both clusters (0.9999 for the cluster with proton transfer and 0.9992 for the cluster without proton transfer). An “extreme” estimate using the total number of intermolecular vibrations (18) yields essentially the same result (0.9736 and 0.9964 for the clusters with and without proton transfer, respectively). Thus, the presence of water at typical atmospheric concentrations is likely to almost completely eliminate the energy nonaccommodation effect for sulfuric acid nucleation.

### C. Possible implications for third partners in $\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ nucleation

If energy nonaccommodation were a significant effect in sulfuric acid–water nucleation, it would also affect the participation of third compounds in ways not directly related to thermodynamic arguments alone. For example, experimental observations<sup>48</sup> that amines such as dimethylamine ( $(\text{CH}_3)_2\text{NH}$ ) may be more important than ammonia as stabilizers of atmospheric clusters might also be explained not only by thermodynamic<sup>40</sup> but also by kinetic factors, as amines possess considerably more vibrational modes than ammonia. We have investigated these possibilities by computing anharmonic vibrational frequencies for  $(\text{CH}_3)_2\text{NH}\cdot\text{H}_2\text{SO}_4$  and  $\text{NH}_3\cdot\text{H}_2\text{SO}_4$  clusters. [See Tables S8–S9 in the supplementary information (Ref. 27).]

To give a rough estimate of the maximal relative role of energy nonaccommodation in  $(\text{CH}_3)_2\text{NH}-\text{H}_2\text{SO}_4$  compared with  $\text{NH}_3-\text{H}_2\text{SO}_4$  nucleation, we computed the ratio of the energy accommodation factors for the  $(\text{CH}_3)_2\text{NH}\cdot\text{H}_2\text{SO}_4$  and  $\text{NH}_3\cdot\text{H}_2\text{SO}_4$  clusters as a function of the coupling limit

described earlier. Unfortunately, the resulting curve was far from monotonic, and the ratio of the accommodation factors varied from 0.636 to 8.81. The few values which were actually below 1.0 were caused by the fact that the acid–amine complex contained many strongly coupled high-frequency modes, which in turn increased the calculated mean frequency and thus decreased the number of critical quanta. This reflects the rather arbitrary nature of the coupling limit, and also the drawbacks of using a single mean frequency for both the dissociative mode and the modes coupled to it. The average value of the ratio for coupling limits between 0 and 20% was 2.3, which is probable a more reasonable estimate of the possible kinetic enhancement than the large range given above.

Based on these results, we can conclude that sulfuric acid–amine nucleation might be kinetically somewhat enhanced (but by less than a factor of 3) compared with sulfuric acid–ammonia nucleation, if the key step in the ternary nucleation process is the collision between an acid monomer and an amine or ammonia molecule. It should be noted that as the accommodation factors computed here depend on the cluster binding energies (and thus the formation thermodynamics), the enhancement effect computed here cannot be considered a “purely” kinetic effect, though it does act in addition to the already demonstrated (and much larger) thermodynamic enhancement.

In any case, accounting for hydration of the sulfuric acid molecules will, as shown in Sec. III B, probably bring all accommodation factors close to 1 and render the difference irrelevant from an atmospheric point of view. (The recent finding<sup>49</sup> that sulfuric acid–amine clusters may remain unhydrated would only serve to decrease any possible difference in energy nonaccommodation between sulfuric acid–amine and sulfuric acid–ammonia nucleation.) Energy nonaccommodation is thus likely to play a role in sulfuric acid nucleation only in artificially dry conditions.

## IV. CONCLUSIONS

The role of energy nonaccommodation in sulfuric acid nucleation has been investigated using bimolecular QRRK theory. Qualitatively reliable anharmonic vibrational frequencies have been computed using at PBE/6-31+G(2d,p) level, and anharmonic couplings have been used to determine the number of accessible vibrational modes needed for the QRRK calculations. The energy accommodation factor for the formation of sulfuric acid dimers is shown to very probably lie between 0.1 and 1, indicating that energy nonaccommodation may play, at most, a moderate role in sulfuric acid nucleation. Energy nonaccommodation might also play a minor role in kinetically enhancing the participation of amines compared with ammonia, in addition to the much larger thermodynamic enhancement due to stronger acid–base binding. However, hydration of the clusters increases the number of accessible vibrational modes dramatically (as well as opening up new channels for energy accommodation via water molecule elimination, which removes excess energy but does not impede the nucleation process), indicating that the role of energy nonaccommodation in atmospheric

conditions, where water is always present, is likely to be very small. Our results demonstrate the importance of accounting for internal degrees of freedom of clusters consisting of complicated polyatomic molecules such as sulfuric acid.

## ACKNOWLEDGMENTS

This research was supported by the Academy of Finland (Project Nos. 1118615 and 1127372) and the Estonian Research Council (Project No. SF0180043s08). P.H.M. and C.K. gratefully acknowledge financial support from the National Science Foundation (Contract Nos. DGE-0114372 and ATM-050067). P.G. gratefully acknowledges hospitality from the University of Helsinki (Dept. of Physics) and financial support from Universidad Complutense de Madrid. Also funding from the Spanish Ministry of Education, Project Nos. FIS2007-6168 and CTQ2008-02578/BQU are acknowledged. We thank the CSC IT Center for Science for computer time.

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