A surface-hopping method for semiclassical calculations of cross sections for radiative association with electronic transitions

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A semiclassical method based on surface-hopping techniques is developed to model the dynamics of radiative association with electronic transitions in arbitrary polyatomic systems. It can be proven that our method is an extension of the established semiclassical formula used in the characterization of diatomic molecule-formation. Our model is tested for diatomic molecules. It gives the same cross sections as the former semiclassical formula, but contrary to the former method it allows us to follow the fate of the trajectories after the emission of a photon. This means that we can characterize the rovibrational states of the stabilized molecules: using semiclassical quantization we can obtain quantum state resolved cross sections or emission spectra for the radiative association process. The calculated semiclassical state resolved spectra show good agreement with the result of quantum mechanical perturbation theory. Furthermore our surface-hopping model is not only applicable for the description of radiative association but it can be used for semiclassical characterization of any molecular process where spontaneous emission occurs.

I. INTRODUCTION

Radiative association is one of the many important processes that contribute to the molecule production in dust-poor regions of interstellar space where there are few competing three-body collisions. Radiative association is hard to study under laboratory conditions due to the small cross sections of the process3,9–17. Experimental studies on radiative rate coefficients have been carried out so far only for a few ionic systems using ion traps or ion cyclotron resonance apparatus3. So far there is no experimental result for the formation of neutral molecules through radiative association. Theoretical modeling of radiative association is highly desirable due to the lack of experimental data. In the case of neutral species it is the only possible way to obtain the rate coefficients3. Good quality potential energy and dipole surfaces are nowadays available from accurate ab initio calculations4–7. Adequate dynamical methods based on ab initio data can provide reliable rate coefficients that can be utilized for kinetic modeling of molecule production in the interstellar medium8.

Most of the previous dynamical calculations have focused on diatomic systems3,9–17. There are only a few dynamical studies where the radiative association of triatomic molecules have been considered18–22. Radiative association is not only difficult to study experimentally, but also theoretically, despite the available global potential energy and dipole surfaces2. There are several reasons which can explain the small number of dynamical studies on polyatomic systems: i) the quantum mechanical treatment of radiative association is a major challenge because we need both bound and unbound states18–22; ii) so far there has been no available semiclassical method which can describe the radiative association of polyatomic molecules with electronic transitions in full dimension; iii) a classical model for the calculation of radiative association in absence of electronic transitions has been recently developed23, but not yet implemented for polyatomic systems. The semiclassical methods are based on classical trajectories and therefore do not contain the resonance structure and the tunneling in the cross sections. In spite of the lack of resonance and tunneling effects, trajectory based methods can provide reasonable results in many cases25–27. The extension of the theoretical studies for polyatomic systems is highly desirable. The bigger the reactants are the more probable radiative association is28–30. Semiclassical and classical methods are the only feasible way to the theoretical modeling of the dynamics of systems which contain more than 3–4 atoms.

The purpose of the current work is to present a new semiclassical dynamical method for the modeling of radiative association with electronic transitions. We use the surface hopping method extended with Fermi’s golden rule which ensures a simple way to the treatment of dynamical coupling of molecular states with electromagnetic fields. The surface-hopping methodology allows the study of radiative association with electronic transitions to be extended to arbitrary polyatomic system.

The surface-hopping method is widely used in the modeling of nonadiabatic molecular processes31–47. The idea of this method originally put forward by Bjerre and Nikitin48 and later advanced by others49–53. The motion of nuclei are described by classical mechanics but the time evolution of the molecular electronic states is treated quantum mechanically. Classical trajectories can take place only on one potential energy surface at a time. Therefore we need a stochastic algorithm that allows the change between potential energy surfaces during the propagation. The branching of the populations due to the dynamical coupling is simulated with this stochastic change in electronic states. Generally the wavefunction of the adiabatic electronic states is used as basis set for the representation of the time-dependent wavefunction. The
population of the electronic states (the hopping probability) can be calculated in each time step from the solution of the time-dependent Schrödinger equation. The ensemble of the independent trajectories extended with stochastic hopping can provide a reliable semiclassical approximation for the simulation of nonadiabatic dynamics.

The surface-hopping method was extended in the last decade for the treatment of arbitrary couplings. Field-induced couplings were the subject of more studies where the absorption spectra or laser-induced transitions were calculated with the surface-hopping methodology. Spin-orbit and dipole couplings have been recently treated simultaneously with surface-hopping methods. In every case the hopping probability is calculated from the numerical solution of the time-dependent Schrödinger equation. To our knowledge, there has been no surface-hopping study so far on radiative association, or on any kind of relaxation process that contains spontaneous emission.

To test our method we calculate the cross sections of radiative association and radiative quenching for the following two reactions:

\[
\begin{align*}
H \left( ^2S \right) + F \left( ^2P \right) & \rightarrow HF \left( A^1\Pi \right) \rightarrow \\
& \rightarrow HF \left( A^1\Sigma^+ \right) + h\omega \\
& \rightarrow H \left( ^2S \right) + F \left( ^2P \right) + h\omega
\end{align*}
\]

\[
\begin{align*}
C \left( ^3P \right) + O \left( ^3P \right) & \rightarrow CO \left( A^1\Pi \right) \\
& \rightarrow CO \left( A^1\Sigma^+ \right) + h\omega \\
& \rightarrow C \left( ^3P \right) + O \left( ^3P \right) + h\omega
\end{align*}
\]

The results of our method are compared to the cross sections calculated with conventional semiclassical and quantum mechanical perturbation theory. Furthermore, the surface-hopping method allows us to calculate the semiclassical quantum state distributions of the stabilized diatom. The quantum state resolved emission spectra and the comparisons with the spectra obtained with quantum mechanical perturbation theory are also presented in section IV.

II. THEORY

Time-dependent perturbation theory provides a very useful approximation for the description of light-matter interaction. This brilliant tool of the time-dependent quantum mechanics is known as Fermi’s golden rule. In fact, the assumptions of Fermi’s golden rule are fulfilled in most of the problems when light absorption or emission considered. It is worth to try to use it in the surface-hopping methodology to avoid the expensive numerical solution of the time-dependent Schrödinger equation in each time step. According to Fermi’s golden rule, the probability of emission from a certain initial state to all possible final states with an energy is lower than \( V_i \) is

\[
P_{em}^{i\rightarrow f} (r) = \sum_{V_j < V_i} 4\frac{\omega^3_{ij} (r)}{3\hbar c^3} \tau (N_{ph} + 1) |\mu_{ij} (r)|^2
\]

where the frequency of the radiation \( \omega_{ij} = \frac{V_i - V_j}{\hbar} \) is defined by the energy of the final and initial state, \( N_{ph} \) is the number of photons in the radiation field, \( \mu_{ij} \) is the transition dipole vector between the initial and the final electronic state, \( \tau \) is the contact-time of the interaction. Eq. (5) is valid for both stimulated and spontaneous emission, the latter one if there is no photon in the radiation field \( (N_{ph} = 0) \). In the remainder of the paper we consider only a two-state system. In the surface-hopping methodology Eq. (5) is used in every time-step to calculate the hopping probability during the motion of the nuclei

\[
P_{em}^{i\rightarrow f} (t) = \frac{4\omega^3_{ij} (t)}{3\hbar c^3} \Delta t (N_{ph} + 1) |\mu_{ij} (t)|^2 = A^{i\rightarrow f} (t) \Delta t
\]

where \( A^{i\rightarrow f} \) is the rate of the emission. In this case the contact-time is the time-step of the integration of the nuclear-motion and the frequency of the emitted photon \( \omega_{ij} (t) = \frac{\max(0, V_i (t) - V_j (t))}{\hbar} \) is the difference of the two potential surfaces and \( \mu_{ij} \) is the transition dipole at the given geometry. With the frequency definition we implicitly assume that the classical Franck-Condon principle is valid for the electronic transition, and the maximum function is introduced to ensure the transition from an upper to a lower state. A uniform random number \( 0 \leq \xi \leq 1 \) is generated in each time step, and the hopping from the initial to the final state is performed if \( P_{em}^{i\rightarrow f} (t) > \xi \). If we study collisions with radiative association, where there are bound states on the bottom potential energy surface, then we need to refine the model. It is possible that the energy of the emitted photon \( (\hbar \omega_{ij}) \) is not high enough for the association of fragments, because after hopping the energy content of the system can be higher than the dissociation energy on the bottom potential energy surface. Thus we need to distinguish the two channels after a hopping:

\[
\text{if } \begin{cases} 
\hbar \omega > E^{tot} _i \text{ and } V^{eff} _f (t) < 0 \text{ then associaton} \\
\hbar \omega < E^{tot} _i \text{ or } V^{eff} _f (t) > 0 \text{ then quenching}
\end{cases}
\]

i) radiative association: if the initial total energy (total energy of the system before collision on the upper potential energy surface) is smaller than the energy of the photon and the bottom effective potential surface has bound states; ii) radiative quenching: the fragments dissociate after the hopping. The former process is illustrated schematically in Fig. V. \( V^{eff} _f (t) \) in Eq. (7) is the effective potential energy surface of the final state when a hopping occurs:

\[
V^{eff} _f (t) = V_f (t) + E_{coll} \frac{\hbar^2}{r^2 (t)}
\]
where $E_{coll}$ is the collision energy, $b$ is the impact parameter of the collision and $r$ is the distance between atoms.

After generation of $N_{tot}$ number of trajectories at a given $(E_{coll}, b)$ pair the probability of the stimulated emission (the opacity function) can be obtained

$$P^r_{rad} (E_{coll}, b) \approx \frac{N_{hop} (E_{coll}, b)}{N_{tot} (E_{coll}, b)}$$

where $N_{hop} (E_{coll}, b)$ is the number of trajectories where hopping was detected. If one would like to simulate spontaneous emission then $N_{ph} = 0$ should be considered. In this case, however, the probability of a transitions would be very small and $10^8 - 10^{10}$ trajectories might be needed to estimate $P^r_{rad}$ in a general molecular system. We can bypass this obstacle if transitions with stimulated emission is calculated even when the aim is spontaneous emission. In every time step we calculate the hopping probability with a certain photon number. To get the probability of spontaneous emission we need to scale down the obtained probability of stimulated emission with the applied photon number

$$P^{sp}_{rad} (E_{coll}, b) \approx \frac{1}{N_{ph} + 1} \frac{N_{hop} (E_{coll}, b)}{N_{tot} (E_{coll}, b)}$$

The trick with the adjustable photon number is profitable in the simulation of spontaneous emission. The required trajectory number in the estimation of $P^{sp}_{rad}$ (and at the same time also the computational time) can be optimized by variation of $N_{ph}$. From this point the cross section of the radiative processes

$$\sigma (E_{coll}) = 2\pi f_{stat} \int b P_{rad} (E_{coll}, b) \, db$$

can be calculated, where $f_{stat}$ is the statistical weight factor for the initial molecular state of the approaching fragments.

It is easy to prove that the surface-hopping method is equivalent with the conventional semiclassical method used in former studies for diatomics\cite{59}. Eq. (10) is considered only for one time-slice of the whole collision process, when Eq. (10) is integrated over the time of the collision then we get $P_{rad}$. If the time-variable is changed to distance in the integral, the Jacobi-determinant of the variable-transformation will be the reciprocal of the velocity. The result of the variable transformation is the well known semiclassical formula

$$P_{rad} = \int A^{i \rightarrow f} (t) \, dt = \int \frac{A^{i \rightarrow f} (r)}{v} \, dr = \sqrt{\frac{\mu}{2}} \int \frac{A^{i \rightarrow f} (r)}{\sqrt{E_{coll} - E_{coll} \frac{k^2}{r^2} - V_{i} (r)}} \, dr$$

as pointed out by Kramers and ter Haar seven decades ago\cite{59}. This allows us to consider the surface-hopping method as the extension of the former semiclassical method in arbitrary dimension.

Furthermore, contrary to the former semiclassical formula the surface-hopping methodology provides real dynamical coupling between molecular states and the radiation field: after hopping we can follow the fate of the trajectory. That means we can characterize the ro-vibrational states of the formed molecules after each re-active hopping. The WKB quantization can be applied for the stabilized diatom (as a rotating anharmonic oscillator) to obtain the semiclassical vibrational quantum number\cite{60}:

$$v' = \sqrt{\frac{2\mu}{\hbar^2}} \int_{r_{min}}^{r_{max}} \left( E_{coll}^{tot} - \frac{L^2}{2\mu r^2} - V_{f} (r) \right)^{\frac{1}{2}} \, dr - \frac{1}{2}$$

where $\mu$ is the reduces mass and $L$ is the angular momentum of the diatom, $r_{min}$ and $r_{max}$ are the turning-points, and $E_{coll}^{tot}$ is the total energy content of the system after a reactive hopping. The quantum state resolved cross sections or emission spectra can be calculated after the semiclassical quantization. That means the surface-hopping method can provide the most detailed levels of the characterization of radiative association using semiclassical mechanics.

The modeling of radiative association with surface-hopping methodology has an additional advantage compared with the conventional surface-hopping method used in the simulation of nonadiabatic dynamics: the scaling of momenta is not needed because the photon takes away energy from the molecular system, equal to the change in potential energy. This is again due to the application of the classical Franck-Condon principle. The former surface-hopping methods (including nonadiabatic and spin-orbit couplings) extended with our model could provide an efficient and complete description of the coupled photophysical processes in molecular collisions or in molecular systems after an electronic excitation.
III. COMPUTATIONAL DETAILS

Hamilton's equations of motion were used in Cartesian coordinates for the calculation of trajectories. A fourth order symplectic integrator was employed for integration with a step size of 0.05 fs. The initial separation between the atoms was fixed at 18 bohr, which guaranteed a negligible initial interaction between the colliding atoms. The hopping probability in each time step was calculated according to Eq. (6) and the cross sections were calculated according to the Eq. (11), where the integral over impact parameter was evaluated with Simpson’s 1/3 rule. The value of $b_{\text{max}}$ (the upper bound) in the integral in Eq. (11) was adjusted at each collision energy to account for all hopping events. $N_{\text{tot}}=1000$ trajectories with adjusted photon number ($N_{\text{ph}}$) were used to estimate the probability of radiation ($P_{\text{rad}}(E_{\text{coll}}, b)$) at each ($E_{\text{coll}}, b$). It should be noted that the photon number used in computation of the stimulated emission, Eq. (6) should be small enough to avoid saturation of the hopping, which in turn results in an underestimation of $P_{\text{rad}}(E_{\text{coll}}, b)$ through the division by $N_{\text{ph}}+1$ in Eq. (10). As a rule of thumb we suggest that the photon number should be set to produce less hopping events than 20-30% of $N_{\text{tot}}$. In the calculation of state-resolved spectra we ran a total of 10$^6$ trajectories to get satisfying statistics. We used a bin size of $\Delta E_{\text{photon}} = 0.1$ eV for the calculation of the spectral densities. The rotational quantum number of the products, $j'$, was calculated from the conventional semiclassical quantization formula $L = b \sqrt{j'(j'+1)}$. The quasiclassical vibrational quantum number was calculated according to Eq. (13) where the integration over the interatomic distance was evaluated with trapezoidal rule. The trajectories were propagated for more 500 fs after a reactive hopping to determine the turning-points used in the calculation of the action-integral. Eq. (13) gives continuous quantum numbers. To obtain discrete quantum numbers we used the standard binning technique: each trajectory contributes $P_{\text{rad}}(E_{\text{coll}}, b)$ with equal weight and the quantum numbers are rounded to the nearest integer. The details of the conventional semiclassical and quantum mechanical perturbation theory used for comparison can be found in Refs. 14,16.

IV. RESULTS

A. Cross sections

First consider the HF test system. Since it contains one low mass atom a significant tunneling effect is expected at low energies. Moreover the potential energy surface of the excited state is almost entirely repulsive. Fig. 2 shows the cross sections of radiative association through Eq. (11) computed with three different methods: quantum mechanical perturbation theory (QM), conventional semiclassical method (SC) and our surface-hopping trajectory method (SHT).

The SHT cross sections perfectly match the curve obtained with the conventional semiclassical method in the whole collision energy range. Resonance structure can not be observed on QM curve because the upper potential energy surface is repulsive. Due to this feature of the HF system the dominant quantum mechanical effect is the tunneling into the repulsive region of the excited potential surface. The semiclassical methods show good agreement with the QM cross sections when $E_{\text{coll}} > 0.2$ eV. The semiclassical methods underestimate the QM results in the low energy domains. This shows the importance of tunneling below $E_{\text{coll}} = 0.2$ eV. Fig. 2 also shows the SHT cross sections for the quenching channel where electronic transition was detected during the collisions but the HF molecules were not able to stabilize due to the remaining high energy content in the system.

The cross section of the quenching channel is smaller almost in the whole energy range with 2-3 orders of magnitude than that of association. Over $E_{\text{coll}} = 10$ eV the quenching process dominates, and at the same time the probability of the association is suddenly diminishing. Above $E_{\text{coll}} = 10$ eV the probability of quenching is an essentially constant function of $E_{\text{coll}}$ and above $E_{\text{coll}} = 11-13$ eV the ionization and electronic excitation of the atoms may play a big role.

The second test system, CO, is somewhat different from HF. The excited potential energy surface is attractive and has many bound states. In this case shape resonances, due to the tunneling into the quasibound states, are expected. The SHT method shows again perfect matching with the conventional semiclassical method (Fig. 6). At high energies good agreement can be found between the QM and the semiclassical methods. The resonance contribution is quite relevant under $E_{\text{coll}} = 1.0$ eV, but the semiclassical methods reproduce the QM base line at energies down to about 0.1 eV. Below $E_{\text{coll}} = 0.1$ eV, however, the SC and SHT cross sections are smaller than that from QM with a factor of 10$^3 - 10^4$. The behavior of the quenching channel is similar to that of the HF system. Below $E_{\text{coll}} = 9.0$ eV the radiative quenching curve shows a falloff shape, at $E_{\text{coll}} = 9.0$ eV it is equally probable as the association channel. The edges of atomic ionization and excitation channels start also about at this energy.
FIG. 3. Cross sections for the radiative association and quenching of C + O collisions according to the reaction (3) and (4), respectively.

FIG. 4. Spectral density for radiative association of HF through reaction (1). The SHT result is computed as explained in section III. The QM result is computed from the QM data presented in Fig. 6 by adding the cross sections in photon energy intervals of $\Delta E_{\text{photon}} = 0.2$ eV and then divided the sum by $\Delta E_{\text{photon}}$.

FIG. 5. As in Fig. 4 but for CO formation through reaction (3). The QM result is computed from the QM data in Fig. 7.

The radiative association process can also be characterized by emission spectra. Fig. 4 shows the collision induced emission spectrum for the HF system at $E_{\text{coll}} = 5.0$ eV. The SHT emission spectrum agrees well with that calculated by quantum mechanical perturbation theory. It means that the SHT method is able to reproduce also the energy distribution of photons, not only the cross sections as a function of $E_{\text{coll}}$. Some differences can be seen in the high energy domains where the QM spectrum has a finer structure that the SHT method misses.

Fig. 5 shows the spectral densities of radiative association for the CO system. The SHT method performs well also for this reaction. The SHT and QM spectra match in the whole energy range.

The surface-hopping method has another big advantage: it allows us to calculate the quantum state resolved spectra or cross sections with semiclassical quantization. Fig. 6 shows the comparisons of the rovibrationally state resolved emission spectra for reaction (1) obtained with SHT and QM method. The envelope of SHT and QM spectra for $v' = 0$ match well. The SHT method slightly underestimates the QM curve only in the high energy region. The QM spectra that corresponds to the higher vibrational quantum states show more complex character. The SHT method can not reproduce the detailed structure of the QM spectra, but overall the spectral distributions are similar. If we add the sticks, each corresponding to one rotational quantum number, then the obtained vibrationally resolved SHT cross sections do agree well with the cross sections of the QM method. Fig. 7 shows the state resolved emission spectra at $E_{\text{coll}} = 2$ eV for reaction (3). The four vibrational states were plotted that have the biggest contribution to the total/unresolved spectrum. These QM spectra have more complex character than in the H + F collisions. In this case the envelopes of SHT and QM curves agree not so well than in reaction (1), but the SHT curves follow the average shape of the QM curves in every case. Most of the products are born with huge rotational and with moderate vibrational quantum number.

These results indicate that the surface-hopping method provides reasonable result even for the most detailed quantum state distributions that characterize the collision induced emission.

V. CONCLUSION

In this work we have presented a semiclassical method based on surface-hopping methodology for the modeling of radiative association with electronic transitions. In the surface-hopping formalism we use Fermi’s golden rule to
calculate the probability of hopping during the propagation of nuclei. Due to Fermi’s golden rule we can avoid to solve numerically the time-dependent Schrödinger equation in each time step. It can be proven that our method, when implemented for two colliding atoms, is equivalent to the established semiclassical formula for diatomic systems. But, contrary to the latter, the surface-hopping methodology allows us to extend the study of radiative association with electronic transitions to arbitrary polyatomic systems, and also to follow the fate of trajectories after a photon emission. Due to this property of the method we can characterize the rovibrational states of the stabilized molecules. To test our method we have calculated the cross sections of radiative association and radiative quenching for two diatomic reactions. The surface-hopping method agrees with the conventional semiclassical formula. This was expected due to the equivalence of the two methods. Moreover the obtained total and the quantum state resolved spectra are compared to the results of a quantum mechanical perturbation theory. These comparisons imply that the surface-hopping method extended with Fermi’s golden rule can provide reasonable result even for the most detailed quantum state distributions for the characterization of radiative association. In addition our surface-hopping model is not only applicable for the description of radiative association but it can be used for a numerically inexpensive semiclassical characterization of any molecular process.

FIG. 6. Rovibrationally state resolved emission spectra for radiative association of HF through reaction (1). The sticks correspond to the \((v', j')\) states.

FIG. 7. Rovibrationally state resolved emission spectra for radiative association of CO through reaction (3). The sticks correspond to the \((v', j')\) states.
where spontaneous emission occurs.

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