Oscillatory reaction cross sections caused by normal mode sampling

Tibor Nagy, Anna Vikár and György Lendvay[a]

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian

Academy of Sciences, Magyar tudósok körútja 2., H-1117 Budapest, Hungary

Abstract

The quasiclassical trajectory (QCT) method is an efficient and important tool for studying the dynamics of bimolecular reactions. In this method, the motion of the atoms is simulated classically, and the only quantum effect considered is that the initial vibrational states of reactant molecules are semiclassically quantized. A sensible expectation is that the initial ensemble of classical molecular states generated this way should be stationary similarly to the quantum state it is supposed to represent. The most widely used method for sampling the vibrational phase space of polyatomic molecules is based on the normal mode approximation. In the present work it is demonstrated that normal mode sampling provides a nonstationary ensemble even for a simple molecule like methane, whose reaction dynamics is widely studied both experimentally and theoretically. The consequences were investigated for reaction $CH_4+H \rightarrow CH_3+H_2$ and its various isotopologs and were found to be dramatic. Reaction probabilities and cross sections obtained from QCT calculations oscillate periodically as a function of the initial distance of the colliding partners and the excitation functions become erratic. The reason is that in the nonstationary ensemble of initial states the mean bond length of the breaking C–H bond oscillates in time with the frequency of the symmetric stretch mode. We propose a simple method, one-period averaging, 1PA, in which reactivity parameters are calculated by averaging over an entire period of the mean C–H bond length oscillation, which removes the observed artifacts and provides the physically most reasonable reaction probabilities and cross sections when the initial conditions for QCT calculations are generated by normal mode sampling.

---

[a] Author to whom correspondence should be addressed. Electronic mail: lendvay.gyorgy@ttk.mta.hu.

I. INTRODUCTION

Theories of elementary gas-phase reactions allow one to rationalize the experimental data and to explore the connection between experimentally measurable quantities and the features of the potential energy surface. The exact theoretical description of the dynamics of elementary reactions requires the use of quantum mechanics. However, for systems involving more than 4 atoms, full-dimensional quantum scattering calculations can only be performed in exceptional cases[1,2]. An often used possibility is the application of reduced-dimensionality quantum mechanical methods in which only the assumedly relevant degrees of freedom are treated explicitly[3,4]. However, with increasing molecular size and flexibility the number of relevant degrees of freedom also quickly reaches the limit above which they cannot be handled explicitly.

On the other hand, classical trajectory calculations can be performed for most molecules relevant in gas-phase chemistry if the potential energy surface (PES) is available. In these calculations, the only limitation in system size is the computational effort necessary to calculate the accurate potential energy surface. Classical mechanics, however, cannot handle quantum effects. The most serious problem is that the concept of zero-point vibrational energy essential in quantum systems is missing from classical mechanics. An *ad hoc* technique is the quasiclassical trajectory (QCT) method[5] in which reactant molecules are prepared in classical states corresponding to a given rovibrational quantum state; their collisions are then investigated with classical dynamics simulations, and the states of product molecules are also characterized by rovibrational quantum numbers. The technique was originally worked out for atom + diatomic molecule systems. The molecular reactant in these systems has only one vibrational degree of freedom plus rotation, and approximate methods such as second-order perturbation theory often provide reasonably accurate ensembles of phase space points corresponding to preselected quantum states[6]. More refined is the technique in which periodic orbits are found for a rotating-vibrating diatomic molecule. According to this method, fast Fourier transformation is used to

identify frequencies and actions corresponding to a quasiperiodic trajectory, and by varying the initial conditions, the trajectory with the desired quantum number is found[7,8].

Rigorous quantization of vibrational motion in polyatomic molecules can be done by using semiclassical methods. Nuclear motion of a polyatomic molecule with N atoms have $f=3N-6$ internal degrees of freedom ($3N-5$ for linear molecules). If the vibrations of a molecule are separable, the Wentzel-Kramers-Brillouin (WKB)[9] semiclassical quantization of the action integral over a period of oscillation can be used for each mode. For molecules with nonseparable but integrable vibrational Hamiltonian the Einstein-Brillouin-Keller (EBK) semiclassical method can be applied, which is based on Einstein's theorem stating that the motion of such systems in phase space is confined to $2f$-dimensional time-invariant tori characterized by the values of the action integrals along f topologically different noncontractible closed loops[10]. For nonintegrable systems, as Einstein proposed, the EBK procedure does not work and a whole new field of physics grew out of the studies on the classical-quantum correspondence in chaotic systems (e.g. Ref. 11).

When an ensemble of phase space points is needed for a semiclassical representation of a molecular vibrational quantum state (for example, to initiate trajectories in a QCT calculation), the torus for which the actions correspond to the desired quantum numbers is located and sampled. The obtained ensemble is a classical representation of the preselected quantum state and is inherently time independent, *i.e.* stationary just like the quantum state itself. In practice, locating the appropriate torus proved to be very difficult for polyatomic molecules with more than 3 atoms and is often not possible because their vibrations are often nonintegrable and chaotic.

A widely used approximation is that the intramolecular phase space is considered separable. Separability provided by the harmonic approximation is the basis of the normal mode sampling method, which is routinely used in QCT calculations to prepare initial states. As long as the normal mode approximation is appropriate for the molecule to be studied, this method will

provide an ensemble of classical states which is a good representation of the desired quantum state. However, the vibrations of polyatomic molecules are usually anharmonic and nonseparable and intramolecular vibrational relaxation takes place due to the coupling between normal modes. Considering the time evolution of a normal mode sampled ensemble on average, the general observation[12] is that the energy flows from high- to low-frequency modes when the molecules are prepared in ground state. If the coupling between modes is strong, the initial distribution of energies will change quickly and the ensemble of molecules will not be stationary even on the timescale of a few vibrational periods.

The stationarity of an ensemble of initial states of a molecule is important if one intends to investigate its reactivity. In QCT calculations of bimolecular reactions, partners are shot together from an initial distance where their interaction can be considered negligible. At the temperatures relevant to chemistry (below 3,000 K) the molecules move relatively slowly and several periods of vibrations can take place during the approach of reactants. During the initial free flight, the energy within the reactant molecules can be reorganized, and depending on the time of flight the reactants will be in different stages of the intramolecular vibrational energy redistribution upon arrival to the strong interaction region, which is expected to affect the calculated reactivity parameters.

Issues with nonstationarity already arose soon after large-scale QCT calculations became possible for the simplest bimolecular reaction, the collinear collision of H_2 molecule and H atom. Careless and Hyatt[13] proposed that the classically accessible region of the quantum distribution of bond extensions should be used for sampling H_2 vibrations to generate initial conditions for quasiclassical trajectory calculations. The reaction probability curve as a function of collision energy they obtained showed features resembling quantum resonances. In subsequent work Bowman et al.[14] pointed out that such selection of initial conditions is physically unacceptable because it leads to a nonstationary ensemble of initial conditions of the H_2 molecule and gives

reaction probabilities which depend substantially on the choice of initial separation between the reactants. They have also shown that the only stationary initial state ensemble will be the accurate solution of the classical equations of motion corresponding to the preselected "quantum numbers", which is a single periodic trajectory. The correct way of calculating reactivity parameters is that the entire periodic trajectory is sampled uniformly.

In ground-state molecules, the relaxation of a normal mode sampled state is manifested as the exchange of zero-point energies (ZPE) of individual normal modes. This is particularly important when, during a classical trajectory, a polyatomic molecule arrives in the strong interaction region, because the ZPE lost from vibrational modes can be utilized to pass over the barrier for reaction, this way unphysically reducing the threshold energy for reaction. Since controlling energy flow is not a trivial problem, a resort is to determine whether the nonstationarity of the normal mode sampled ensemble (*i.e.* intramolecular vibrational relaxation) influences the QCT reactivity parameters and if so, how much. Xie *et al.*[15] investigated the classical energy relaxation of the state of CH_4 in which one of the triply degenerate stretch modes was excited by one quantum. They considered the relaxation particularly likely because sharing energy between modes of same frequency (within harmonic approximation) was usually rapid. They pointed out that the short interaction time of hyperthermal collisions, relevant in the methane+H atom reaction, lessens the concern. For the estimation of this time period, they selected the initial separation of the centers of mass of the CH_4 and H reactants to be 9 a_0 and an initial relative kinetic energy of 1.52 eV. For this setup, reactants reach the strong interaction region in roughly 10 fs. So, the practical concern about relaxation of vibrationally excited CH_4 is limited to this relatively short time scale. They followed the average energy of the selected excited normal mode in a standalone CH_4 molecule in 41 trajectories and found on average less than 20% energy loss from the mode up to 25 fs. They concluded that this approach is still realistic to model the effect of excitation on reactivity. Note, however, that the 20% loss of mode

energy in fact corresponds to 30% loss of the excitation energy that makes this conclusion less convincing.

Czakó et al.[16] monitored the conservation of normal mode vibrational quantum numbers of CHD_3 after exciting the nearly local C–H stretch mode ν_1. They followed the dynamics of methane with $\nu_1=1$ excitation in 100 trajectories for 360 fs and found that the average normal mode quantum numbers were conserved satisfactorily well at least for a time scale used in the QCT calculations. However, examining their results, one can see that on average, significant transfer of energy from other stretch modes (mean quantum number change $\Delta\nu_{mean} = -0.1$) to the bending modes ($\Delta\nu_{mean} = +0.3$) took place in the investigated period, indicating that the final reactivity data might have been biased by relaxation.

Camden et al.[17,18] used a different scheme to avoid problems caused by nonstationarity of the ensembles generated by normal mode sampling in their investigation of the dynamics of $CD_4+H\rightarrow CD_3+HD$ reaction. For generating initial conditions corresponding to the vibrational ground state of CD_4, an intramolecular trajectory was started from the equilibrium geometry of CD_4, placing the entire zero-point energy of each mode into kinetic energy. This "root" trajectory was integrated for a long period covering many vibrational periods. CD_4 coordinates and momenta corresponding to randomly selected phases of this trajectory were used as initial conditions in QCT calculations. Since the root trajectory is very long, the initial ensemble is thought to be stationary. The procedure, however, cannot be used in cases when the corresponding intramolecular trajectory displays significant relaxation, because then the excitation energy or a significant part of it leaks out of the desired mode during the evolution of the root trajectory and gets distributed among all degrees of freedom.

The purpose of the present work is the investigation of the nonstationarity of the ensembles of phase space points generated by normal mode sampling. We also assess the influence of nonstationarity on the calculated value of the most important reactivity parameters, namely,

reaction probabilities and reaction cross sections. Based on the observations from these studies, we propose a correction scheme that allows one to avoid the problem of nonstationarity and to derive physically meaningful reactivity parameters. Our test molecule is methane and the test reaction is the abstraction one of its H atoms by an attacking H atom:

$$CH_4 + H \rightarrow CH_3 + H_2. \tag{R1}$$

The paper is structured as follows: in Sec. II the standard methods applied in QCT calculations, including the principles of normal mode sampling are briefly reviewed and some methodological details are listed. In Sec. III we demonstrate the nonstationarity of ensembles of classical states generated by normal mode sampling to describe the vibrational ground state of various methane isotopologs (CH_nD_{4-n}, $n=0,..,4$); then the impact of nonstationarity, manifested as oscillation in reactivity parameters is presented. This is followed by the evaluation of sampling techniques that could serve as possible improvements to normal mode sampling (WKB quantization, energy homogenization). In Sec. IV a simple method is proposed to remove reactivity oscillations that allows one to produce the physically most meaningful reactivity data; and finally we investigate the range of systems and conditions where reactivity oscillations are expected to emerge.

II. THEORY

A. Normal mode sampling

Normal mode sampling (NMS) used in QCT calculations to generate initial ensembles of states is based on the harmonic approximation in which the potential energy $V(\mathbf{x})$ is approximated with its Taylor expansion up to second order around the equilibrium geometry ($\mathbf{x}_e$). Then in Cartesian coordinates both the kinetic and the potential energy in Hamiltonian H are quadratic:

$$H(\mathbf{x},\mathbf{p}) = \tfrac{1}{2}\mathbf{p}^{\mathrm{T}}\mathbf{M}^{-1}\mathbf{p} + V(\mathbf{x}) \approx \tfrac{1}{2}\mathbf{p}^{\mathrm{T}}\mathbf{M}^{-1}\mathbf{p} + \tfrac{1}{2}\left(\mathbf{x}-\mathbf{x}_{\mathrm{e}}\right)^{\mathrm{T}}\mathbf{F}_{\mathrm{e}}\left(\mathbf{x}-\mathbf{x}_{\mathrm{e}}\right), \qquad (1)$$

where for an N atom system $\mathbf{x}=(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and $\mathbf{p}=(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ are the $3N$-component coordinate and momentum vectors consisting of those of individual atoms ($\mathbf{r}_i=(x_i,y_i,z_i,)$ and $\mathbf{p}_i=(p_{ix},p_{iy},p_{iz})$), $\mathbf{M}=\mathrm{diag}(m_1,m_1,m_1, \ldots, m_N,m_N,m_N)$ is the diagonal $3N\times3N$ mass matrix and $\mathbf{F}_{\mathrm{e}}$ is the force constant matrix. Due to the pure quadratic form of the Hamiltonian, it is possible to transform the deformations and momenta into coordinates Q_i and momenta P_i, in which the cross terms disappear both in the kinetic and the potential energy (see details in the supplemental material[19]), so that the Hamiltonian becomes a sum of $3N$ one-dimensional harmonic oscillator Hamiltonians:

$$H^{\mathrm{1D}}_{\mathrm{harm},i} = \tfrac{1}{2}P_i^2 + \tfrac{1}{2}\omega_i^2 Q_i^2 . \qquad (2)$$

In this decomposition procedure, called normal mode analysis[20], the system is formally decomposed into independent harmonic oscillators, called normal modes. The $3N$ frequencies ω_i are positive except 6 (5 in linear molecules), which are zero. The zero-frequency modes correspond to overall translation and rotation. When a quantum state is characterized by a set of vibrational quantum numbers n_i, each vibrational normal mode is given an energy according to the exact quantum mechanical harmonic oscillator expression:

$$E^{\mathrm{1D}}_{\mathrm{harm},i} = \hbar\omega_i\left(n_i+\tfrac{1}{2}\right) . \qquad (3)$$

For a harmonic oscillator this coincides with the expression provided by the semiclassical WKB quantization condition[9]. In the NMS procedure the phases of these oscillators are sampled randomly from uniform distributions, and the corresponding deformations and momenta are converted to Cartesian coordinates and momenta, and summed up. This way phase space points $(\mathbf{x},\mathbf{p})$ are obtained, which we shall refer to as classical states. In order to investigate the average behavior of the quasiclassically quantized system, ensembles of classical states are generated by normal mode sampling (hereafter referred to as NMSE). When the quantum state of the molecule

is to be determined, the inverse procedure can be used. The details of these steps are given in the supplemental material[19].

B. Quasiclassical trajectory calculations

Two of the analytical potential energy surfaces available for reaction R1 were used in the present study, those developed by Corchado *et al.* (denoted as CBE)[20] and by Zhang *et al.* (called ZBB3)[21]. The ZBB3 PES is globally more accurate. Its disadvantage is that the calculation of the forces is two orders of magnitude slower than on the CBE PES, making the latter more suitable for method development. Using the standard normal mode sampling procedure, ensembles of classical states of methane molecules representing the rovibrational ground state were prepared. The number of intramolecular and collision trajectories (N_{traj}) was varied between 10^3–10^4 and 10^4–4×10^5, respectively. For the collision trajectories, the sampled methane molecules were randomly oriented in uniform distribution using Euler rotations. For reaction cross section calculations the impact parameter (b) was sampled uniformly from the [0, 4.5 a_0] interval (in the calculations and in this paper we use atomic units a_0=0.5291772 Å, τ_0=2.419×10^{-17} s and E_h=27.2114 eV for distance, time and energy, respectively). The initial center of mass (c.m.) distance of reactants (R_{ini}) was scanned starting from 12 a_0, up to 24.9 a_0 in 0.3 a_0 steps (unless stated otherwise). In this region the initial interaction energy is negligible (≤0.1 mE_h) compared to the vibrational zero-point energy of methane (~40 mE_h, 1.09 eV) and to the applied collision energies. Collision energies (E_{coll}) were scanned in 5-10 mE_h steps between 10 and 90 mE_h covering the range of previous measurements and calculations[1,2,15,17,18,21–23]. The lower limit is much below the classical barrier height of the reaction (cca. 24 mE_h) because we wanted to characterize the entire reactive range in which classical mechanics provides reaction. In the evaluation of reaction probabilities and cross sections, all trajectories were included and no attempt was made to investigate the final states of products. In the figures we report error bars

corresponding to 2σ Monte Carlo error, generally only for a short abscissa range to ensure transparency.

For the simulation of collisions, Hamilton's equations of motion were integrated in Cartesian coordinates using the Runge-Kutta method by adapting the step size to guarantee energy conservation within 0.05 mE_h throughout each trajectory. For the integration of intramolecular trajectories the time step was 1 τ_0, with which constants of motion were conserved (*e.g.* the energy within 0.001 mE_h) for 10^6 τ_0-long trajectories.

In the following, when intramolecular trajectories of methane isotopologs are discussed, H$_n$–CD$_m$ will denote the average length of n H–C bonds, and H$_n$C–D$_m$ will stand for that of the m C–D bonds. When reaction probabilities (P_r) and cross sections (σ_r) for abstraction reactions of methane isotopologs are discussed, H$_n$–CD$_m$ will denote that one of the n H atoms, and H$_n$C–D$_m$ that one of the m D atoms is abstracted. The identical isotopes of H in methane were not distinguished and the total reactivity including all of them was considered. However, to enable direct comparisons, these data were divided by the number of identical H isotopes n or m to obtain quantities called "reaction probability per bond" (P_r per bond) and "cross section per bond" (σ_r per bond).

III. RESULTS

### A. Nonstationarity of ensembles generated by normal mode sampling

A crucial criterion for ensembles of initial states in QCT calculations is that they should be stationary. For such ensembles the distribution of the properties does not change in time, apart from the statistical fluctuations which scale inverse squarely with the sample size. Sampling a stationary ensemble produces reactivity parameters that do not depend on the initial separation of reactants.

The evolution of the NMSEs of rovibrationally ground-state methane molecules was investigated by the integration of ensembles of 10^4 and 10^3 intramolecular trajectories for 10^6 τ_0 and 10^5 τ_0 on the CBE and the ZBB3 PESs, respectively. The calculations were performed for five isotopologs of methane (CH_nD_{4-n}, $n=0,..,4$).

One can expect that in reaction R1 the length of the breaking bond participating in the H-atom abstraction will influence the magnitude of the reactivity parameters. The ensemble average of the carbon-hydrogen bond length in methane isotopologs is shown as function of relaxation time (t_{relax}) in Fig. 1 obtained on the CBE PES. The mean C–H bond length was obtained by averaging over all C–H bonds in the molecule; the average C–D bond lengths were determined analogously. For symmetry reasons the influence of the nonsymmetrical modes cancels out, and the data obtained this way correspond to the global average phase of the corresponding local C–H or C–D ($n=1$) or the appropriate symmetric C–H_n or C–D_n ($n>1$) stretch mode at the given point in time of ensemble evolution.

Remarkably, in the initial section of the ensemble evolution, the mean C–H bond extension oscillates with a large amplitude (as large as 0.025 a_0), implying phase coherence between the stretch vibrations of individual samples. The period of the oscillation is τ_{CH}=450 to 480 τ_0 and τ_{CD}=630 to 665 τ_0 for C–H and C–D bond lengths, respectively, depending on the isotope combination. Converting these to wavenumbers, one gets approximately 2900-3050 cm^{-1} and 2090-2190 cm^{-1} respectively, which are, as expected, in good agreement with those of the corresponding local or symmetric C–H and C–D stretch modes, or with the nondegenerate symmetric stretch frequencies when multiple identical H isotopes are present in the molecule (for details see Table S1 in supplemental material[19]). During the initial 10^4 τ_0 period, the oscillation is
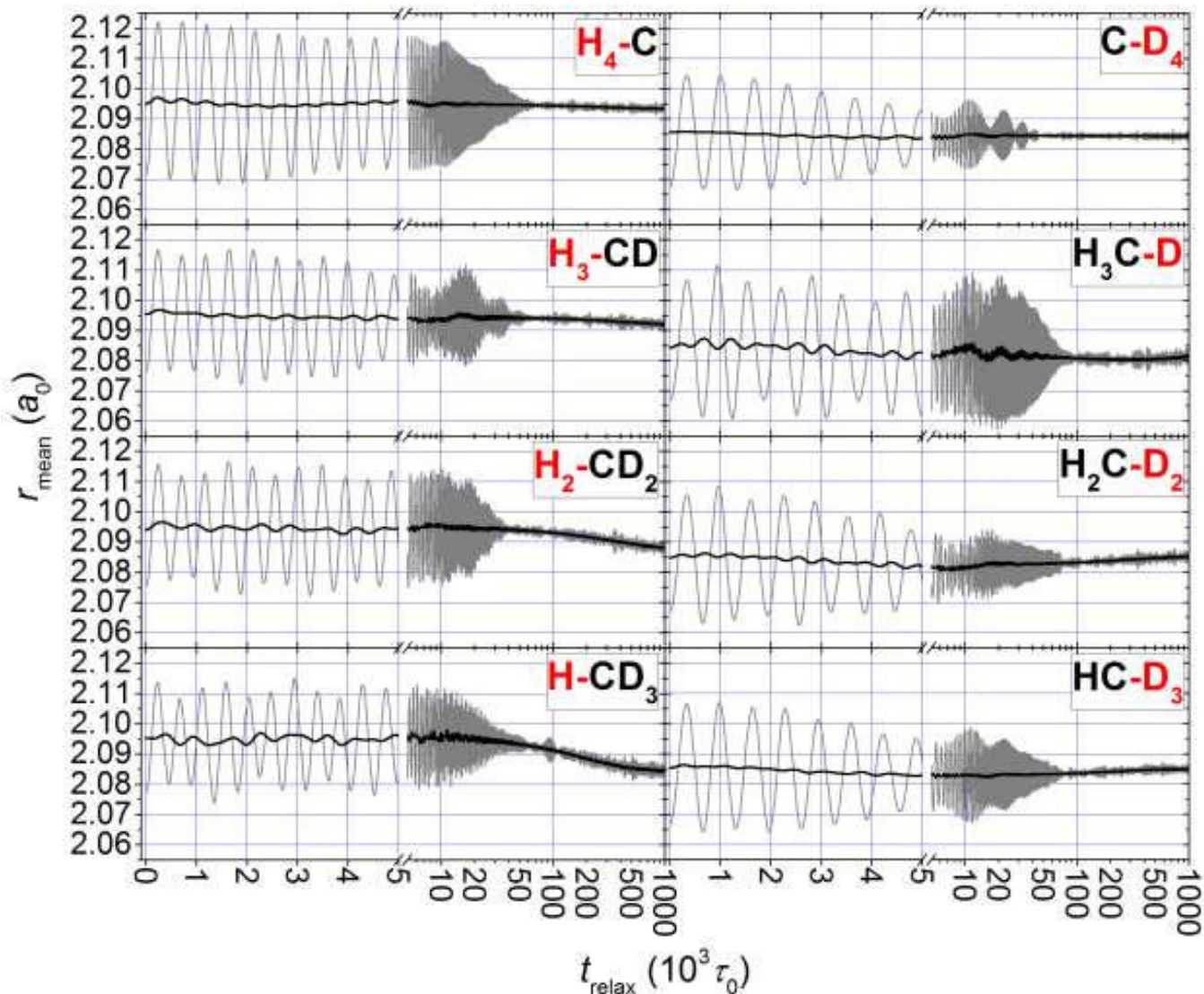
**FIG. 1.** Time dependence of the mean C–H (left panel) and C–D (right panel) bond lengths (gray lines; equilibrium value: 2.0579 a_0) on the CBE PES in ground-state methane isotopologs CH_nD_{4-n} ($n=0,..,4$), obtained from the time evolution of 10^4 normal mode sampled states. There is a scale change at 5×10^3 τ_0 from linear to logarithmic. The black curve is the moving average with a one-period wide time window.

close to sinusoidal in CH_4. In the other isotopologs the amplitude slightly varies on this time scale and even beating can be observed (e.g. in H_3–CD, C–D_4, HC–D_3), indicating that energy is exchanged between the stretch and the other modes. The amplitude of the C–H bond length oscillation in the first 10^4 τ_0 time period is significant which, as will be shown later, induces drastic changes of the reactivity parameters. Later during ensemble evolution, the amplitude of the oscillation decays to low values by 5×10^4-10^5 τ_0. The relatively large amplitude oscillations visible in the 10^5 to 10^6 τ_0 period are statistical fluctuations; their magnitude decreases with increasing sample size.

Fig. 1 also shows running averages (black lines) calculated over a one-period wide ($1\,\tau_{CH}$ or $1\,\tau_{CD}$) moving time window. Note that the average C–H and C–D bond extensions in the NMSE at zero time are about $0.02\,a_0$ and $0.01\,a_0$, respectively, with respect to the equilibrium length of $2.0579\,a_0$, while their running averages vary within the 0.035–$0.040\,a_0$ (C–H) and 0.025–$0.028\,a_0$ (C–D) ranges. This is not surprising: the initial coordinates and momenta are generated assuming a quadratic PES around the equilibrium geometry, thus the normal mode extensions are too short and the contractions are too long with respect to those corresponding to the same energy level on the anharmonic potential surface. As soon as dynamics are started, the bond lengths tend to oscillate around the values dictated by the anharmonic PES.

The moving average of the mean bond length is approximately constant in the first $10^4\,\tau_0$ period and remains close to this value in the whole simulation time. The slow changes taking place during the first $10^6\,\tau_0$ include a negligibly small drift in the CH_4 and CD_4 isotopologs, suggesting a slight energy loss from symmetric stretch to other modes. More complicated patterns are observed in the mixed isotopologs, the largest change being a reduction of the average C–H bond length from about 2.095 to $2.085\,a_0$ after $10^6\,\tau_0$, which is not negligible. Overall, the moving average C–H bond length decreases, that of the C–D bond increases, which indicates a minor symmetric C–H to symmetric C–D stretch energy transfer. Similar behavior was observed on the ZBB3 PES (see Fig. S1 in the supplemental material[19]).

Since the methane initial state ensembles are designed to correspond to specific quantum states, the time development of the quantum numbers in each vibrational mode is one of their most important characteristics. The evolution of ensemble average normal mode quantum numbers calculated using the method described in the supplemental material[19] on the CBE PES for the CH_4 isotopolog are shown in Fig. 2 together with the evolution of the mean C–H bond length serving as a clock.
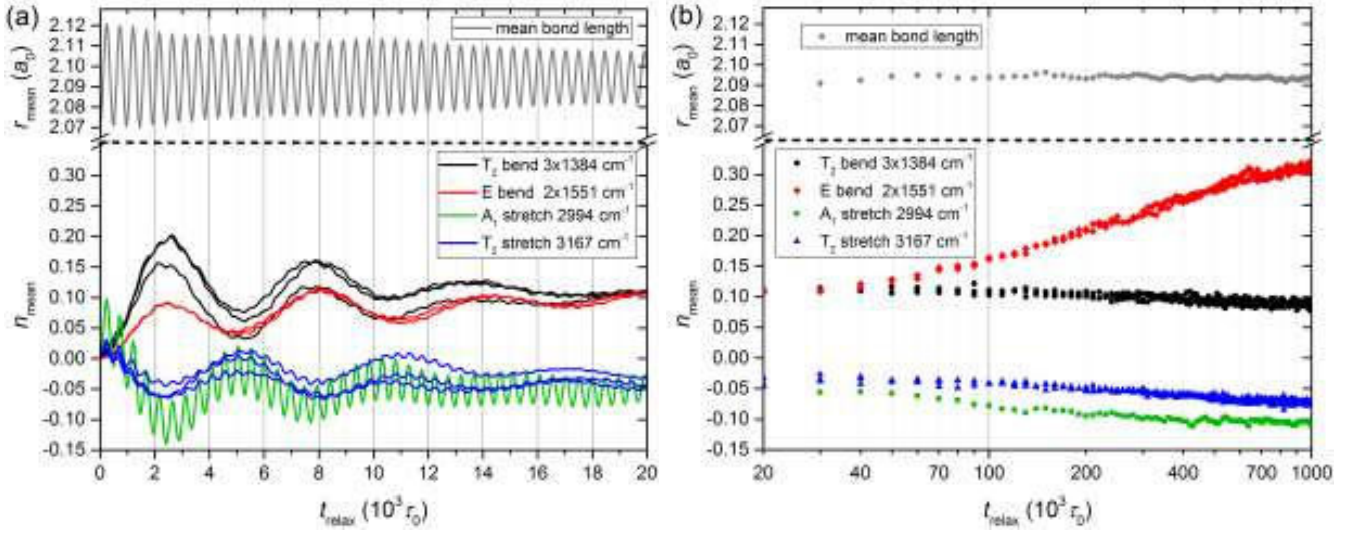
FIG. 2. (a) Evolution of the mean bond length (upper panels) and the mean normal mode quantum numbers (lower panels) of CH_4 in ground-state on the CBE PES obtained from the trajectory simulation of 10^4 normal mode sampled states for $2 \times 10^4 \, \tau_0$. (b) Same as (a), but data is shown at every $10^4 \, \tau_0$ between $2 \times 10^4 - 10^6 \, \tau_0$ using logarithmic time scale.

The behavior of quantum numbers also proves that the NMSE is nonstationary. In the first 3,000 τ_0 period the quantum numbers of the high-frequency stretch modes decrease, whereas the low-frequency bending modes gain energy. Such behavior has also been mentioned in the literature (see e.g. Ref. 12). During the first 20,000 τ_0, a long-period damped oscillation can be observed, which starts from the "stretched state" represented by the initial NMSE. The temporal change of the average quantum numbers of the stretch versus bending modes is completely synchronous but the phases are opposite. This damped beating with an approximate time period of 5,000 τ_0 is an obvious sign of strong stretch-bend coupling within CH_4. It is worth mentioning that a short-period oscillation which is synchronous with that of the ensemble average bond lengths is superimposed on the damped oscillatory quantum number curves, but the long-period quantum number oscillation is not reflected in the bond-length oscillations (the amplitude of which decays four or five times slower than the quantum number oscillation). The overall temporal evolution of the normal mode quantum numbers clearly indicates that the classical normal mode approximation is not appropriate for the description of the vibration of methane. The ensemble average quantum numbers for stretch modes (which are nominally zero for the ground state of methane) change within a single stretch period by more than 0.05 and vary

between 0.1 and -0.15 during the first 5 or 6 stretch oscillations. This means that the "quantum state" of methane, represented by the ensemble, will change during the initial "free" flight of the reactants when collisions are simulated by trajectories.

B. Oscillatory reactivity as a consequence of nonstationarity of ensembles generated by normal mode sampling

When the C–H bond extension contributes significantly to the reaction coordinate in a reaction, the large-amplitude oscillation of the ensemble average bond length can have profound consequences on the reactivity. This is the case for reaction R1. The reactivity is expected to be larger when the system enters into the strong interaction zone in the stretched phase of the bond length oscillation than when it arrives in the contracted phase. The change of the phase of the mean C–H bond length oscillation during the "free" flight is determined by the value of R_{ini}. This is demonstrated schematically for reaction $CH_3H'+H''\rightarrow CH_3+H'H''$ in Fig. 3, which shows individual trajectories calculated on the CBE PES corresponding to head-on collisions ($b=0$, $E_{coll}=40$ mE_h, 1.09 eV) for which the initial conditions were the same, except that R_{ini} was varied between 12.0 a_0 and 14.2 a_0 in 0.2 a_0 steps. In this, otherwise typical, methane state, the breaking C–H' bond was approximately pointing towards the attacking H'' atom.
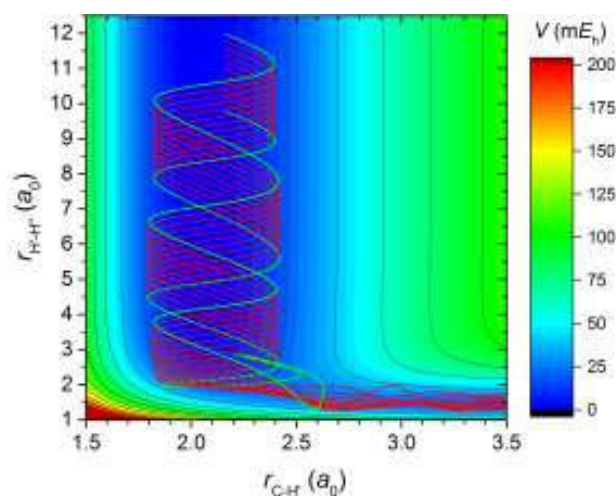

FIG. 3. Traces of a series of trajectories starting from the same initial state of methane at R_{ini} varying between 12.0 and 14.2 a_0 together with a contour plot of the CBE PES for reaction $H_3CH'+H''\rightarrow H_3C+H'H''$, plotted as a function of the H'–H'' and C–H' distances. The potential energy was calculated at geometries with C_{3v} symmetry and fixing the H_3C fragment at its equilibrium geometry within methane. Reactive and nonreactive trajectories are drawn in red and green, respectively. The green trajectory which starts at around 10 a_0 H'–H'' separation corresponds to $R_{ini}=12$ a_0. The impact parameter is zero and the collision energy is 40 mE_h (1.09 eV).

15

The trajectories are projected on the plane of the breaking C–H' and forming H'–H" bond lengths together with the contours of the respective section of the PES at a collinear H_3–C–H'–H" arrangement while constraining the H_3C moiety fixed at its equilibrium geometry within methane. Trajectories plotted in red are reactive, and for clarity, only two nonreactive trajectories are shown (in green, representing the edges of the nonreactive segment). One can see that trajectories arriving at an H'–H" distance between 4.5 and 2.5 a_0 when the C–H' oscillation is at the outer turning point are reactive, those that arrive at this phase between r(H'–H")=5.5 and 4.5 a_0 are nonreactive. Since the mean C–H bond length in the NMSE oscillates similarly to the bond length in individual molecules, one can expect that similar phase dependence will be manifested in the behavior of ensembles, inducing a dependence of reactivity parameter on the duration of the initial free flight time which translates to dependence on R_{ini}. This can be seen in Fig. 4(a), showing the per bond reaction probabilities for reaction R1 as a function of R_{ini}. The reaction probability P_r shows large-amplitude sinusoidal oscillations extending from 0.95% to 1.58%. This means that if P_r is calculated by starting trajectories at a given R_{ini}, one is faced with as large uncertainty as 60% (between minimum and maximum value) in the theoretical determination of the reaction probability with QCT calculations.

Fitting a sine function to the first four periods, the wavelength was found to be $\lambda_{Pr} \approx 3.2\ a_0$. From the collision energy and the reduced mass of the colliding partners, this wavelength can be converted to a flight time period of 480 τ_0, matching exactly the period of ensemble average bond length oscillations in CH_4. Fig. 4(b) shows the evolution of the ensemble average C–H bond length as a function of flight time plotted to match the reactivity oscillation. The synchronization was performed based on the assumption that large bond extension corresponds to large P_r, and on the observation that the mean C–H bond length performs about two oscillations before the strong interaction region is reached by the trajectories starting at R_{ini}=12 a_0.
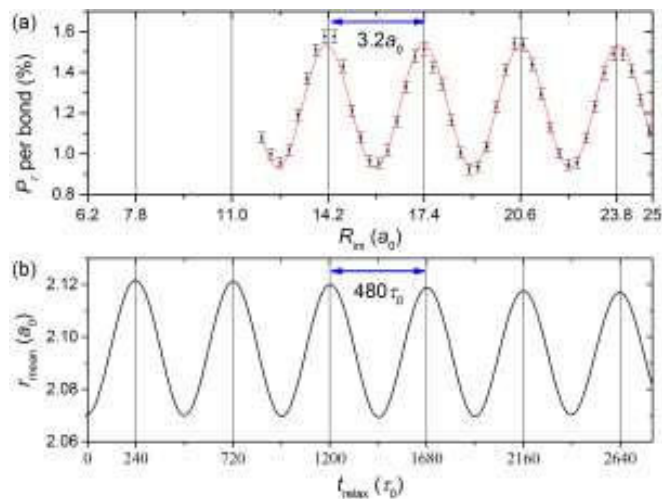
FIG. 4. (a) Oscillatory reaction probability as a function of the initial distance of reactants for the $CH_4+H\rightarrow CH_3+H_2$ abstraction reaction on CBE PES at 40 mE_h collision energy and zero impact parameter obtained for 10^4 trajectories. A fitted sine function is also shown in red. (b) The corresponding evolution of the mean bond length in the same but freely evolving ensemble of CH_4 molecules (see text for details).

From this, one can conclude that the CH_4 molecules react around 1,000-3,000 τ_0 after their preparation if the initial separation is varied in the 12.0-24.9 a_0 range. The perfect match of the reactivity and mean bond length oscillation suggests that, as expected, it is the latter that determines the reactivity. Remarkably, there is no sign of the damped oscillation that occurs during the evolution of normal mode quantum numbers, which means that the mode energies and amplitudes do not affect directly the reactivity. A consequence of this is that by monitoring the evolution of the normal mode quantum numbers one cannot decide whether the NMSE is stationary with respect to reactivity in the time range of collisions.
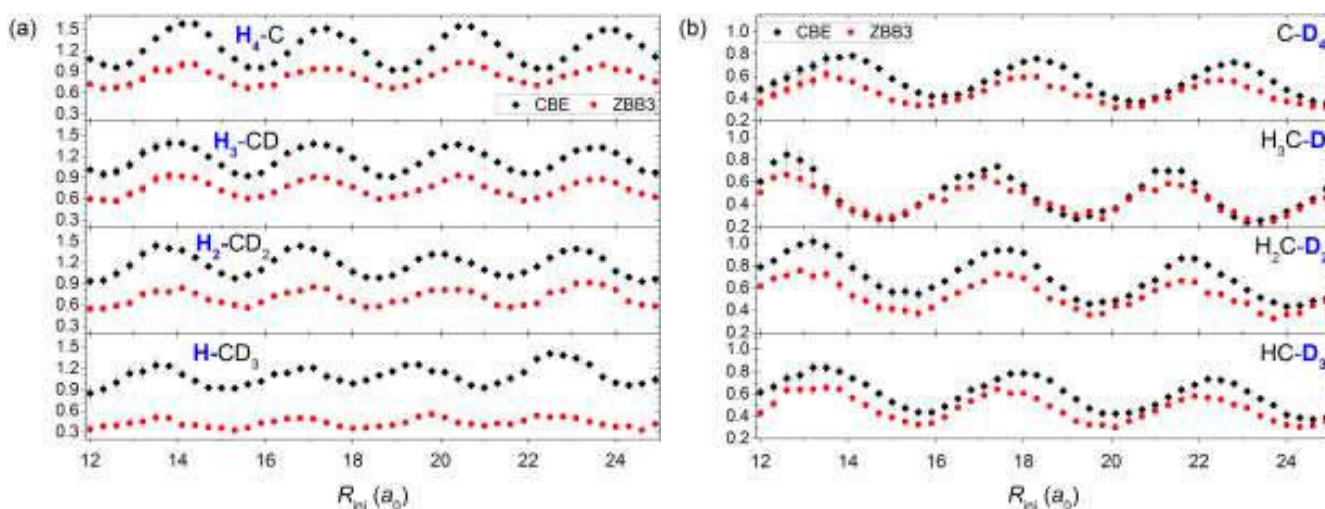
FIG. 5. Oscillatory reaction probability as a function of initial distance of reactants for (a) H and (b) D atom abstraction in the $CH_4+H\rightarrow CH_3+H_2$ reaction with various methane isotopologs on the CBE and ZBB3 PESs at 40 mE_h collision energy and 0 impact parameter, obtained from 4×10^4 trajectories.

On the CBE PES significant reactivity oscillations can be observed for other methane isotopologs, too (Fig. 5). Results for the more realistic ZBB3 PES also show the oscillations with the same wavelength and approximately in phase with those of the CBE PES, but with slightly smaller amplitude. The wavelength is approximately 3.2 a_0 for all C–H and 4.4 a_0 for all C–D stretch modes. The goodness of the match of the time periods of the reactivity and mean bond length oscillations is shown for all isotopologs in Table S1 and in Fig. S2 in the supplemental material[19].

The reaction probability oscillations are carried over into the reaction cross sections calculated as a function of R_{ini} (Fig. 6), which show the same kind of oscillation as reaction probabilities do. The amplitude is approximately constant and the period of oscillations in time is identical to that of the mean bond length oscillation.
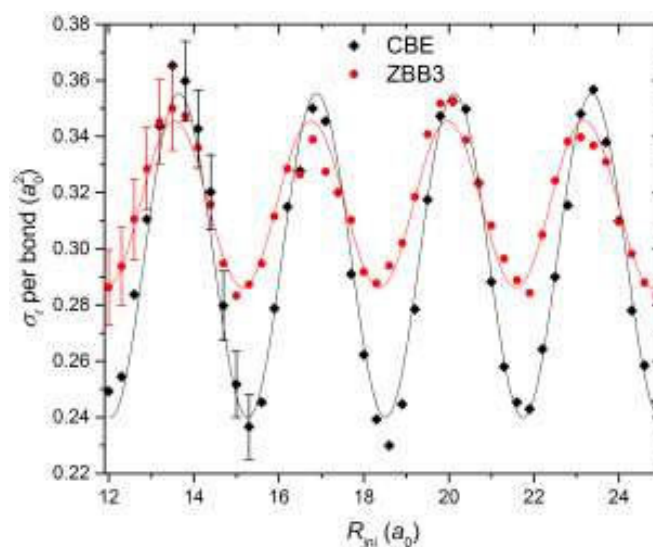
FIG. 6. Oscillatory reaction cross section as a function of initial distance of reactants for the $CH_4+H \rightarrow CH_3+H_2$ abstraction reaction on CBE and ZBB3 PESs at 40 mE_h collision energy. For each initial distance between 12.0-24.9 a_0 in 0.3 a_0 steps, 10^5 trajectories were calculated. Impact parameters were sampled uniformly in the interval of [0, 4.5 a_0]. Sine functions fitted to each data series are shown with solid lines.

The behavior is qualitatively the same on both the CBE and ZBB3 PESs except that the amplitude of the oscillation is smaller on the ZBB3 PES. The uncertainty (maximum/minimum value) induced by the nonstationarity of the NMSE are rather large, 50% and 20% for CBE and ZBB3 PESs, respectively. The uncertainty for isotopolog reactions can be expected to be even larger, recalling the amplitudes of the reaction probability oscillations in Fig. 5.

To summarize: the investigation of the reaction probabilities and cross sections indicates that the nonstationarity of the ensembles of classical CH_4 states generated by NMS induces oscillatory reactivity parameters as a function of R_{ini}. The oscillation is a consequence of that of the mean bond lengths and prevents the accurate calculation of the reaction probabilities and cross sections in QCT calculations performed in the conventional way, namely, by starting all trajectories at the same R_{ini}. This problem will also rise in the calculation of excitation functions unless some ways to generate stationary ensembles are found.

C. Testing advanced sampling techniques

The nonstationarity of the ensembles obtained by NMS is connected to the failure of the normal mode approximation. There are two factors that may contribute to the oscillation of average properties and can be corrected relatively easily: diagonal anharmonicity and the spread of the initial energies within the ensembles generated by normal mode sampling.

The diagonal anharmonicity, which is the anharmonicity of the potential energy along the normal coordinates determined in the harmonic approximation, can be taken into account using the Wentzel-Kramers-Brillouin (WKB) semiclassical quantization scheme[9]. The idea is that instead of using Eq. (3) for quantization, for each normal mode one finds the one-dimensional oscillation in the anharmonic 1D potential along the given normal mode coordinate for which the classical action (S_i) for a whole period fulfills the WKB quantization criterion

$$S_i = \oint P_i(Q_i)\,dQ_i = h\left(n_i + \tfrac{1}{2}\right). \tag{4}$$

In principle, this way one gets closer to the respective invariant torus in phase space (as long as it exists at all). Note that the definition of the normal coordinates is kept the same as is generated by the quadratic PES assumption.

We generated ensembles of states of methane by finding and randomly sampling periodic orbits corresponding to each normal mode in phase space and summing up the Cartesian

deformations and momenta from all modes (see details in the supplemental material[19]). If coupling between normal modes plays a minor role, the sampling of the 1D periodic orbits is expected to provide stationary ensembles for short times.

Conventional NMS suffers from another inconsistency: the ensembles it generates are not monoenergetic because the real, anharmonic potential energies differ from those obtained from the harmonic formula. For the NMSE of ground-state CH_4 molecules on the CBE PES, the energy distribution is close to Gaussian ($\exp(-(E-\mu)^2/2\sigma^2)/(2\pi\sigma^2)^{1/2}$), with a significant, around 5% relative standard deviation (μ=45.0 m$E_{\rm h}$, σ=2.4 m$E_{\rm h}$). Since reactivity is highly sensitive to the energy of the methane molecule and only a small number of the CH_4+H collisions (~5%) lead to reaction at $E_{\rm coll}$=40 m$E_{\rm h}$, the calculated reaction probability might be significantly affected by the large-energy samples, even if their number is relatively small. A possible way of making the ensemble monoenergetic is scaling all deformations ($\mathbf{x}$-$\mathbf{x}_{\rm e}$) and momenta ($\mathbf{p}$) with a common factor[24–26] to make the total energy of each sample match the same sum ($E(\mathbf{n})$) of the mode energies $E_i(n_i)$ of the desired quantum state $\mathbf{n}$=($n_1,\ldots,n_{3N-6}$). Factor α need to be found for each sample separately by solving the nonlinear equation:

$$E(\mathbf{n}) = \sum_{i=1}^{3N-6} E_i(n_i) = H(\mathbf{x}_{\rm e} + \alpha(\mathbf{x} - \mathbf{x}_{\rm e}), \alpha\mathbf{p}) . \qquad (5)$$

The method can be applied after normal mode sampling performed both with the harmonic oscillator (Eq. (3)) and the general WKB quantization rule (Eq. (4)).

The calculations of the evolution of ensemble average bond length and reaction cross sections as a function of $R_{\rm ini}$ shown in Figs. 1 and 6 for harmonic quantization (HARM) have been repeated with the WKB quantization rule (denoted WKB). In addition, both sampling methods were combined with deformation and momentum scaling (HARM SCL and WKB SCL, respectively). The results are summarized in Fig. 7.
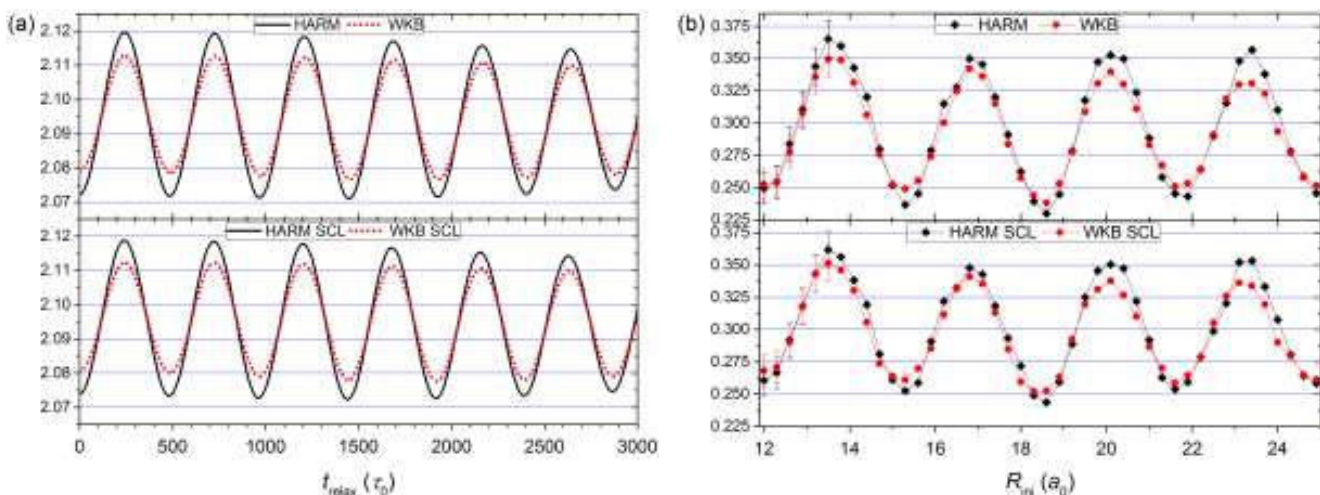
FIG. 7. (a) The ensemble average bond length as a function of the relaxation time ($N_{\text{traj}}=10^4$) and (b) the reaction cross section per bond ($E_{\text{coll}}=40$ mE_{h}, $N_{\text{traj}}=4\times10^5$) as a function of initial distance of reactants for reaction $CH_4+H\rightarrow CH_3+H_2$ on CBE PES. The initial ensemble of methane molecules were sampled with normal mode sampling (HARM, with harmonic oscillator quantization rule) and with the WKB quantization rule (WKB). Both methods were also combined with momentum and deformation scaling (HARM SCL, WKB SCL).

Both the ensemble average bond length and the reactivity show similar oscillations with all four sampling methods. The oscillations have approximately the same wavelength and are in phase for the initial few periods. The mean values obtained by averaging over a complete oscillation period with the four methods are the same within the Monte Carlo error. The amplitude of the mean bond length oscillation that is critical for QCT calculations is only slightly reduced with the WKB and SCL corrections. This reduction is reflected in the reactivity oscillation curves, but the amplitude remains significant. One can conclude that neither the WKB method nor the removal of the energy spread of the NMSE can help in removing the oscillations observed with standard normal mode sampling. This means that the main cause of oscillations is the nonseparability of those vibrational normal modes that directly affect the reactivity.

IV. DISCUSSION

A. A method for the calculation of physically meaningful excitation functions

The sinusoidal oscillation of the ensemble average C–H bond extension in methane is reflected in the R_{ini}-dependence of the reaction cross sections calculated at a given collision

energy. The wavelength of the $\sigma_r - R_{ini}$ oscillation varies as a function of E_{coll}. As a result, if one starts the attacking H atoms from the same R_{ini}, the swarms of trajectories with different E_{coll} will arrive at the strong interaction region at different phases of the average C–H bond extension. This results in an erratic excitation function displaying unphysical maxima and minima because the cross section oscillation at each collision energy is superimposed on the real, smooth excitation function. This is demonstrated in Fig. 8, where the excitation functions are shown for reaction R1 calculated with various R_{ini} values on the CBE and ZBB3 PESs.
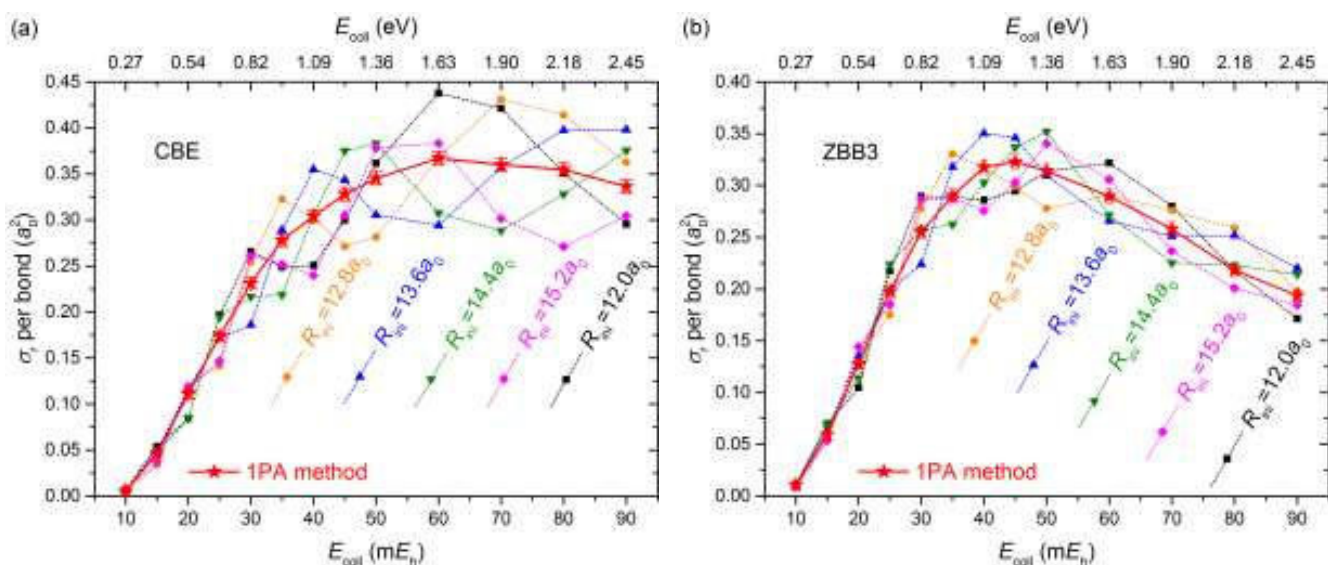
FIG. 8. Dependence of the excitation function for the $CH_4+H \rightarrow CH_3+H_2$ reaction on the initial distance of reactants on the (a) CBE and (b) ZBB3 PESs. At each initial distance and collision energy, 4×10^5 and 2×10^5 trajectories were calculated on the two PESs, respectively. The thick red lines represent the excitation functions obtained at a fixed initial separation of 12 a_0 with averaging over a period of the average C–H bond length oscillation (see text for details).

One can see that the location and magnitude of the local minima and maxima also changes with R_{ini}. The reason for this is that the phase of the mean C–H bond length oscillation upon arrival to the strong interaction zone also varies with the initial reactant separation. As a result, one can get any cross section within a wide range depending on R_{ini}. The uncertainty of the calculated cross sections caused by the nonstationarity of the NMSE can be as high as 50% and 30% for CBE and ZBB3 PESs, respectively.

We have seen that the oscillation of the ensemble average C–H bond length is almost perfectly sinusoidal in the first few periods, and such are the reactivity oscillations. This is the

manifestation of the coherence in the evolution of the NMSE. It is reasonable to assume that the NMSE in the early part of its evolution, although is not stationary, still remembers the kind of motion generated by the semiclassical prescription. A complete period of the C–H bond length oscillation will cover all phases of the early, quasiperiodic evolution of the ensemble. Accordingly, averaging over a complete oscillation period will produce physically meaningful and smooth reactivity functions that do not depend on the initial separation as if the ensemble of initial states were stationary. This way, the erratic features of, for example, the excitation functions will also disappear.

In practice this averaging can be performed by starting trajectories from initial distances sampled uniformly from an interval corresponding to a flight time equal to one period of the average bond length oscillation. The width of the R_{ini} interval obviously depends on the collision energy. An equivalent possibility is that initially only the vibrations of methane molecules are propagated for different random fractions of a whole C–H oscillation period, and all collision trajectories are started from the same initial distance. The two options differ only technically and yield identical results as long as the initial distance of reactants is large enough. Hereafter, this method will be referred as one-period averaging, and will be abbreviated as 1PA.

The excitation functions for reaction R1 on the CBE and ZBB3 PESs obtained by averaging over one complete period of oscillation ($\sim 480\ \tau_0$) at a fixed $R_{ini}=12\ a_0$ are shown as thick red lines in Fig. 8. The averaged excitation functions are smooth and pass in the middle of the uncertainty bands spanned by those obtained at various fixed initial distances without averaging. This observation holds not only for reaction R1 on both the CBE and the ZBB3 PESs but also for other isotopologs of the reaction.

We think that this kind of averaging is not only a formal removal of the uncertainties in the determination of the reaction cross sections and excitation functions induced by the coherence in the relaxation of NMSEs, but also provides the physically most faithful reactivity parameters,

23

based on the following reasoning. The NMS procedure deploys the semiclassically prescribed energy in the vibrations approximated as normal modes. In the initial segment of the evolution of a NMSE, the motion of the atoms in the molecule can be expected to remain close to this prescription. These states are very probably closer to the respective quantum state than, for example, the classical states obtained after a long time evolution on the anharmonic PES, leading to significant energy exchange between modes. As a consequence, in the initial stages of NMSE evolution, the average C–H bond length that determines the reactivity in reaction R1 and similar abstraction processes will be realistic. Based on this one can say that the excitation function obtained by averaging will be the physically most meaningful within the harmonic normal mode approximation.

B. When should one watch for artificial reactivity oscillations?

As shown in Sec. III, unphysical reactivity oscillations emerge when the ensemble average of a geometrical parameter of the reactant that is critical to the reaction oscillates as a function of time. In reaction R1 the length of the breaking C–H bond is such a parameter, and in the ensembles generated by normal mode sampling its mean value was found to oscillate as a function of time. The oscillation of average bond length, however, will not necessarily lead to that of the calculated reactivity parameters as a function of R_{ini} because not only the existence of the oscillation, but also its rate is important. The temporal oscillation of the bond length is manifested as an oscillation of reactivity as a function of R_{ini}, the wavelength of which varies according to the collision energy and the combination of masses. In reaction R1, when the ensemble arrives in the phase corresponding to stretched (compressed) C–H bond length at a critical intermolecular separation range where the outcome of the collision is determined, one expects large (small) reactivity. When the wavelength of oscillation becomes commensurable with the size of the critical distance range, the effect washes out because the critical range "samples" both the stretched and the compressed phases. In what follows we give a more

quantitative account on and estimate the conditions where the artificial oscillations appear and corrections are needed. For the quantitative treatment we use equation

$$CX_4 + Y \rightarrow CX_3 + XY \qquad (R1')$$

to distinguish different isotopes of the atoms participating in the reaction: X is the abstracted and Y is the attacking atom.

The wavelength (λ_{reac}) of the reactivity oscillation as a function of R_{ini} is the product of the period (τ_{vibr}) of the important vibrational mode and the relative velocity (v_{rel}) of the reactants. For example, in CX_4 this mode is the symmetric stretch. The period of this mode is proportional to the square root of the mass m_X of the abstracted atom (the carbon atom does not move in this mode, thus its mass is irrelevant). The relative velocity of the reactants is $v_{rel}=(2\mu E_{coll})^{1/2}$, $\mu=m_{CX4}m_Y/m_{CX4Y}$ being the reduced mass of the collision partners. The mass and collision energy dependence of λ_{reac} is then determined by Eq. (6).

$$\lambda_{reac}=v_{rel}\tau_{vibr}\propto\sqrt{E_{coll}\frac{m_{CX4Y}m_X}{m_{CX4}m_Y}} \qquad (6)$$

To illustrate the effect caused by mass changes, reaction probabilities were calculated as a function of the initial distance of reactants (at $b=0$ and $E_{coll}=40$ mE_h) for reaction R1' on the CBE PES, assigning masses of H, D and 4, 8, 19 dalton to the Y atom, denoted by ^{1}H, ^{2}H, ^{4}H, ^{8}H and ^{19}H, respectively (Fig. 9).

The wavelength of the oscillation of the per bond reaction probability is found to change as a function of m_Y in accordance with Eq. (6). The amplitude of probability oscillation decreases from about 0.6 to about 0.07 when the mass of the attacking atom increases from $m_Y=1$ to 19 dalton (we forbear from the discussion of the small concomitant change of the average reactivity). The amplitude is roughly inversely proportional to the mass m_Y. When λ_{reac} decreases to about 1 a_0, the amplitude of oscillation approaches the error bar of a less precise QCT calculation, where this oscillation would be buried in the noise (note that the very accurate
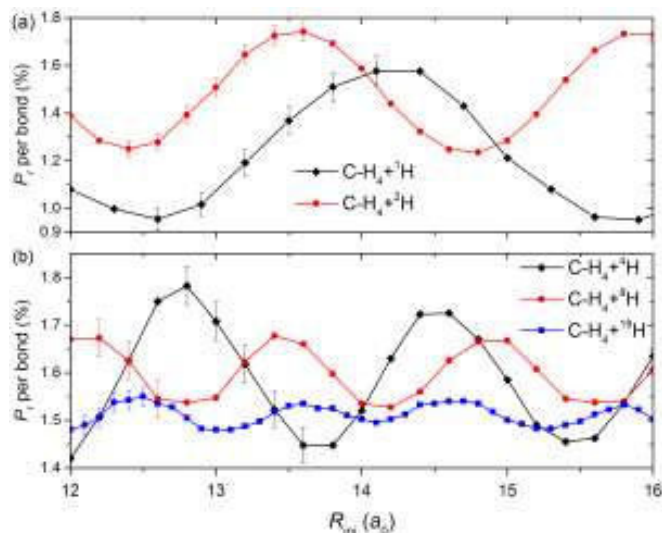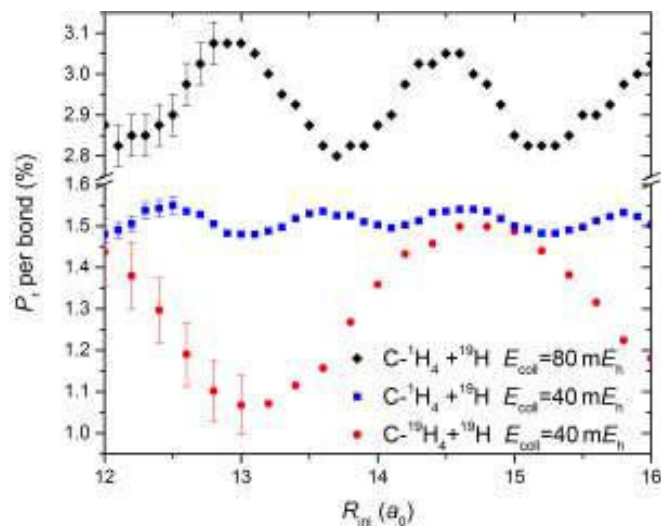
FIG. 9. Oscillatory reaction probability as a function of initial distance of the reactants for reaction R1' on the CBE PES with X=H and Y being (a) natural H and D (^{1}H, ^{2}H) and (b) hypothetically heavy (^{4}H, ^{8}H, ^{19}H) isotopes at 40 mE_h collision energy and zero impact parameter. The results are determined from 10^4 trajectories (10^5 for ^{19}H). Note, (a) spans twice as large range in reaction probability as (b).

m_Y=19 dalton curve was obtained from 10^5 trajectories per point). Accordingly, in reactions of CH$_4$ with halogen atoms such as those discussed by Czakó and Bowman[27] one does not expect to see reactivity oscillation.

It should be noted, however, that according to Eq. (6), the wavelength of the reactivity oscillation varies both with E_{coll} and τ_{vibr}, determined by the isotope combination of the reactant. Consequently, if no reactivity oscillation can be seen for a given system at some E_{coll} and τ_{vibr}, it may reappear at a higher value of one of them. This is illustrated by Fig. 10, where the per bond reaction probability is shown for reaction C^{1}H$_4$+^{19}H at E_{coll}=40 mE_h compared with that obtained after doubling E_{coll} or changing the mass combination to C^{19}H$_4$+^{19}H. In the first case, the wavelength increases by a factor of $2^{1/2}$ and the amplitude of the reaction probability oscillations increases from 0.07 to 0.27 %. In the second case, τ_{vibr} of symmetric stretch mode increases by a factor of $19^{1/2} \approx 4.4$ and v_{rel} decreases by a factor of 1.34, resulting in a P_r amplitude enhancement to 0.42.

We have seen that the reactivity oscillation becomes insignificant when the wavelength is small because the periods of the mean bond length oscillation in the ensembles of CX$_4$+Y trajectories follow each other so closely that one entire or even more periods fit into the critical

FIG. 10. Oscillatory reaction probability as a function of initial distance for reaction $C^1H_4 + {}^{19}H \rightarrow C^1H_3 + {}^1H^{19}H$ at $E_{coll} = 80$ mE_h ($N_{traj} = 4 \times 10^4$) and for the $C^{19}H_4 + {}^{19}H \rightarrow C^{19}H_3 + {}^{19}H_2$ reaction at $E_{coll} = 40$ mE_h ($N_{traj} = 10^5$) at 0 impact parameter. For comparison, the results for reaction $C^1H_4 + {}^{19}H \rightarrow C^1H_3 + {}^1H^{19}H$ at $E_{coll} = 40$ mE_h are also repeated (from Fig. 9).

c.m. separation range of the reactants that determines the outcome of the collision. Based on the results shown in the previous paragraphs, the width of the critical zone is in the range of 1 a_0. The position and the width of the dynamically defined critical zone, however, cannot be determined accurately in polyatomic systems; it is necessarily a diffuse range. The reason for this is twofold. First, the intermolecular separation is not a single parameter that characterizes where the fate of the trajectory is decided and second, that only the ensemble average of the bond length oscillation show coherence. Even at a fixed collision energy and impact parameter, the individual trajectories represent different phases of the other degrees of freedom such as the instantaneous orientation of CX_4 and its remaining vibrational modes when arriving in this region. Because of this, one cannot expect that all such collisions are controlled by a single c.m. separation, even if all of them arrives at the same phase of the C–H stretch at a given distance. The other factor contributing to the diffusivity of the critical separation range is that the initial distance between the attacking Y and the abstractable X is not fixed even in a zero impact parameter situation, and this diffusivity prevents that all trajectories arrive at a selected distance in the same phase, which decreases the amplitude of oscillations by an inherent time averaging. This latter contribution can be modeled quantitatively, as presented in the Appendix.

V. CONCLUSIONS

The purpose of normal mode sampling (NMS) in QCT calculations is the semiclassical representation of quantum states of polyatomic molecules. The ensembles of classical states generated this way are, however, nonstationary, because the ensemble adapts to the potential surface which is anharmonic in contrast to being quadratic that serves as the basis of NMS. When an ensemble generated by NMS (an NMSE) evolves in time, initially it relaxes coherently, a consequence of which is that the ensemble average of some (e.g. geometric) parameters characterizing the motion of the polyatomic molecule shows large-amplitude oscillations. If a reaction is sensitive to one of such parameters of the reactant polyatomic, the reaction probabilities and cross sections will also oscillate as a function of the flight time of the reactants from the starting initial distance to the strong interaction zone. This can be observed as an oscillation of the reactivity parameters as a function of the initial distance between the reactants (R_{ini}). For example, for CH_4, the average C–H bond length oscillates with a frequency of the symmetric stretch mode. Since reaction R1 ($CH_4 + H$) is sensitive to the length of the breaking C–H bond, the oscillations of the ensemble average bond length are carried over to the reaction probabilities and cross sections, which were found to oscillate as a function of the initial $CH_4 -$ H distance. When a QCT calculation is performed with a fixed initial reactant separation, the sensitivity of the reactivity parameters to R_{ini} introduces a significant uncertainty in the values the QCT calculation yields for them. It also distorts the excitation function since the oscillations are superimposed on the real excitation function and unphysical minima and maxima appear, whose positions will depend on the choice of R_{ini}. The magnitude of uncertainty depends on the potential energy surface, the collision energy, the reduced mass of reactants and the period of vibrational mode to which the reaction is sensitive. For the CH_4+H system the amplitude of reactivity vs. initial distance oscillations were found to become negligible when their wavelength is around 1 a_0 or less. The oscillatory behavior of ensembles generated by normal mode

sampling is very probably not restricted to methane and can be expected to cause significant uncertainty in the QCT determination of reactivity parameters for many other reactions.

The uncertainty caused by the nonstationarity of the ensembles generated by NMS can be removed based on the following reasoning. As long as the amplitude and the mean value of the oscillation of the average bond length does not decay significantly on the time scale of molecular collisions, it is reasonable to assume that a complete period of the initial virtual oscillation describes more-or-less faithfully the properties of intramolecular motion in the sense that it has not yet relaxed and reflects the properties of the vibrational state with the desired quantum numbers. It has been shown for reaction R1 that by calculating the reactivity parameters with initial states sampled from the evolution of an NMSE over a period of oscillation of the ensemble average molecular property that determines the reactivity, the oscillation of reaction probabilities and cross sections as a function of R_{ini} can be smoothed out. This procedure, called one-period averaging (1PA) method, is not only a virtual and purely aesthetic cure to the problem but it will provide the closest possible description of the reactivity of the selected quantum state within the normal mode approximation.

The observation of large-scale oscillation of reactivity parameters (reaction probabilities and cross sections) as a function of flight time in QCT simulations of CH_4+H collisions highlights an issue virtually forgotten when QCT simulations switched from atom+diatom systems to reactions of polyatomic molecules. Namely, it is important to pay more attention to whether the ensemble of initial conditions used for the characterization of the initial quantum state of the polyatomic molecule is physically meaningful. Before trajectory simulations, it is advisable to get convinced that the method used to generate initial conditions produces a stationary ensemble. When the semiclassical initial conditions are generated with the widely used normal mode sampling technique, it is desirable to test whether the initial ensemble changes during the initial free flight. As the oscillations universally appear in all reactivity parameters, a quick and easy test is that

one calculates any cheap reactivity measure (for example, the reaction probability for head-on collisions) as a function of R_{ini}. For systems displaying oscillatory reactivity the proposed systematic 1PA method is an easy-to-use procedure that requires little extra computational cost in trajectory integration time, on average, is increased only by an extra half period of the identified oscillation.

ACKNOWLEDGEMENTS

APPENDIX: REDUCTION OF REACTIVITY OSCILLATION AMPLITUDES DUE TO SPREAD IN ATTACKING AND ABSTRACTED ATOM INITIAL DISTANCES

One contribution to the decay of reactivity oscillations comes from the inherent averaging due to a spread in reaction times caused by the differences in other degrees of freedom (not in the C–H stretch coordinate) between the molecules in the ensemble of reactive trajectories, even when all of them starts from the same initial c.m. distance at the same relative velocity. Histograms of initial distances of abstracted atoms from the attacking H' atom in reactive head-on collisions between $C^1H_4+^1H'$ and $C^1H_4+^{19}H'$ (CBE PES, E_{coll}=40 mE_h, R_{ini}=12 a_0, N_{traj}=10^4) are shown in Fig. 11.
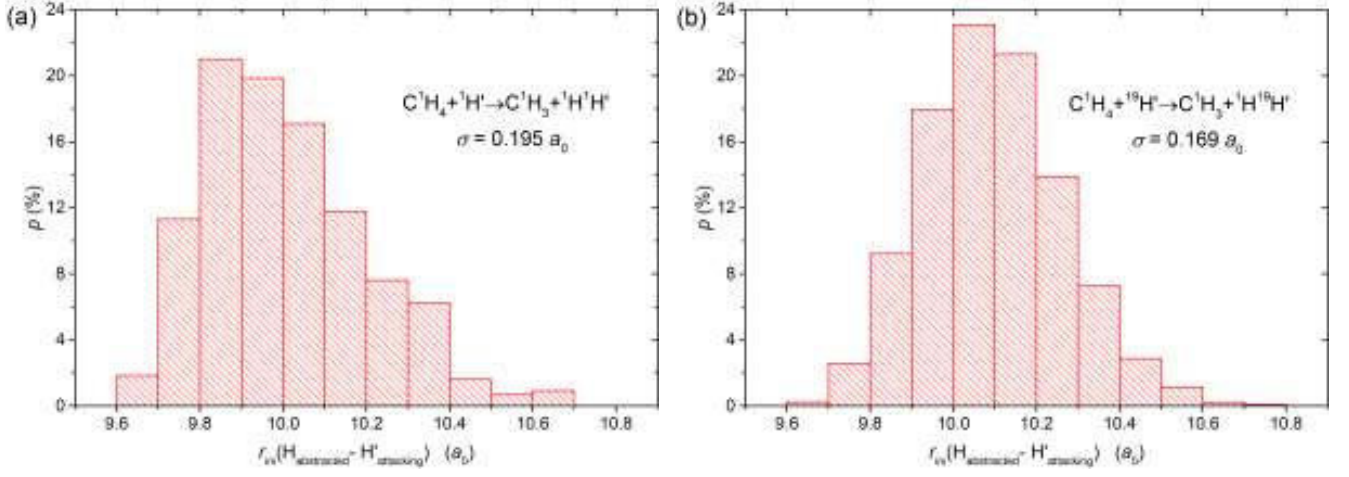
FIG. 11. Histograms of initial distances between the abstracted H atom and the attacking H′ atom for the reactive head-on collisions between (a) $C^1H_4+^1H′$ and (b) $C^{19}H_4+^{19}H′$ (CBE PES, $E_{coll}=40$ mE_h, $R_{ini}=12$ a_0, $N_{traj}=10^4$).

Both distributions are bell-shaped, centered around $\mu \approx 10$ a_0 with significant standard deviations implying differences in reaction times. The reaction probability observed for a given initial c.m. distance is actually a weighted average over initial H–H′ distances, where the weighting functions are the observed distributions. Approximating the reactivity oscillations with a sine function ($\sin(2\pi R_{ini}/\lambda_{reac})$, amplitude $A=1$, λ_{reac} wavelength) and the distribution with a Gaussian function (with parameters μ and σ), the change in the amplitude can be obtained from:

$$\int_{-\infty}^{\infty} \sin\left(2\pi \frac{R_{ini}-y}{\lambda_{reac}}\right) \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(y-\mu)^2}{2\sigma^2}\right) dy = \exp\left(-\frac{2\pi^2\sigma^2}{\lambda_{reac}^2}\right) \sin\left(2\pi \frac{R_{ini}-\mu}{\lambda_{reac}}\right). \quad (B1)$$

The resulting function is also a sine function of R_{ini}, but its phase is shifted and its amplitude is reduced. In the case of $C^1H_4+^1H′$ ($\lambda_{reac} \approx 3.24$ a_0 at 40 mE_h, $\sigma=0.19$ a_0) the convolution causes a decrease of 7% in the amplitude, whereas for the case of $C^1H_4+^{19}H′$ ($\lambda_{reac}=1.07$ a_0, $\sigma=0.17$ a_0) 40% decrease is predicted (in agreement with Fig. 9).

REFERENCES

[1] G. Schiffel and U. Manthe, J. Chem. Phys. **133**, 174124 (2010).

[2] R. Welsch and U. Manthe, J. Chem. Phys. **137**, 244106 (2012).

[3] G. Nyman, in *Theory Chem. React. Dyn. NATO Sci. Ser.*, edited by A. Laganà and G. Lendvay (Kluwer, Dordrecht, 2004), pp. 253–278.

[4] D.H. Zhang, M. Yang, M.A. Collins, and S.-Y. Lee, in *Theory Chem. React. Dyn. NATO Sci. Ser.*, edited by A. Laganà and G. Lendvay (Kluwer, Dordrecht, 2004), pp. 279–304.

[5] L.M. Raff and D.L. Thompson, in *Theory Chem. React. Dyn. Vol III.*, edited by M. Baer (CRC Press, Boca Raton, Florida, 1985), pp. 1–122.

[6] R.N.R. Porter, L.M.L. Raff, and W.H. Miller, J. Chem. Phys. **63**, 2214 (1975).

[7] G.C. Schatz, Comput. Phys. Commun. **51**, 135 (1988).

[8] C.W. Eaker and G.C. Schatz, J. Chem. Phys. **81**, 2394 (1984).

[9] H.A. Kramers, Z. Phys. **39**, 828 (1926).

[10] J.B. Keller, Ann. Phys. (N. Y). **4**, 180 (1958).

[11] M.C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer New York, New York, NY, 1990).

[12] D. Lu and W.L. Hase, J. Chem. Phys. **89**, 6723 (1988).

[13] P.N. Careless and D. Hyatt, Chem. Phys. Lett. **14**, 358 (1972).

[14] J.M. Bowman, A. Kuppermann, and G.C. Schatz, Chem. Phys. Lett. **19**, 21 (1973).

[15] Z. Xie, J.M. Bowman, and X. Zhang, J. Chem. Phys. **125**, 133120 (2006).

[16] G. Czakó and J.M. Bowman, J. Chem. Phys. **131**, 244302 (2009).

[17] J.P. Camden, W. Hu, H. a Bechtel, D.J.A. Brown, M.R. Martin, R.N. Zare, G. Lendvay, D. Troya, and G.C. Schatz, J. Phys. Chem. A **110**, 677 (2006).

[18] W. Hu, D. Troya, G.C. Schatz, J.P. Camden, H.A. Bechtel, D.J.A. Brown, M.R. Martin, and R.N. Zare, J. Phys. Chem. A **110**, 3017 (2006).

[19] See supplemental material at (n.d.) for normal mode analysis, normal mode sampling and assigment of normal mode quantum numbers; frequencies (and periods) of mean bond length and reaction probability oscillations along with normal mode and experimentally determined values; evolution of mean bond length in the NMSEs of methane isotopologs on the ZBB3 PES;

correlation between the frequencies of reactivity and mean bond length oscillations for NMSE of methane isotopologs.

[20] E.B. Wilson, J.J.C. Decius, and P.C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra* (Dover Publications, New York, 1980).

[21] J.C. Corchado, J.L. Bravo, and J. Espinosa-Garcia, J. Chem. Phys. **130**, 184314 (2009).

[22] X. Zhang, B.J. Braams, and J.M. Bowman, J. Chem. Phys. **124**, 021104 (2006).

[23] W. Zhang, Y. Zhou, G. Wu, Y. Lu, H. Pan, B. Fu, Q. Shuai, L. Liu, S. Liu, L. Zhang, B. Jiang, D. Dai, S. Lee, Z.Z. Xie, B.J. Braams, J.M. Bowman, M.A. Collins, D.H. Zhang, and X. Yang, Proc. Natl. Acad. Sci. U. S. A. **107**, 12782 (2010).

[24] S. Chapman and D.L. Bunker, J. Chem. Phys. **62**, 2890 (1975).

[25] C.S. Sloane and W.L. Hase, J. Chem. Phys. **66**, 1523 (1977).

[26] W.L. Hase and D.G. Buckowski, Chem. Phys. Lett. **74**, 284 (1980).

[27] G. Czakó and J.M. Bowman, J. Phys. Chem. A **118**, 2839 (2014).