

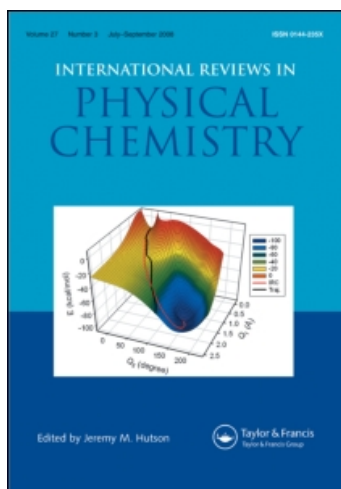
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Dynamics simulations of atmospherically relevant molecular reactions

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Dynamics simulations of atmospherically relevant molecular reactions

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This article offers an overview of the recent progress in theoretical modelling of molecular reactions of atmospheric interest. The review covers processes in isolated molecules, e.g. vibrational overtone-induced processes in HNO₃ and H₂SO₄. Another focal topic is thermally, as well as overtone-induced processes of NO_x, HNO_x and other atmospherically relevant species in water clusters, the latter serving as models for water surfaces, aerosols and other water environments. Among the processes examined in water clusters are separations of NO_x and HNO_x into ion pairs in contact with water, and the reverse processes of anion/cation recombination to form neutral molecules. Physical insights into the mechanisms and properties of the processes, as extracted from theoretical simulations, are analysed. The methodology discussed in the review is mostly classical molecular dynamics simulations, using potentials directly from electronic structure methods. The merits and limitations of different electronic structure methods for the systems of interest are discussed. Limitations and open problems with regard to the classical dynamics approximation are also briefly examined. Concluding remarks are presented on the usefulness of classical dynamics with *ab initio* potentials for reactions of atmospheric chemistry. Possible directions for future progress are suggested.

Keywords: atmospheric chemistry; molecular dynamics; *ab initio*; *ab initio* molecular dynamics; NO_x molecules; H₂SO₄; water clusters

Contents	PAGE
1. Introduction	208
2. Computational methods	209
2.1. Electronic structure methods	209
2.2. ‘On-the-fly’ dynamics simulations	212
2.3. Sampling of initial conditions	212
3. Applications	213
3.1. Processes induced by vibrational overtone excitation	213
3.2. Recombination of protons and NO ₃ ⁻ anions in water clusters	217
3.3. Ionisation of NO _x species in contact with water	218

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4. Concluding remarks	219
Acknowledgements	220
References	220

1. Introduction

The intensive activity in atmospheric chemistry in recent years has led to a great interest in a wide range of reactions that play a major role in the field [1,2]. The rates, mechanisms and properties of atmospherically relevant processes have become the topics of extensive research, and are being pursued mostly by laboratory and field experiments. Great progress was made towards the understanding and characterisation of many reactions, yet this field is still at a relatively early stage of development and an extremely large number of open problems remain to be addressed. An example of a broad class of reactions of which relatively little is known as yet are processes taking place at surfaces and interfaces. Reactions at water films or on aerosols belong in this class [3]. Complete characterisation and understanding of such reactions is not available, and typically only very limited information is at hand. This provides motivation for an attempt to pursue computational studies to provide data and understanding for reactions in atmospheric chemistry. First-principles modelling of molecular reactions is a difficult task even for isolated species in the gas phase, but the growing power of computational tools provides increasing possibilities.

This article is a review of recent attempts to contribute to knowledge of both gas-phase and interfacial reactions in atmospheric chemistry, using first-principles simulations of the processes. This research direction is but several years old. Encouragement can be drawn from major progress made in the last decade or so on simulations of structural and thermodynamical properties of atmospherically relevant systems, including interfaces. A useful example is the study of salt aerosols and their properties. Knipping *et al.* [4] carried out laboratory experiments on reactions of OH radicals with aqueous NaCl aerosols, in which chlorine is formed. The combination of experimental observation with computer kinetic modelling of the system, and with molecular dynamics (MD) simulations of salt in water droplets strongly suggests that chemistry at the surface of the aerosol is responsible for the observed production of Cl₂ [4]. The MD description of the NaCl aqueous aerosols (modelled as clusters of the order of 10³ atoms only) shows that there is a relative excess of Cl⁻ anions at the interface, which provides a microscopic explanation for the mechanism. This gave impetus to a series of illuminating MD studies of the microscopic structures of different salts in water, and especially at water surfaces [5–8]. Such MD simulations of structural and thermodynamical properties at equilibrium are tremendously useful for suggesting consequences for chemical behaviour, but in themselves do not treat molecular reactions. In addition to properties of systems at thermal equilibrium, MD simulations were also extensively applied in recent years to calculations of physical processes in atmospherically relevant systems. We use the terminology of ‘physical processes’ here for processes that do not involve chemical change, the making or breaking of chemical bonds. A physical process that has been the target of several MD studies in the last several years is the uptake of molecules from the gas phase

by water and other liquid surfaces [9–14]. The issues of mass accommodation, trapping and absorption into the bulk at gas–liquid interfaces continue to present important challenges, but major progress has been made, and MD has emerged as a very powerful tool for addressing these processes.

The power of MD as a simulation tool for equilibrium properties and for physical processes is a consequence of the availability of suitable interaction potentials for modelling the systems of interest. In the above examples, as in most other applications, the interactions used are taken from empirical, and most often analytical, force fields [15]. While doubts about the quantitative accuracy of the empirical force fields remain for certain properties and certainly can be a serious issue in specific cases, the rich spectrum of applications and comparisons with experiment supports their adequacy for calculations of structural and thermodynamical properties. The interactions that govern these systems are non-covalent forces, specifically electrostatic and dispersion interactions of several kinds, and the classical force fields model these potentials very effectively. In addition, the classical force fields are computationally very efficient, making it possible to simulate sufficiently large models for describing condensed-phase systems.

The issue of availability of suitable interaction potentials is of the essence for the topic of the present review, description of chemical reactions for atmospherically relevant systems. Standard force fields cannot describe making or breaking of chemical bonds. Several empirical force fields have been suggested that support treatment of at least certain types of reactions. The applicability of these force fields to systems and processes as discussed here is not known at this stage. It is possible that this may become a useful direction in the future.

At the present stage, force fields that can describe chemical reactions come from electronic structure theory. The use of such potentials is computationally very demanding, compared with empirical force fields. This severely limits the size of systems that can be employed as computational models. The question of finding models realistic enough for calculations that correspond to condensed-matter experimental systems is a major challenge. Also, not for all types of chemical reactions are there electronic structure methods that permit reliable calculations even for small systems. The objective of this review is to examine methods of dynamics with potentials from electronic theory that were applied to atmospherically relevant systems. We examine the models that were used, the classes of processes treated so far and the insights that were gained into the chemistry of realistic cases. We will attempt to identify major needs for further progress, in a field that is just in an early formative stage.

2. Computational methods

2.1. *Electronic structure methods*

It is useful to examine the applicability of different electronic structure methods in dynamics in the context of the type of reactions that are targeted, and of the models that can be useful in describing the corresponding realistic systems. The description of excited electronic state interactions, as pertinent to photochemical reactions, is extremely demanding computationally, and there are open questions of the expected accuracies of

the leading available methods. There are virtually no applications of the state-of-the-art methods for photochemical processes for the targeted systems. This is largely the case also for open-shell systems in the ground state, though in this case the problems are somewhat less severe. A possible tool for dynamics simulations of open-shell and possible excited state systems, is the Multi-Configuration SCF (MCSCF) method, in the algorithm developed by Chaban *et al.* [16], and implemented in GAMESS [17]. This algorithm has a degree of computational effectiveness that should render it applicable for molecules of up to 10 atoms or so. A major difficulty is, however, that the accuracy of MCSCF is insufficient for quantitative description of the potential energy surface, and the forces acting on the nuclei, which are the derivatives of the potential. For this purpose, dynamical correlations, not present in MCSCF, seem essential. For single point calculations, that is for a fixed molecular geometry, such methods are available and successful in use: Complete Active Space with Second-order Perturbation Theory (CASPT2) and Multi-Reference Configuration Interaction (MRCI). However, computational application of this method to direct dynamics is outside the realm of feasibility, at least presently. Another very promising tool for photochemistry and excited state dynamics is time-dependent density functional theory (TDDFT) [18]. A very illuminating application to a system related to the topic of the review is by Röhrig *et al.* [19] on excited state dynamics of acetone in water. The acetone molecule is treated in this example by TDDFT, while the water molecules are described by an empirical force field [19].

Clearly, simulations of reactions in excited electronic states are an important frontier, and there are some promising directions that are being pursued. However, computational studies of atmospheric reactions have so far been confined almost entirely to processes taking place in the ground electronic state. There are several electronic structure methods that are applicable to broad classes of ground state reactions, and furthermore these methods are feasible for direct use in dynamics simulations of realistic systems. However, not all types of chemical processes in the ground electronic state can be treated by the available methods, as will be discussed later.

An electronic structure algorithm that we consider as probably the most accurate feasible method in the present state-of-the-art for many of the processes discussed here is the second-order Möller–Plesset theory, MP2. An important class of systems, where strong evidence points to reliability of MP2 are water clusters, including neutral molecules and ions in water clusters. A major advantage of MP2 for such systems, as pointed out by Riley and Hobza [20], is that it offers a reasonably accurate and balanced description of the electrostatic and dispersion non-covalent interactions in these systems. MP2 can be in error in treating interactions in dispersion-dominated systems [20,21], however, with careful attention to the basis set used, the method is found to perform very well in cases where electrostatics provide the main non-covalent forces, with dispersion playing a non-negligible but secondary role. Much of the evidence for the validity of MP2 comes from vibrational spectroscopy of systems such as $\text{Cl}^-(\text{H}_2\text{O})$, $\text{F}^-(\text{H}_2\text{O})$, $\text{HNO}_3(\text{H}_2\text{O})$, $(\text{SO}_4^{2-}) \cdot (\text{H}_2\text{O})_n$, $(\text{H}_2\text{O})_2$, H_5O_2^+ , $(\text{HNO}_3) \cdot (\text{NO}_2)$, $(\text{NO}_3^-) \cdot (\text{N}_2\text{O}_4)$, and quite a few others [22–30]. Vibrational spectroscopy thus strongly supports the reliability of MP2 potentials for the systems of interest, but the method is computationally relatively expensive, which limits its use for large systems. To study molecular processes in a water environment, applications of dynamics with MP2 potential surfaces used clusters of water molecules as model systems [31,32]. The interactions in water clusters are, of course, similar to those

at water surfaces or in bulk water. It is obvious, however, that for many properties, such a long-range structure, clusters are inadequate as models for liquid water or ice. This is not expected to be the case for many molecular reactions in water. Local reactions can be greatly affected by hydrogen bonding of the reagent species, and perhaps of the transition state, with neighbouring water molecules. Such electrostatic effects are expected to be at least semi-quantitatively similar for clusters, interfaces and bulk, starting sometimes from modest numbers of water molecules in the cluster. Indeed, sometimes the water effect upon a reaction becomes appreciable already at the level of one or two water molecules. We will later discuss examples which point to the usefulness of water clusters as model systems for molecular reactions in condensed phases of water, for some types of processes. A possible alternative to using water clusters as such is to embed the latter in a large environment of molecules modelled by empirical force fields. This has not been done yet for the systems discussed in this review. Density functional theory (DFT) methods have probably been employed more extensively to date than any other electronic structure method for 'on-the-fly' simulations of chemical dynamics. This is thanks to the pioneering contribution of Car and Parrinello [33] who introduced a first approach for *ab initio* MD. The original variant of the Car–Parrinello Molecular Dynamics (CPMD) method is still extensively in use, though additional techniques were introduced in which the dynamics algorithm, and the incorporation of the DFT method into the scheme, are different. Essentially, all the schemes employ a convenient calculation of the forces from DFT, by evaluation of analytical gradients. A variety of energy density functionals were employed, and these determine to a large extent the accuracy of the treatment. The most extensively used DFT functionals in dynamics simulations seem to have been of B3LYP or the HCTH type [34–44], which are generalised gradient approximation (GGA) DFT methods. Very few simulations in the field of applications considered here were carried out to date with B3LYP/DFT, which employs a hybrid energy density functional. Direct tests of the DFT-based calculations for reaction dynamics are few and partial, but comparisons to spectroscopic and other experimental properties seem to support the DFT predictions. It should be noted that quantitative spectroscopic tests for water clusters, ions in water clusters and several other relevant systems suggest that MP2 is somewhat superior to B3LYP in accuracy, and substantially better than HCTH or BLYP [45–47]. However, it is not clear at this point how significant is the greater accuracy of MP2 for the actual description of chemical dynamics. The advantage of MP2 over the DFT methods may be partly due to the role of dispersion interactions, which are not included in BLYP, HCTH or B3LYP. Recently, several new variants of DFT have been proposed, which include the dispersion-type contributions [48–50], and applications of these to reaction dynamics calculations in water and similar media should be of considerable interest.

Another class of electronic structure methods used in dynamics simulations of atmospheric reactions are the semi-empirical methods, specifically PM3 [51,52]. Applications of PM3 to direct dynamics simulations, both for atmospheric [53,54] and for other reaction processes [55,56], so far employed the standard variant of PM3 [52]. However, for semi-empirical potentials, the possibility of re-parametrising them for specific applications seems very attractive. This could be viewed as developing a reactive force-field, based on PM3, and adapted empirically for the field of application. Adaptation of PM3 in such an approach for vibrational spectroscopy proved to be very encouraging [57], and work along similar lines for dynamics of atmospheric processes is under way in the group of

the author. However, applications of ‘standard’ PM3 for several atmospheric reactions [51,52] seem to yield results in at least semi-quantitative accord with experiment.

2.2. ‘On-the-fly’ dynamics simulations

The most straightforward approach to ‘on-the-fly’ dynamics simulations, the so-called Born–Oppenheimer methods, combines Newton’s equations of motion:

$$M_\alpha \frac{d^2 \mathbf{R}_\alpha}{dt^2} = \mathbf{F}_\alpha \quad (1)$$

with the force computed directly from electronic structure theory, via the Hellman–Feynman relation:

$$\mathbf{F}_\alpha = -\text{grad}_\alpha W(R) = -\langle \Phi(r, R) | \text{grad}_\alpha \text{He} | \Phi(r, R) \rangle_r \quad (2)$$

In the above equations, \mathbf{R}_α is the position vector of atom α , M_α is the mass and \mathbf{F}_α the force acting on the atom at time t . R denotes collectively the nuclear positions and $W(R)$ is the multi-dimensional potential energy surface. $\Phi(r, R)$ is the electronic wavefunction, r denoting collectively the electronic coordinates. $\text{He}(r, R)$ is the electronic Hamiltonian which depends parametrically on R .

In the Car–Parrinello approach the form of the dynamical equation is different, since a Lagrangean scheme is followed to simultaneously determine the trajectory and optimise the orbitals (DFT) [33]. This leads to a fictitious mass in the dynamical equations, but with careful choice of this parameter, its effect on the physical properties is negligible.

For equilibrium ‘on-the-fly’ simulations, where the purpose is optimisation of the structure of the system or determination of thermodynamic properties, the computed trajectory (or trajectories) serves for physical insights, but are not always of quantitative importance. For non-equilibrium processes, the properties of the trajectories are of the essence.

2.3. Sampling of initial conditions

Insights into the dynamics of a process, e.g. ionisation of a neutral acid molecule in water, can be obtained sometimes from very few trajectories [39]. In some cases even a single trajectory may suffice. On the other hand, quantitative calculations of rates and timescales generally require an ensemble of trajectories computed for a suitable set of initial conditions. This obviously implies much greater computational demands. The sampling of initial conditions is of central importance in this context.

Consider the sampling of initial conditions for a reaction in thermal conditions. If the reaction is sufficiently slow compared with the equilibrium timescale of the system (10–20 ps at least for the cases considered in the review), then an essentially random selection of the initial conditions will lead, after sufficient propagation of the trajectory, to equilibration. After equilibration is real ‘snapshots’ of the trajectory can be randomly sampled, and a set of positions and momenta of the particles is thus harvested from each snapshot. Each set of positions and momenta is then used to propagate a long trajectory, to explore the reaction. This, of course, is a standard MD algorithm. The difficulty is that

relatively large simulations are required, and such simulations are computationally very expensive for DFT or MP2 potentials. Also, for reactions that are fast, the assumption of equilibration prior to reaction may not be justified.

A more approximate method can be used for fast reactions at thermal (or at fixed energy conditions), and was applied for a number of processes in clusters [31,32]. A set of local minimum structures (as well as the global minimum structure) are computed. A set of low lying minima are selected. For each local minimum, velocities that correspond to the temperature are assigned to the particles, and the dynamics is propagated from the local minimum structure. For systems such as water clusters or other hydrogen-bonded complexes, the set of local minima to be sampled is vast, and the assumption is that a set of a few tens of local minima is sufficiently representative. The set can, of course, be tested for convergence by examining the contribution of additional minima. Low-lying minima are expected to be significantly populated in the real system, since the density of states (classical) at these configurations is high.

The case of reactions induced by vibrational overtone excitation requires a very different sampling of the initial states, compatible with the different experimental preparation, in this case of the activated reagent [53,54]. The following approach was used in [53,54]. The overtone-excited vibrational state was computed. From the vibrational wavefunction, initial configurations were sampled. The weighting function used for the sampling was:

$$P(\mathbf{q}) = |\Psi_\nu(\mathbf{q})|^2 \quad (3)$$

where $\mathbf{q} = (q_1, \dots, q_N)$ denotes the vibrational coordinates of the molecule, and ν denotes the vibrational level. In [53,54], the separable vibrational self-consistent field (VSCF) approximation was used. In this case, for each sampled value of \mathbf{q} , a corresponding value of the momentum \mathbf{p} can be assigned, by a semi-classical approximation:

$$p_1 = \pm\sqrt{2m_1(\epsilon_1 - V_1(q_1))} \quad (4)$$

here V_1 is the potential pertinent to mode 1, ϵ_1 is the vibrational energy of that mode and m_1 the corresponding effective mass. This is applied to each mode, the sampling of the overtone-excited mode being the most important. The above procedure has an unsatisfactory feature in that \mathbf{q} and \mathbf{p} are not treated symmetrically in the sampling. As an alternative for this sampling, the Wigner distribution can be computed from the vibrational wavefunction, and employed for the sampling [55,56]. This was pursued for other types of molecules [55] than are discussed here, but tests have shown that the two sampling methods yield very similar results.

3. Applications

3.1. Processes induced by vibrational overtone excitation

Donaldson *et al.* [58,59] and Vaida [60] put forward a very interesting mechanism for the possible induction of chemical reactions in the atmosphere by solar light in the visible range. In molecules such as H–O–NO₂, absorption of light into an overtone of the OH stretch may lead, after intramolecular energy transfer, to dissociation of the relatively weak O–N bond adjacent to the OH. This, of course, builds on studies of

overtone-induced reactions in laboratory conditions, where lasers are conveniently used to excite these weak transitions. Direct evidence for such reactions in field conditions is extremely hard to provide. However, a combination of spectroscopy estimates of yields of excitation at atmospheric conditions and laboratory experiments add up to a strong case for a possible significant role of overtone-induced reactions for molecules such as HNO_3 and H_2SO_4 in the atmosphere [58–65]. On-the-fly simulations are a very suitable tool for exploring overtone-induced reactions, since these processes take place on the electronic ground state potential surface, so the electronic structure methods for the previous section may apply [31,32,53,54]. However, this must be examined with caution for each process. The reaction $\text{HONO}_2 \rightarrow \text{HO} + \text{NO}_2$ does indeed take place upon overtone excitation. However, this is a hemolytic bond-breaking reaction, and the standard closed-shell variant of MP2, B3LYP or PM3 cannot be assumed to describe it properly [53]. Thus, Miller *et al.* [53] assumed that if the O–N bond in HONO_2 is stretched up to a certain critical distance, the dissociation will take place. That critical distance was estimated from multi-reference CASPT2 calculations to lie in the range where PM3 is still valid to good approximation. Thus, ‘on-the-fly’ simulations using PM3, in combination with an estimated ‘critical distance’ made possible the calculation of dissociation timescales [53]. In ‘on-the-fly’ simulations of high-overtone ($\nu \geq 5$) excitations of the O–H stretch on HONO_2 , an interesting effect was found in all computed trajectories [53]. Figure 1 shows snapshots from one of the trajectories.

As shown in Figure 1, the H atom becomes delocalised following the excitation, and ‘hops’ from the first oxygen to another oxygen atom. For example, following excitation into $\nu=7$, approximately three ‘hopping’ events take place (on the average) in the first 20 ps, then an average of 1.5 ‘hopping’ events take place in the next 20 ps, and the process goes on for very long durations of time. This ‘hopping’ process is obviously much more

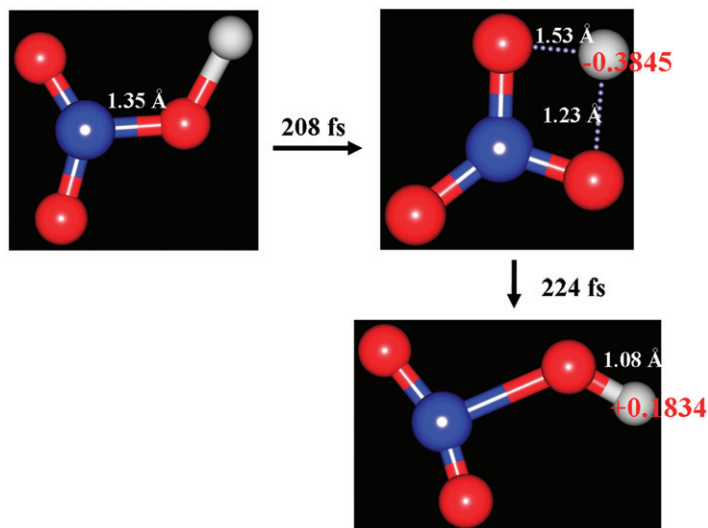


Figure 1. [Colour online] Snapshots of overtone-excited ($\nu=6$) HNO_3 – the transition state is the intermediate step shown.

efficient than the competing chemical reaction of dissociation into OH and NO₂. The mean time for dissociation, following excitation into $\nu=7$, is 36 ± 4 ps. The predicted migration of the H atom in HNO₃ between the O atoms is supported in part by experiments of Donahue *et al.* [66]. In these molecular beam experiments, a collision complex of OH \cdots NO₂ is formed. Isotope effects show that the O of the OH collider is not generally the same as the O of the product OH [66]. This, of course, is not a case of overtone excitation but the collision complex must represent a vibrationally highly excited species. A very interesting finding from the simulations is on the nature of the transition state for the hydrogen hopping. The intermediate snapshot in Figure 1 was identified by us as being essentially the transition state configuration. Very interestingly, the partial charge of the H atom at that configuration is *negative*, representing a hydridic transition state. This seems surprising since, at equilibrium, the H of HNO₃ is acidic. However, in the transition state the H is bound to two O atoms, which results in a net partial negative charge on H. Such a finding probably depends on using an electronic structure method for the potential, as it makes possible the calculation of partial charges along the dynamics. In [53], a variety of isomerisation processes of HONO and HNO₃, as well as dissociation processes, induced by overtone excitation, are computed. Several of these can be viewed possibly as ‘surprising’ predictions. An example is the formation of the species HOON, following overtone excitation of HONO. This particular process, net of high yield, is not expected to be of atmospheric importance. However, this is again a result made possible by ‘on-the-fly’ simulations using *ab initio* potentials, as opposed to calculation with fitted potentials. When potentials are fitted to the available data, the potentials are unlikely to contain and reveal surprising features. ‘On-the-fly’ simulations explore a much richer landscape of possibilities, as included in electronic structure theory. Atmospheric chemistry, with the large number of still unknown mechanisms in the field, is very likely to benefit from the possible discovery of as yet unrecognised intermediates. There may be also some ‘disappointments’. For example, simulations of overtone excitations of the complex HNO₃ \cdots H₂O show that no chemical reaction takes place [53]. Instead, the O–H stretching energy is transferred to intermolecular soft modes, leading to dissociation of these hydrogen-bonded clusters. This is a useful result, since it was suggested that the chemical reaction takes place also for the complex. The reason for the ‘suppression’ of the chemical reaction is, by the calculations, a consequence of the strong coupling on HNO₃ \cdots H₂O between the OH stretch and the intermolecular modes [53]. In fact, so strong is this coupling that it is predicted that narrow-bond overtone transitions will not be observable at all.

Another system of considerable atmospheric relevance in this context is H₂SO₄ [54]. This is among the systems for which Vaida *et al.* [61] proposed an overtone-induced reaction. ‘On-the-fly’ dynamics simulations using PM3 potentials were pursued [32]. Tests were carried out to test the PM3 method for this system against higher-level methods. It seems that PM3 is indeed valid in this case. Indeed, the simulations carried out for the $\nu=6$ excitation of an OH stretching vibrations shows that this leads to the reaction H₂SO₄ \rightarrow SO₃ + H₂O. Hydrogen-hopping events between different O atoms were observed for part of the trajectories. Figure 2, from [54], shows snapshots from a trajectory in which the dissociation is relatively fast.

In fact, the calculations show that there are two dynamical mechanisms: direct ($t < 40$ ps, or so), and ‘delayed’ dissociation, for which the lifetime is much longer. In the

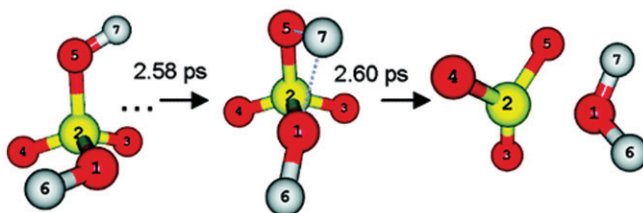


Figure 2. Snapshots of the dissociation of H_2SO_4 into SO_3 and H_2O .

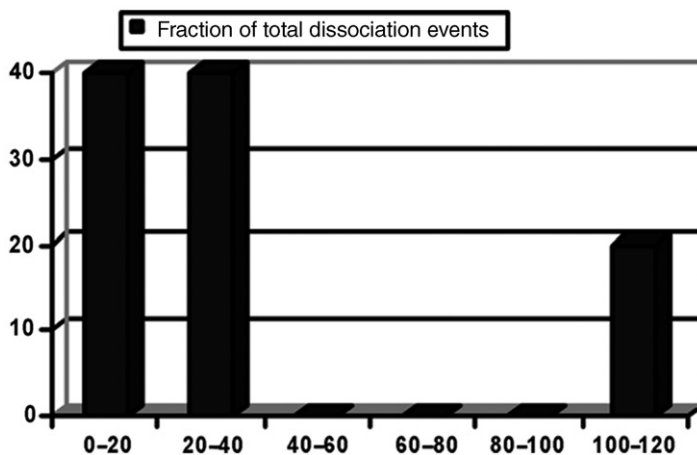


Figure 3. [Colour online] The distribution in time (picoseconds) of dissociation events of H_2SO_4 into SO_3 and H_2O during the simulations.

‘delayed’ mechanism, much of the overtone excitation energy is redistributed among essentially all the degrees of freedom, in the spirit of Rice–Ramsperger–Kassel–Marcus (RRKM), [32]. The lifetime distribution is shown in Figure 3.

Miller *et al.* [67] combined rate calculations for isolated H_2SO_4 molecules with radiation data in atmospheric conditions, to compute the calculation of the overtone-induced process at different altitudes. The results indicate that for H_2SO_4 the overtone-induced mechanism is of atmospheric importance [67]. For $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$, the overtone-induced reaction mechanism seems inapplicable, [32]. The reason, as in the case of $\text{HNO}_3\text{-H}_2\text{O}$, seems to be very strong coupling between the OH stretch and the intermolecular coupling in the cluster, which leads to dissociation of the latter. Very recently, Takahashi *et al.* [68] reported ‘on-the-fly simulations’ on the vibrationally induced elimination of HF from CH_2FOH , and from its complexes with water. In this case, complexation with H_2O does not seem to suppress the process. In fact, hydrogen bonding to water in these cases lowers the barrier for the elimination reaction [68]. Also Takahashi *et al.* [69] explored the decarboxylation of pyruvic acid, induced by overtone excitation [69]. A very interesting result of this study, that combines ‘on-the-fly’ simulations with experiments, is that the properties of the overtone excitation for two different conformers of pyruvic acid are very different.

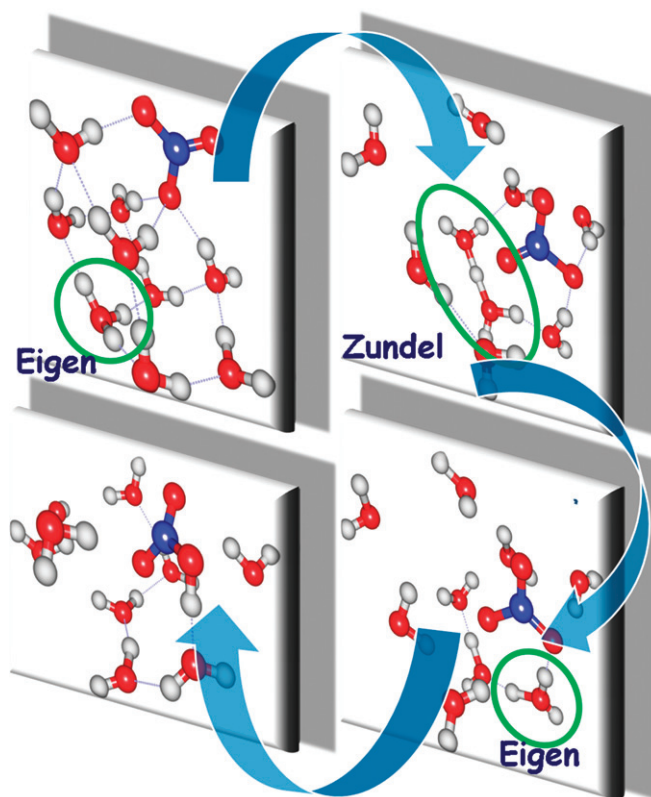


Figure 4. Snapshots of the recombination of H^+ with NO_3^- in $(\text{H}_2\text{O})_9$.

3.2. Recombination of protons and NO_3^- anions in water clusters

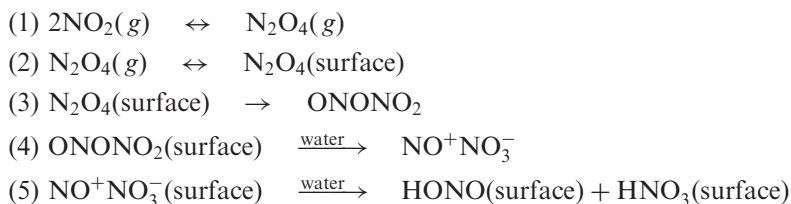
Ionisation of acids, and the reverse process of neutralisation by recombination of the proton with an anion, is among the fundamental processes in condensed phases of water, and at water and ice surfaces. This topic has been the subject of extensive studies in recent years, also including investigations by ‘on-the-fly’ simulations [34–36,38–40,70,71].

The example we will present from this subject deals with the recombination of H^+ and NO_3^- in water clusters [31]. In addition to the relation of the process in clusters to the corresponding one in liquid water, the process in clusters is of intrinsic interest. The question investigated is basically: What is the lifetime of an ion pair in a water cluster of a given size? This question is very relevant to the nucleation of water and to the role of ion pairs and of neutral acids in inducing the process. Miller and Gerber studied the recombination of H^+ with NO_3^- in $(\text{H}_2\text{O})_g$ clusters, using ‘on-the-fly’ simulations with MP2 potentials. As noted in Section 2.1, ‘on-the-fly’ dynamics simulations using MP2 are computationally relatively demanding. This is compensated by the expected accuracy of the approach, since the ‘track record’ of MP2 for water clusters and for ions in water clusters is emphasised in Section 2.1. A set of trajectories were computed, starting from different (low-energy) local minima, for providing a model of the initial state. Snapshots of the recombination from one of the trajectories are shown in Figure 4.

It is found that recombination, although not instantaneous (i.e. not femtosecond timescale), is very fast [31]. The mean computed lifetime is 1.2 ps. The implication is that H^+ and NO_3^- ion pairs do not live long enough in small water clusters for this to enhance their possible role as nucleation centres. Upon recombination, which in this case is exoergic, one or more water molecules evaporate from the cluster. The simulations are initiated with the proton as a part of an H_3O^+ cation. As the snapshots in Figure 4 show, the proton propagates in the cluster by a succession of transfers that can be described by: $\text{H}_3\text{O}^+ \rightarrow \text{H}_5\text{O}_2^+ \rightarrow \text{H}_3\text{O}^+$, etc. The mean probabilities at any time of finding H_3O^+ , or H_5O_2^+ (Zundel ion) are of the same magnitude roughly. However, the neutralisation of the proton with NO_3^- always takes place with H_3O^+ [31]. Evidently, H_3O^+ is a much more effective proton donor than H_5O_2^+ in this system. It is of considerable interest to determine how general this finding is, also for other anions. Many proton/anion ion pair systems in clusters are of considerable interest and remain to be investigated. This is one of the topics where there is a large scope for future ‘on-the-fly’ studies.

3.3. Ionisation of NO_x species in contact with water

Separation of NO_x species into pairs of ions in contact with water is not an intuitively expected process, since these molecules are not viewed as electrolytes. However, several mechanisms that have been proposed in heterogeneous atmospheric chemistry include an assumption of ionisation, specifically of N_2O_4 [72]. A process of considerable atmospheric importance in atmospheric chemistry is the hydrolysis of NO_2 (in fact, of its dimer N_2O_4) at water films. The following mechanism for hydrolysis was proposed by Finlayson-Pitts and coworkers:



This mechanism was not, however, confirmed yet directly by experiment. Steps (3) and (4) of the mechanism are the most debatable, and we examined here step (4). ONONO_2 is an asymmetric isomer of (symmetric) N_2O_4 , and considerably more stable. Miller *et al.* [32] carried out ‘on-the-fly’ simulations of ONONO_2 in water clusters, in the range of $n = 1-8$ molecules to explore if the ionisation assumed in step (4) does indeed take place, and what are the timescales and the properties of the process on the detailed molecular level. The simulations were carried out using MP2 potentials which are expected to be very reliable for this type of system.

First, dynamics simulations were carried out for isolated ONONO_2 at 300 K, as a calibration. No ionic pair states could be harvested from the simulation for any significant duration of time.

Figure 5 shows snapshots from a trajectory computed for $\text{ONONO}_2\text{-H}_2\text{O}$, starting from a local equilibrium structure (it seems that this is the lowest ‘neutral’ state minimum). An ensemble of trajectories was computed, but the behaviour seen in Figure 5

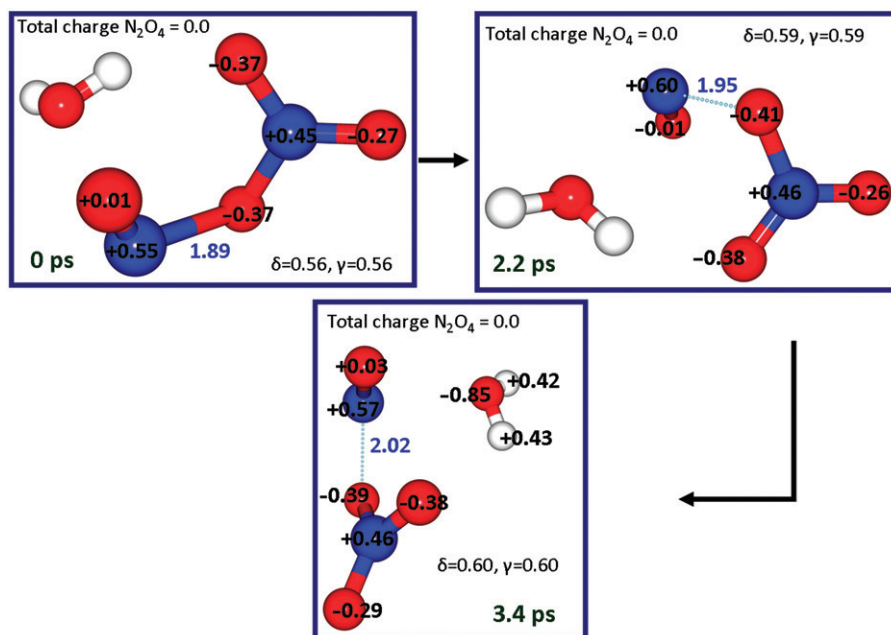


Figure 5. [Colour online] Snapshots of the ionisation of ONONO_2 complexed with a single H_2O molecule.

seems typical. After some thermally induced motion in the cluster, configurations are reached in which the H_2O molecule interacts more strongly with the ON part of $\text{ON}\cdots\text{ONO}_2$. This is the case in the intermediate step of Figure 5. The electrostatic field due to the H_2O (partial charges) seems strong enough to induce some lengthening of the $\text{ON}\cdots\text{ONO}_2$ bond. The magnitudes of the partial charges on the two groups are increased. Finally, an essentially separate state of $(\text{ON})^{+\delta}\cdots(\text{NO}_3)^{-\delta}$ is reached, within a timescale of 3.5 ps. This separated ion-pair structure is stabilised via solvation in the water molecule.

The picosecond timescale for ionisation is also found for the $n=2$ cluster [32]. For clusters with $n \geq 3$ molecules, the timescale for ionisation decreases dramatically to a few tens of femtoseconds. The process for $n \geq 3$ is thus essentially spontaneous [32]. On the whole, these results support the kinetic mechanism of [72]. The important difference is that for systems where N_2O_4 is in contact with more than two water molecules, ONONO_2 , if formed, is an essentially transient and not a proper chemical intermediate. It can be argued that symmetric N_2O_4 , when 'trying' to isomerise into ONONO_2 , separates directly into NO^+ and NO_3^- .

4. Concluding remarks

Progress in dynamics simulations of chemical reactions has reached a stage where realistic applications are feasible for processes of importance in atmospheric chemistry. Reactions of other disciplines of chemistry are, of course, equally in the range of applications in the present state-of-the-art. The challenge of atmospheric chemistry is that a very broad range

of assumed reaction mechanisms need to be tested, supported or perhaps disregarded, and theoretical simulations could play a major role, especially since experimental molecular level studies are exceedingly difficult in many cases. Though gas-phase reactions still present in cases pose many unsolved riddles, one of the main current challenges is reactions of heterogeneous atmospheric chemistry, that is, at surfaces. We believe that one lesson of this review is that water clusters can provide useful insights also for water surfaces, a system of key interest, and probably also for reactions in bulk liquid water.

The progress on simulations of reaction dynamics is largely through the advent of 'on-the-fly' trajectory methods. This defines also an important direction for future progress. *Ab initio* methods, effective enough for simulations of realistic systems, are not available in particular for excited electronic states. Photochemistry is clearly a frontier and a major challenge, a field of many potential applications to atmospheric chemistry. Methods have been proposed, but things are very far from a situation where applications are possible as a routine. Hopefully, this will be addressed in the near future.

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