



A flexible transition state searching method for atmospheric reaction systems



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ABSTRACT

The precise and rapid exploration of transition states (TSs) is a major challenge when studying atmospheric reactions due to their complexity. In this work, a Monte Carlo Transition State Search Method (MCTSSM), which integrates Monte Carlo sampling technique with transition state optimization methods using an efficient computer script, has been developed for transition state searches. The efficiency and the potential application in atmospheric reactions of this method have been demonstrated by three types of test suits related to the reactions of atmospheric volatile organic compounds (VOCs): (1) OH addition, (2) OH hydrogen-abstraction, and (3) the other reactive group (e.g. Cl, O₃, NO₃), especially for the reaction of β-pinene-sCl (stabilized Criegee Intermediates) with water. It was shown that the application of this method with effective restricted parameters has greatly simplified the time-consuming and tedious manual search procedure for transition state (TS) of the bimolecular reaction systems.

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1. Introduction

Volatile organic compounds (VOCs) are essential components of tropospheric chemistry and play a critical role in atmospheric chemistry [1–4]. Goldstein and Galbally estimated that there were 10,000 to 100,000 different organic compounds in the atmosphere [3]. Each VOC can produce a series of oxidized products through a number of atmospheric degradation processes. The products formed in the subsequent chemistry processes can contribute to secondary organic aerosol (SOA) formation and growth [5–7] and will thus directly impact air quality and the global climate [8–10], as well as human health and the environment [11–13]. The reactions of VOCs are primarily initiated by OH, O₃, NO₃, and Cl oxidants [14]. Among of them, the hydroxyl radical (OH) is particularly important because it controls the removal of most atmospheric pollutants, such as carbon monoxide (CO) and VOCs [15,16]. These reactions are often accompanied by a series of subsequent oxidation steps, such as alkyl, alkoxy, alkylperoxy and Criegee intermediates reactions, which make the chemical transformation mechanisms very intricate [1]. It is usually difficult to obtain a clear picture of various reaction channels simply from experimental studies and generally requires theoretical explanation or predication.

To explore reaction processes, where the rate-determining step is particularly important, the elusive transition state structures must be found. A transition state (TS) which can be determined by searching for the first-order saddle points on potential energy surfaces (PES), is the state corresponding to the highest energy along a particular reaction coordinate and is essential for analyzing the reaction path and rate. Usually, the determination of a TS is performed via manual searching, which begins from guessing a possible structure based on the reactant and product configurations. The performance of manual searching typically requires one should be familiar with the reaction mechanism and with good chemical intuition. However, this is not true in most cases, especially for those unknown chemical reactions. In addition, chemical reactions may contain multiple transition state structures and a variety of intermediates exist on the reaction pathways due to the complexity of the reaction systems. Even researchers specialized in chemical reactions may have difficulty in finding out all transition states. To determine the correct transition states is usually a tedious, time-consuming, and error-prone process. Therefore, a systematic and effective TS search method is urgently needed for the automatic exploration of transition state structures.

In this work, we developed a simple and efficient method called Monte Carlo Transition State Search Method (MCTSSM) which combines the Monte Carlo sampling technique and the TS optimization methods to determine the transition states of complex atmospheric reactions. Similar to our successful Basin-Hopping (BH) method with the Monte Carlo sampling technique and a local

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optimization method to obtain global minimum structures of atomic and molecular clusters [17–25], the MCTSSM method started from a Monte Carlo randomly generated initial guess based on the reactant configurations, and the initial guess was then optimized via local TS optimization methods implemented in quantum chemistry package like Gaussian [26]. MCTSSM can be combined with Gaussian 09 [26] or DMol³ [27,28]. In principle, any TS optimization algorithm implemented in Gaussian or DMol³ can be employed in combination with the MCTSSM method. In the present work, we chose the default Beryny optimization algorithm [29] implemented in Gaussian 09 for TS optimization. To save computational cost, Hartree–Fock (HF) theory and Density Functional Theory (B3LYP) with small basis set were chosen for initial TS optimization. Then, all the TSs found from MCTSSM using HF or B3LYP were re-optimized using the higher-level theory recommended in the relevant literature for a particular system.

Many different strategies for finding TS have been suggested [29–43]. The MCTSSM presented here differs from previous efforts in two ways: (1) The Monte Carlo sampling technique and TS optimization method (which is implemented in widely used quantum chemistry package like Gaussian) are integrated via a computer script. This manner is flexible and allows for changes to the script, suggesting it can be easily improved in the future. (2) The initial guesses are generated via Monte Carlo sampling with simple parameters, and this gives the guarantee to find enough TSs. The MCTSSM strategies on the combination of Monte Carlo sampling technique and TS optimization method are summarized in Section 2. Then examples of applications of the method are discussed in Section 3. The reactions of OH radicals with the general atmospheric VOCs are primarily considered to be the test suites. Other attack group reactions, such as O₃, NO₃, Cl and H₂O, are also studied. Additionally, the reaction of β-pinene-sCI (stabilized Criegee Intermediates) with water is chosen as a new system for testing.

2. Methods

Our successful Basin-Hopping method has been widely used on structure exploration of atomic clusters and molecular clusters [17–25]. Here we present a new method applying a Monte Carlo sampling technique and TS optimization method for automatically searching the TS for resolving complex atmospheric reactions. To start TSs searching, only the reactant structures are needed as initial inputs for the Monte Carlo random sampling; *a priori* knowledge of the products is not required. Fig. 1 shows the flowchart of the method. The method for finding TSs can be summarized as follows:

- (1) Input the known reactants structure (Cartesian coordinates of reactant A and reactant B) and some simple parameters. (Sampling parameter R represents an initial distance between atoms, M represents the number of TS searches.)
- (2) Start from the given reactants structure, the initial random guess is generated automatically via Monte Carlo sampling.
- (3) Invoke Gaussian 09 (or other quantum chemistry package) to optimize the initial guess with the key words “opt = (ts, calcfc, maxcyc = 500) freq” in our script and calculate the frequency with low-cost electronic structure methods such as HF or DFT (method and basis set are set by the users in step (1)).
- (4) Read the output frequencies. If the list of output frequencies has only one imaginary frequency (IF), then the optimized geometries with sampling parameter $R = R'$ are saved, and $R = R'$ replaces $R = R_0$ as the initial distance in the next cycle. If not, sampling continues with parameter $R = R_0$ until the structure with only one IF is found.

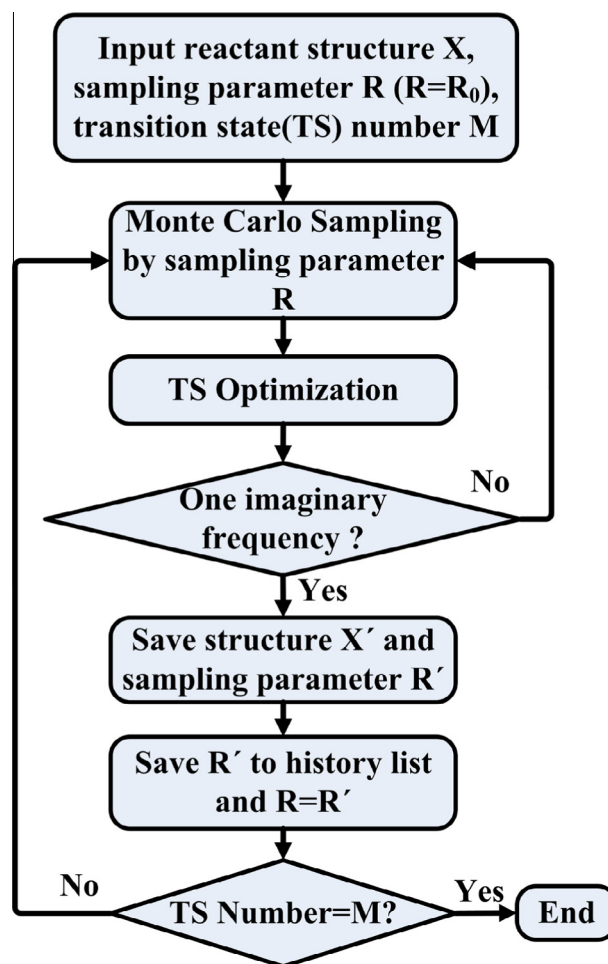


Fig. 1. Flowchart of the Monte Carlo Transition State Search Method (MCTSSM).

- (5) Terminate the search. The TS searching number M is set to terminate the search. M defined by the user is based on the size of the system.

Sampling parameters are very important. The efficiency of the MCTSSM depends heavily upon the effective sampling. The initial guess generated via Monte Carlo sampling is completely random, thus structures taken from Monte Carlo (MC) sampling are often deviate from true TSs. As a result, the self-consistent field (SCF) or TS optimization calculation often fails to converge, which adds additional cost for finding the true TSs. Therefore, we introduced some reasonable empirical parameters to constrain traditional MC sampling. Such a sampling is not completely random and we call it “restricted” or “constrained” MC sampling. “Restricted” MC sampling can generate “higher quality” initial guesses which probably are located in the limited zone near the true TS.

Different from traditional Basin-Hopping (BH) method, which allows each atom to move independently, here we consider that the reaction system consists of two molecules, that is reactant A (such as OH radical) and reactant B (such as dimethyl ether). Generally, we designated reactant A (such as OH radical) as attacking molecule which attacked towards reactant B and rotate randomly around B (such as dimethyl ether), but the relative positions of atoms in A are fixed, and it is the same for molecule B. So the MCTSSM moves each molecule as an entirety, and that is to say, the relative positions of atoms in the same molecule are kept fixed. Sampling parameter R represents an initial distance between atoms which has been defined in step (1). In principle, there are

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