

Mixed Quantum/Classical Theory for Collisional Quenching of PAHs in the Interstellar Media

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Abstract: Computationally affordable methodology is developed to predict cross sections and rate coefficients for collisional quenching and excitation of large molecules in space, such as PAHs. Mixed quantum/classical theory of inelastic scattering (MQCT) is applied, in which quantum state-to-state transitions between the internal states of the molecule are described using time-dependent Schrodinger equation, while the scattering of collision partners is described classically using mean-field trajectories. To boost numerical performance even further, a decoupling scheme for the equations of motion, and a Monte-Carlo sampling of the initial conditions, are implemented. The method is applied to compute cross sections for rotational excitation and quenching of benzene molecule C_6H_6 by collisions with He atoms in a broad range of energies, using a very large basis set of rotational eigenstates up to $j = 60$, and close to one million non-zero matrix elements for state-to-state transitions. The properties of collision cross sections for $C_6H_6 + He$ are reported and discussed. The accuracy of approximations is rigorously tested and is found to be suitable for astrophysical/astrochemical simulations. The method and code developed here can be employed to generate a database of collisional quenching rate coefficients for PAHs and other large molecules, such as iCOMs, or for molecule-molecule collisions in cometary comas.

Keywords: inelastic scattering, rotational excitation, state-to-state transitions, rotational states, inelastic cross-sections, MQCT, benzene, C_6H_6

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INTRODUCTION

Inelastic collisions between molecules and background gasses, such as He and H₂, play an important role in the interstellar media, because these energy-transfer processes contribute to the rates of gas cooling and thus influence the processes of formation of pre-stellar cores and protoplanetary discs.¹⁻³ Moreover, observation of molecular transitions in space provides a unique tool for quantitative analysis of physical conditions in various astrochemical environments, permitting to constrain temperature, density, and chemical composition of the emitting gas, which in turn helps to describe evolution of these objects.⁴⁻⁶ Quantitative analysis in these and other applications is only possible if the rate coefficients (or cross sections) are known for the collisional quenching and excitation of astrochemically important molecules.⁷ This information becomes critical for the environments that are far from thermodynamic equilibrium, such as in proto-stellar shocks and bipolar jets (chemically rich outflows of forming stars).⁸⁻¹⁰

Experimental measurements of inelastic collision cross sections in the lab are possible but are challenging,¹¹ so, the astronomers often rely on results of computational modeling of these processes. Unfortunately, classical trajectory methods, often employed to predict the rates of chemical reactions, are not directly suitable for the spectroscopic applications mentioned above, where transitions between the individual quantized states of molecules (rotational, vibrational) are considered. On the other extreme, the full-quantum mechanical calculations of molecular state-to-state transitions are affordable only for the simplest molecules (diatomic and triatomic)¹²⁻¹⁵ and the lightest collision partners (diatomic at most). For small polyatomic molecules such calculations are affordable in the very low energy regime only.^{16,17} As complexity of the astrochemical environments grows, with more complex, larger, and heavier molecules being detected in space, one starts begging for a practical computational tool, capable of predicting the rates of molecular excitation and quenching in a satisfactory manner. Among the largest targeted molecules, one finds the interstellar complex organic molecules (iCOMs),^{18,19} unsaturated linear carbon chains,²⁰⁻²² and polycyclic aromatic hydrocarbons (PAHs).²³ The last group spans an impressive range of sizes and masses, going from smaller molecules with well-known shapes (such as naphthalene, anthracene, etc.) all the way up to the carbon sheets in the nanometer size range (several hundred atoms),^{24,25} where even the identification of relevant isomers becomes challenging. How possibly can we solve the inelastic scattering problem for at least some of these targets?

During the last decade we developed a mixed quantum/classical approach for the description of molecule + atom and molecule + molecule collisions.^{26–31} In our method the internal (rotational and vibrational) states of molecules are treated quantum mechanically, which permits to predict observables for quantum transitions, such as state-to-state specific cross sections. At the same time, the translational motion of collision partners is described classically using the mean-field trajectories, which captures the most important information about the scattering process, enabling massive parallelism and thus offering a very substantial computational advantage. We showed that the mixed quantum/classical theory (MQCT) is quite accurate for small molecules (when the full-quantum results are available for comparison)^{32–34} and remains computationally affordable even for the largest systems ever studied in this context, such as collisional excitation of methyl formate by helium ($\text{CH}_3\text{COOH} + \text{He}$)²⁶ or collisional quenching in water vapor ($\text{H}_2\text{O} + \text{H}_2\text{O}$)^{35,36} in cometary comas. The first user-ready version of our code, named MQCT, was recently made available to the community.³⁷

In this paper our goal is to make the first step in the application of our theory and code to the collisional quenching of PAHs, by doing MQCT calculations for the smallest member of this group, the benzene molecule, collided with helium atom: $\text{C}_6\text{H}_6 + \text{He}$. For this, we compute cross sections for rotational excitation and quenching of benzene by helium in a broad range of collision energies using large rotational basis set, up to $j_k = 60_{60}$. Quantum propensity rules are determined and discussed, and an efficient simplified approach for such calculations is developed. To our best knowledge, no quantum mechanical calculations of inelastic cross sections for benzene have ever been attempted before.

MQCT METHODOLOGY

Here we briefly summarize the equations of motion propagated within framework of the mixed/quantum classical theory. Rigorous derivation of these formula is available from literature.^{26–36}

The relative motion of two collision partners is described classically by vector $\vec{R}$ in the laboratory-fixed reference frame that connects their centers of mass. The length R of this vector and its azimuthal angle Φ (related to the deflection angle) evolve according to the following classical-like equations of motion:^{29,30}

$$\dot{R} = \frac{P_R}{\mu} \quad (1)$$

$$\dot{\Phi} = \frac{P_\Phi}{\mu R^2} \quad (2)$$

$$\dot{P}_R = - \sum_n \sum_{n'} e^{i\varepsilon_n^{n'} t} \sum_m \frac{\partial M_n^{n'}}{\partial R} a_{mn}^* a_{mn} + \frac{P_\Phi^2}{\mu R^3} \quad (3)$$

$$\begin{aligned} \dot{P}_\Phi = & -i \sum_n \sum_{n'} e^{i\varepsilon_n^{n'} t} \sum_m M_n^{n'} \\ & \times \left[a_{m-1,n'}^* a_{mn} \sqrt{j'(j'+1) - m(m-1)} \right. \\ & + a_{m+1,n'}^* a_{mn} \sqrt{j'(j'+1) - m(m+1)} \\ & - a_{mn}^* a_{m-1,n} \sqrt{j(j+1) - m(m-1)} \\ & \left. - a_{mn}^* a_{m+1,n} \sqrt{j(j+1) - m(m+1)} \right] / 2 \end{aligned} \quad (4)$$

where P_R and P_Φ are two generalized momenta associated with R and Φ .

In these formula $\varepsilon_n^{n'}$ describe energy differences between the initial (lower index, unprimed) and the final (upper index, primed) internal states of the system, say rotational or ro-vibrational states with energies E_n and $E_{n'}$. Index m labels projections of the total molecular angular momentum j onto the molecule-quencher axis $\vec{R}$ (which is the quantization axis z in the body-fixed reference frame). Multiple sums in Eqs. (3) and (4) go over all quantum states of the system. Time evolution of probability amplitudes $a_{mn}(t)$ for these molecular quantum states (rotational, ro-vibrational) is described in the body-fixed reference frame, tied to the molecule-molecule vector $\vec{R}$, and is given by the following quantum-like system of coupled equations:^{29,30}

$$\begin{aligned} \dot{a}_{mn} = & -i \sum_{n'} e^{i\varepsilon_n^{n'} t} \sum_m M_n^{n'} a_{mn'} \\ & - i\dot{\Phi} \left[a_{m-1,n} \sqrt{j(j+1) - m(m-1)} \right. \\ & \left. + a_{m+1,n} \sqrt{j(j+1) - m(m+1)} \right] / 2 \end{aligned} \quad (5)$$

Second term in Eq. (5) describes transitions between the rotational states with $\Delta m = \pm 1$, driven by the classical orbital angular velocity $\dot{\Phi}$, which is the Coriolis coupling effect. First term in Eq. (5) includes the potential coupling matrix $M_n^{n'}$ that depends parametrically on R (omitted for clarity). This matrix is real-valued time-independent and is diagonal in m (also omitted for clarity):

$$M_n^{n'}(R) = \langle \Psi_{n'}(\Lambda) | V(R, \Lambda) | \Psi_n(\Lambda) \rangle. \quad (6)$$

Wavefunctions $\Psi_n(\Lambda)$ and $\Psi_{n'}(\Lambda)$ correspond to the initial and final states, respectively. They describe rotations of the molecule relative to the molecule-quencher axis R using a set of Euler angles $\Lambda = \{\alpha, \beta, \gamma\}$. In particular, for symmetric-top rotor molecules (such as benzene), the rotational states of given parity p (+ or $-$) are used to represent the basis set of molecular eigenstates:

$$\Psi_{k,m}^{j,p}(\Lambda) = \sqrt{\frac{2j+1}{16\pi^2(1+\delta_{k0})}} [D_{+k,m}^j(\Lambda) \pm D_{-k,m}^j(\Lambda)]. \quad (7)$$

where the usual Wigner D -functions are used but k is non-negative. The integrals of Eq. (6) are computed numerically using a multi-dimensional quadrature over angles Λ , for a grid of points R_i along the molecule-quencher distance R . When trajectories are propagated, these pre-computed values of $M_n^{n'}(R_i)$ are splined to give a smooth continuous dependence of $M_n^{n'}(R)$. It should be stressed that since the ro-vibrational motion of the molecule is treated quantum mechanically, the so-called “leakage” of zero-point energy (known to cause serious problems in the purely classical trajectory simulations) does not happen in the mixed quantum/classical calculations, where these internal states are quantized.

The equations of motion (1-5) are propagated through the interaction region and the values of inelastic transition cross sections are computed from the final probability amplitudes as [38]:

$$\sigma_{n \rightarrow n'} = \frac{\pi}{(2j+1)k^2} \sum_{J=0}^{J_{max}} (2J+1) \sum_{m=-j}^j \sum_{m'=-j'}^{j'} |a_{m'n'}^{(i)}|^2. \quad (8)$$

This expression includes the usual sum over final and average over initial values of m' and m (respectively) in the ranges determined by the final and initial values of molecular angular momenta j' and j (respectively) that correspond to the final and initial states n' and n (in general, can be ro-vibrational states). The outer sum is over the total angular momentum of the molecule-quencher system varied through the range $0 \leq J \leq J_{max}$, so, J_{max} is a convergence parameter, just as in the full-quantum methods. Index i labels trajectories propagated for each initial m state of given j and for each value of the orbital angular momentum of collision l that changes through the range $|J - j| \leq l \leq J + j$, for each J . The value of l determines classical initial conditions for angular momentum, $P_\Phi = \hbar\sqrt{l(l+1)}$. The radial component of momentum P_R is set to satisfy energy balance $P^2 = P_R^2 + P_\Phi^2/R^2$, where $P = \sqrt{2\mu U}$ is the total initial momentum related to the kinetic energy U of trajectory. Classical impact parameter b can be obtained from $P_\Phi = bP$. Thus, the impact parameter b is related to l , but also depends on energy and reduced mass of the system: $b = \hbar\sqrt{l(l+1)/(2\mu U)}$. Although classical impact parameter is not used anywhere in the equations of motion, it is a useful property for setting up the initial conditions.

In theory, the propagation of each trajectory of this “batch” is required only if the differential and/or elastic cross sections are needed, since those are sensitive to the quantum phase shifts (not discussed here, see Ref. [38]). If only the integral inelastic transition cross section are of interest, as here, the sampling of initial conditions can be replaced by a more efficient multi-dimensional Monte-Carlo procedure as follows: Draw randomly and uniformly the initial m from the range $-j \leq m \leq j$, draw the initial J value from the range $0 \leq J \leq J_{max}$, and finally draw the value of l from the range $|J - j| \leq l \leq J + j$, and use these random numbers to set up the trajectory i . Cross section is computed as average over the sample using:

$$\sigma_{n \rightarrow n'} = \frac{\pi}{k^2} \cdot \frac{J_{max}}{N} \sum_{i=1}^N (2J^{(i)} + 1) |a_{m'n'}^{(i)}|^2. \quad (9)$$

where the number of trajectories N in the random sample is another convergence parameter. Note that if the quencher is also a molecule, such as H_2 , then two angular momenta are introduced for the initial state of the molecule-molecule system, j_1 and j_2 , and the procedure starts with a random sampling of j_{12} from the range $|j_1 - j_2| \leq j_{12} \leq j_1 + j_2$, then sampling m_{12} from the range $-j_{12} \leq m_{12} \leq j_{12}$, then random initial J , and only then the initial value of l from the range $|J - j_{12}| \leq l \leq$

$J + j_{12}$. This replaces a four-dimensional sampling of the initial conditions by one Monte-Carlo sampling, which is very efficient.

Even more speed up can be obtained by decoupling²⁸ the propagation of quantum equations (5) from the classical equations (1-4). This can be done by, first, propagating the whole system of coupled equations (1-5) together, but using a small basis set of the internal molecular states (to make these calculations fast). Probability amplitudes a_{mn} of the quantum states are disregarded after this first run, and only the evolution of classical variables R , Φ , P_R and P_Φ is recorded. During the second run the internal molecular basis set size is increased to the desired value, and only the quantum equations (5) for the evolution of probability amplitudes a_{mn} are propagated, using the values of classical variables saved during the first run. The limiting case of this approach, when the first run is done using only the basis set of degenerate m states of the initial j channel, corresponds to the rotationally adiabatic trajectory method, which we named AT-MQCT.²⁸ This method was found to be sufficiently accurate and very efficient for $\text{H}_2\text{O} + \text{H}_2$ and for $\text{H}_2\text{O} + \text{H}_2\text{O}$ collisions and will be tested below for the $\text{C}_6\text{H}_6 + \text{He}$ collisions. Note that AT-MQCT can be used in conjunction with the Monte-Carlo sampling described above.

RESULTS

For these calculations we used an existing *ab-initio* potential energy surface (PES) from literature for the interaction of C_6H_6 with He atom.³⁹ Six-fold symmetry of the interaction potential leads to non-zero matrix elements only for transitions with $\Delta k = \pm 6$, where k is projection of j on the symmetry axis of benzene (perpendicular to the plane of the molecule). Also, since the PES is symmetric with respect to the plane of the molecule, only the transitions with $\Delta j = \pm 2$ are allowed, just as in the case of a diatomic molecule. Therefore, for calculations in which the initial state is the rotational ground state $j_k^p = 0_0^+$ (where p is parity) we included in the rotational basis set only the states with $k = 0, 6, 12$ etc. (up to $k = j$) with even j values up to $j = 60$, and only the states of positive parity (+). This resulted in 176 non-degenerate quantum states in the basis set (channels). The rotational constants $A = B = 0.18960 \text{ cm}^{-1}$ and $C = 0.09480 \text{ cm}^{-1}$ were used for the oblate symmetric top model of benzene,⁴⁰ with the highest energy state $j_k^p = 60_0^+$ at 693.936 cm^{-1} . The inclusion of degenerate m -states leads to the total of 14036 quantum states in the calculations, and 970628 non-zero matrix elements for state-to-state transitions.

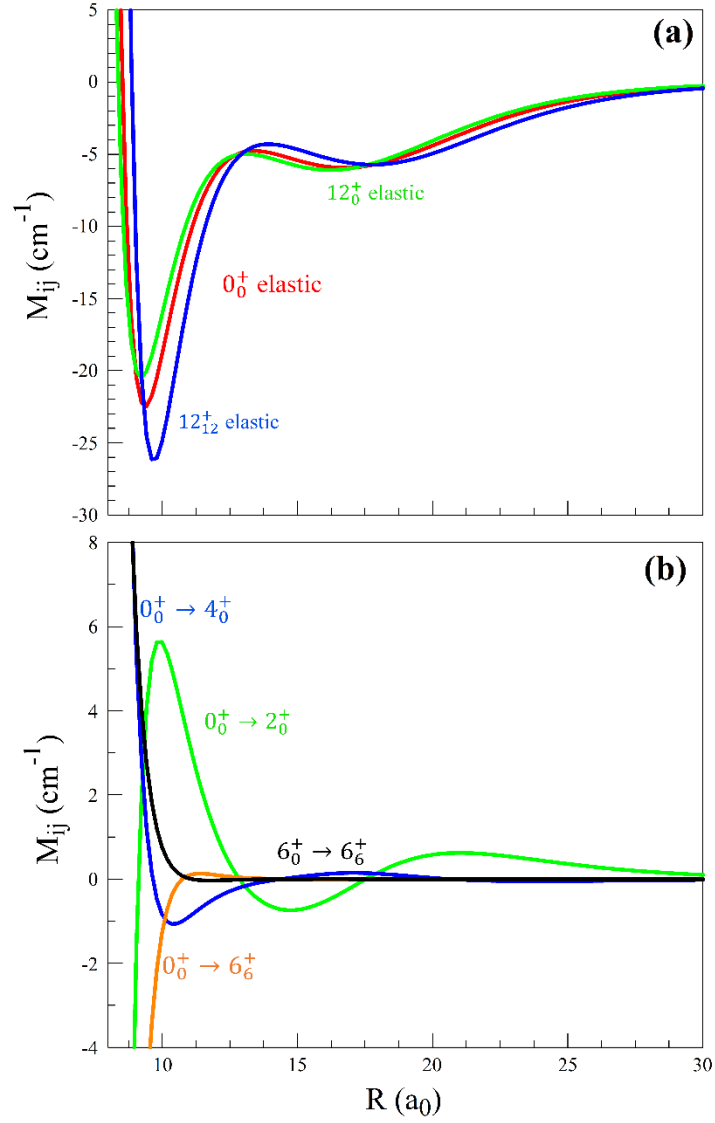


Figure 1: Several diagonal (a) and off-diagonal (b) matrix elements for $\text{C}_6\text{H}_6 + \text{He}$ system. Long-range interaction well is clearly seen. Inelastic transitions remain important up to $R = 30 a_0$ range of the molecule-quencher distances. Only the case of $m = 0$ is shown, the matrix elements for other values of m look similar.

To ensure that symmetry properties were taken into account correctly, we also tried to include in the basis set all states (with all values of j and k , and of both parities p) and, using a multi-dimensional quadrature, computed all state-to-state matrix elements. We found that for all transitions we neglected the matrix elements are indeed near numerical zero, thus, including these states would not lead to any state-to-state transitions anyway. Figure 1 gives several examples of non-zero diagonal and off-diagonal matrix elements for the $\text{C}_6\text{H}_6 + \text{He}$ system. The diagonal matrix elements reflect long-range interaction that extends far into the molecule-quencher distance, through $\sim 30 a_0$. Therefore, the values of $R_{\max} = 50 a_0$ was used, which, in conjunction with $b_{\max} = R_{\max}$ leads to $J_{\max} = 125$ for collision energy $U = 100 \text{ cm}^{-1}$, $J_{\max} = 397$ for collision energy $U = 1000 \text{ cm}^{-1}$, and $J_{\max} = 1257$ for collision energy $U = 10000 \text{ cm}^{-1}$. Note that the full-quantum calculations of inelastic scattering would hardly be possible for these large values of J . From figure 1 we also see that the off-diagonal matrix element for $\Delta j = 2$ transition also exhibits a long-range behavior. This is due to a pronounced anisotropy of the PES for this system, which exhibits a potential well over 80 cm^{-1} deep at the symmetry axis (at the “poles”) but is much shallower in the plane of the molecule (in the “equatorial” plane). As we will see below, this polar anisotropy will result in a long ladder of $\Delta j = 2$ transitions.

Our standard full-coupled CC-MQCT calculations, that are expected to serve as a reference and thus need to be perfectly converged, were carried out in a usual way, using 4th-order Runge-Kutta integrator with a constant time-step set to a rather small value, $\Delta t = 50 \text{ a.u.}$ Convergence of the approximate AT-MQCT calculations with adiabatic step-size predictor²⁸ was also rigorously checked, by varying the value of accuracy ϵ (see Ref. [28] for details). The results presented in figure 3 are found to be entirely converged when $\epsilon = 10^{-3}$.

In the literature there is only one example of scattering calculations for $\text{C}_6\text{H}_6 + \text{He}$ system⁴¹ using a simplified isotropic potential, which can only give the *elastic* cross section. Interestingly, the results of those calculations were found to be in good agreement with experimental results for the *total* cross section (reported in the same paper). This is quite possible, since all inelastic cross sections are much smaller than the elastic one (by at least an order of magnitude, see below) and because experimental results were scaled to match the results of calculations (as experiment of Ref. [41] doesn’t give the absolute values). Therefore, we decided to run, first of all, some comparison of our results vs. those data available from literature. In figure 2 we present the

dependence of elastic cross section on the speed of collision, replicated from Ref. [41]. Their experiments were conducted with room-temperature C_6H_6 target molecules. Therefore, for our calculations of elastic cross sections, we have chosen several highly excited rotational states at energy near 200 cm^{-1} , which corresponds to kT at 300 K. We found that the values of elastic cross sections for all such states are very similar. In figure 2 we present the dependence of elastic cross section for 30_0^+ and 36_{24}^+ states of C_6H_6 at energies 200.218 and 197.942 cm^{-1} , respectively. Note that one of them has $k = 0$, while the other has very large $k = 24$, still, the dependencies of elastic cross sections on collision energy are nearly identical. In order to mimic the elastic calculations of Ref. [41] by our MQCT calculations, we reduced the basis set to only one (elastic, initial) channel, but included all degenerate m states. From figure 2 we see that the positions of peaks, and the overall shapes of dependencies, are very similar here and in Ref. [41], but the magnitudes are different by a factor of 3 to 4. This difference is likely to occur due to the fact that an approximate averaged potential was used in Ref. [41], while here we use an accurate PES that exhibits significant anisotropy³⁹. Also, quite unfortunately, it is unknown what theoretical method was used in Ref. [41] for the calculations of scattering. In order to eliminate a possibility that something is wrong with our MQCT code, we carried out an additional set of elastic scattering calculations using a well-known full-quantum code MOLSCAT⁴², for the same states of benzene: 30_0^+ and 36_{24}^+ (such calculations become affordable if just one quantum state is included). These data are also presented in figure 2. They are very similar to our MQCT results, with maximum difference $\sim 13\%$ at low collision energies, which represents a successful test of our mixed quantum/classical methodology.

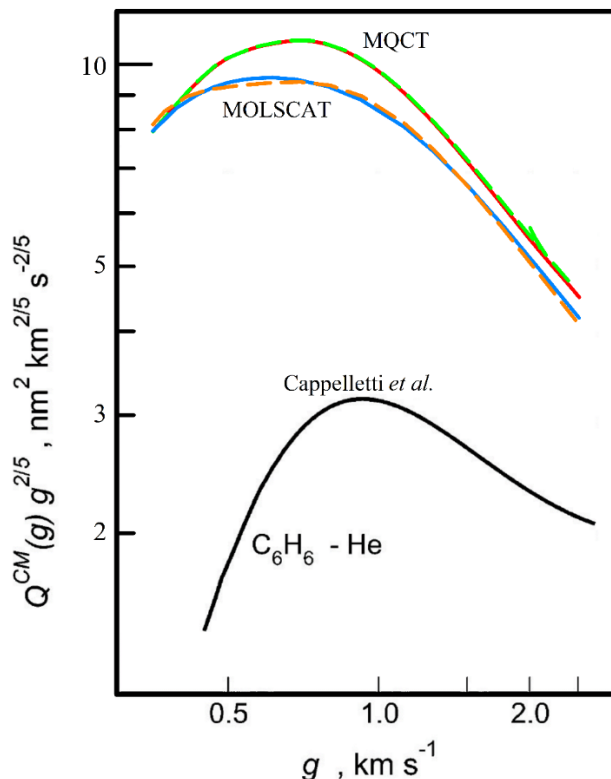


Figure 2: Dependence of elastic cross sections on the speed of collision similar to figure 2 of Ref. [41]. The black solid line is the result obtained from Ref. [41]. The solid red and blue lines represent results for initial state 30_0 for MQCT and MOLSCAT, respectively. The dashed green and orange lines represent results obtained for initial state 36_{24} with MQCT and MOLSCAT, respectively.

Next, we looked in detail at the rotational excitations from the ground state of the system, 0_0^+ . Figure 3 in the main text and figure S1 in the *Supporting Information* (SI) report cross sections for 200 state-to-state transitions, including the elastic channel, for two values of collision energy $U = 100 \text{ cm}^{-1}$ and $U = 1000 \text{ cm}^{-1}$, respectively. One can see that the results of approximate AT-MQCT method (dashed lines) follow closely the trend of benchmark CC-MQCT data (solid lines with symbols) through all transitions and all collision energies, systematically. We did not find even one transition where the adiabatic trajectory method would fail badly. Note that the values of cross sections in figure 3 and figure S1 vary through seven orders of magnitude range. Still, the results of the approximate AT-MQCT method remain very close to the results of the full-coupled CC-MQCT method, even for very small cross sections.

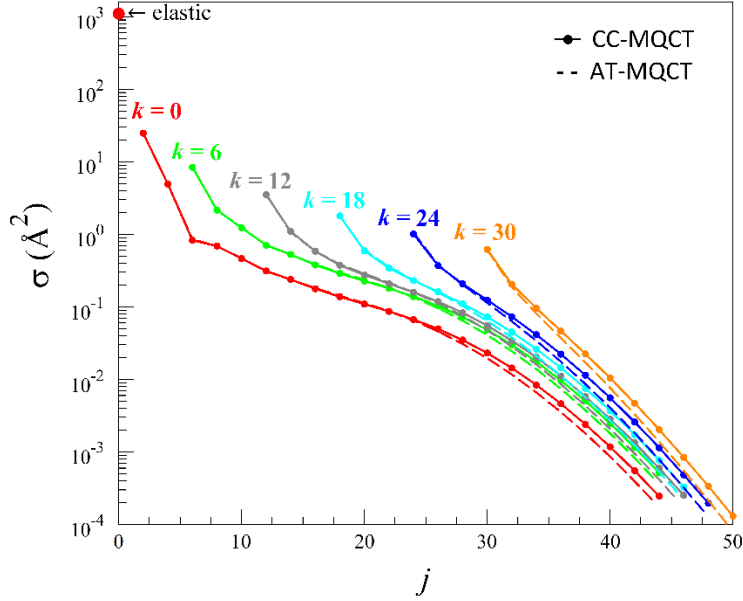


Figure 3: Comparison of results of the approximate AT-MQCT method (dashed line) against the full-coupled CC-MQCT calculations (solid line with symbols) for rotational excitation of the ground state 0_0^+ of C_6H_6 at collision energy of 100 cm^{-1} . Quantum numbers j of the final rotational states are listed along the horizontal axis, while their quantum numbers k are indicated by color. The values of collision cross sections are plotted along the vertical axis using log scale. The value of elastic cross section is also shown.

In figure 4 we present the error (in percent) of AT-MQCT cross sections relative to the CC-MQCT benchmark data, for collision energy $U = 100 \text{ cm}^{-1}$. The case of $U = 1000 \text{ cm}^{-1}$ is reported in figure S2 of SI. These data indicate that for larger, practically important cross sections (up to $J = 24$ or so) the difference between AT and CC versions of theory remains within 5% of the cross-section values. Only when the value of cross section drops by several orders of magnitude, the difference starts increasing, reaching 40% for the weakest (basically negligible) transitions. But even in this case the error of the AT method does not “explode”. It grows linearly with J and remains tolerable. These results are encouraging and justify the use of adiabatic trajectory approximation for this system. In what follows, AT-MQCT version will be used. One advantage of AT-MQCT is computational speed up which, for this system, is a factor of ~ 16 at

$U = 100 \text{ cm}^{-1}$, and a factor of ~ 19 at $U = 1000 \text{ cm}^{-1}$. These speed-up data were determined by running MQCT calculations on Cori Haswell machine (2.3 GHz Intel Xeon Processor E5-2698 v3) at the National Energy Research Scientific Computing Center (NERSC), using 1 node (32 processors). At lower (higher) collision energy the AT-MQCT method took only 3.42 min (8.33 min) of the wall clock time.

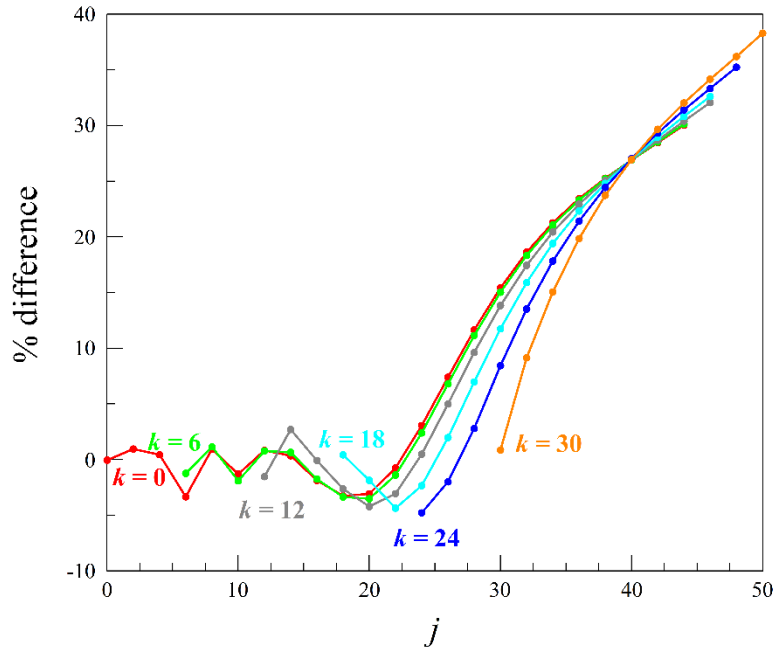


Figure 4: Relative deviation of AT-MQCT results from CC-MQCT results (% error) for all cross sections presented in figure 3 for the rotational excitation of 0_0^+ state of C_6H_6 by He impact at collision energy 100 cm^{-1} . Quantum numbers j of the final rotational states are listed along the horizontal axis, while their quantum numbers k are indicated by color.

Another advantage of the adiabatic trajectory version of our theory is that it permits to expand MQCT calculations into the regime of low collision energies, dominated by quantum scattering resonances. While the trajectory based MQCT method is not expected to capture every individual scattering resonance accurately, it permits to mimic resonant behavior at low energies, on average. Figure 5 reports energy dependence of several state-to-state transition cross sections in a broad range of collision energies, starting from the process threshold at low energies and going

up to 10000 cm^{-1} . We see that slightly above excitation threshold, and typically below 50 cm^{-1} , each curve passes through a series of peaks. Each peak is produced by one characteristic value of impact parameter that leads to the formation of a long-lived orbit, a phenomenon studied in detail in Ref. [38]. In the full-coupled CC-MQCT version of theory such orbiting trajectories can be permanently trapped (due to inelastic energy exchange), while in the AT-MQCT version of theory they will typically leave after a few periods of orbiting, which permits us to run the final state analysis and compute inelastic cross sections at low collision energies, which is an important practical advantage.

It should be noted that not all cross sections in the high energy part of figure 5 are entirely converged with respect to the basis set size. Indeed, energies of the eigenstates in our rotational basis set reach, roughly, 700 cm^{-1} , which is a huge basis set taking into account small rotational constants of C_6H_6 . Still, this is smaller than the range of collision energies in figure 5. We tried to vary the basis set size and found that all important state-to-state transition cross sections are well converged up to collision energy $\sim 2000 \text{ cm}^{-1}$. Above this energy, as one may notice from figure 5, the energy dependencies of inelastic cross sections are not entirely smooth, they exhibit some (relatively small, residual) oscillations. These oscillations represent a vestige of an insufficient basis set size (at high energy). When the basis set size is increased, these oscillations vanish and the energy dependence becomes smooth, which is the behavior expected at high collision energies.

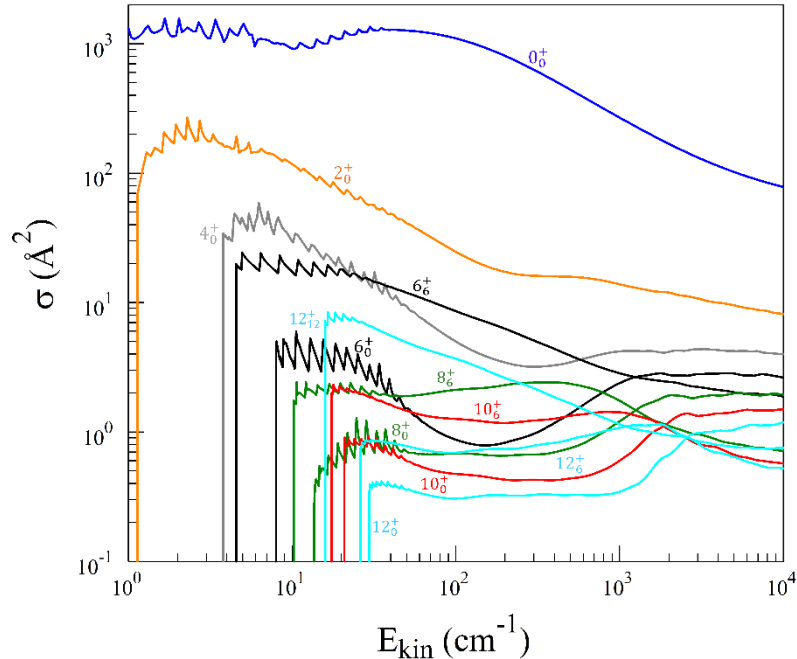


Figure 5: Energy dependence of excitation cross sections for several rotational states of C_6H_6 starting from the rotational ground state 0_0^+ , collided with He atom. The dependence of elastic cross section is also shown.

One important measure of the accuracy of MQCT method is the deviation of state-to-state transition cross sections from the values that obey the principle of microscopic reversibility:

$$(2j + 1)\sigma_{j \rightarrow j'} = (2j' + 1)\sigma_{j' \rightarrow j} \quad (8)$$

It is known that while the full-quantum methods satisfy this condition automatically, the trajectory-based semi-classical methods often violate this relationship to some extent. Our MQCT method is not an exception. Therefore, the property of Eq. (8) has to be checked and, if needed, one of the known procedures has to be employed³⁶ to symmetrize the state-to-state transition matrix, before it can be used in the kinetics simulations. Figure 6a compares cross sections for the rotational $0_0^+ \rightarrow 10_6^+$ transition, as a function of energy computed directly (by excitation of the 0_0^+ initial state) with that computed indirectly (in the “reverse”, using Eq. (8) and the data from the MQCT calculations of quenching $10_6^+ \rightarrow 0_0^+$ carried out separately). We see that although the microscopic reversibility principle is not exactly satisfied, the two sets of results remain very close to each other through the entire range of collision energies, from $U = 1 \text{ cm}^{-1}$ to 10000 cm^{-1} . Similar behavior is seen in figure 6a for the quenching $10_6^+ \rightarrow 0_0^+$ transition, which means that a meaningful symmetrization procedure can be carried out to enforce the microscopic reversibility principle in the final data produced by MQCT. Figure 6b gives the same information for transitions between two excited states, $10_6^+ \rightarrow 12_0^+$ and $12_0^+ \rightarrow 10_6^+$, and these data look similar to those of figure 6a. Importantly, the deviation of MQCT results from the principle of microscopic reversibility is manageable and appears to decrease at higher collision energies, as expected for a trajectory-based method with a classical component. Figure 6c gives yet another example, for transitions between 2_0^+ and 10_6^+ , where the difference between the direct and reverse calculations appears to be larger, particularly at low collision energies.

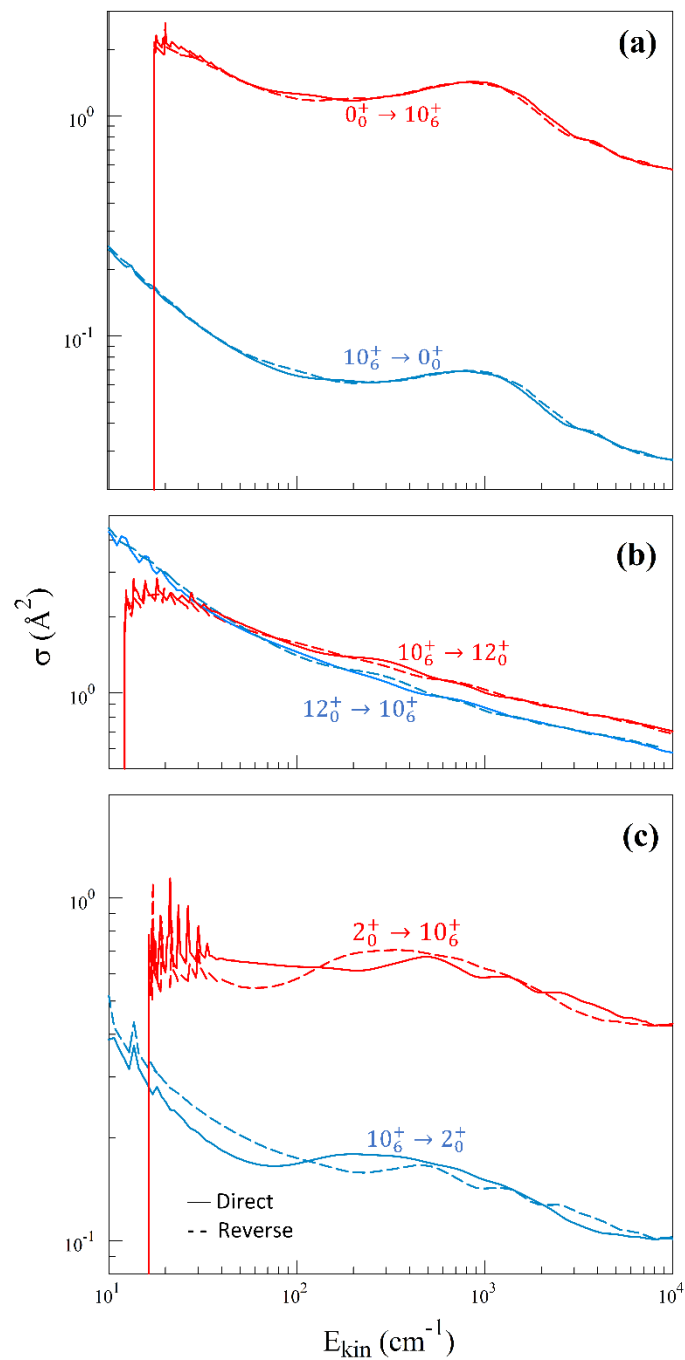


Figure 6: A test of the microscopic reversibility principle for transitions between several rotational states of C_6H_6 collided with He atom. The values of cross sections are plotted as a function of collision energy. The data obtained by direct calculations are shown by solid lines, while the results of “reverse” calculations are shown by dashed lines.

State-to-state cross sections for quenching of several excited rotational states of C_6H_6 by He are presented in figure 7 for collision energy $U = 100 \text{ cm}^{-1}$. The case of $U = 1000 \text{ cm}^{-1}$ is reported in figure S3 of SI. It should be mentioned that for the initial states with larger values of j the regular MQCT calculations are heavier, since we must propagate trajectories with all $2j + 1$ values of the initial quantum number m , to account for the second summation in Eq. (6), over $-j \leq m \leq j$. When the initial state corresponds to $j > 10$, the numerical cost of such calculations increases by at least an order of magnitude.

To overcome this problem, one can employ the random Monte-Carlo sampling of initial conditions (over both m and l) and use Eq. (7) to compute cross sections. Data presented in figure 7a demonstrate the performance of such Monte-Carlo sampling, within AT-MQCT method, for the initial states 12_0^+ (circles), 12_6^+ (diamonds) and 12_{12}^+ (squares) of C_6H_6 . In these calculations we reduced the maximum value of impact parameter to $b_{max} = 25a_0$ and propagated only 100 randomly sampled trajectories, instead of ~ 1800 trajectories in the regular AT-MQCT calculations. We see that the results of random sampling (dashed lines, empty symbols) are close to the benchmark data of regular calculations (solid lines, filled symbols) systematically through all transitions and all collision regimes. Differences between the two sets of data, on average, are about 10% of cross section values, which seems to be acceptable, especially if one takes into account a substantial speed up, by a factor of close to ten.

In figure 7b we present the total quenching cross sections for several initial states of C_6H_6 , summed over the final j_k^+ states with j and/or k values smaller than those of the initial state. Here x-symbols correspond to regular AT-MQCT calculations, whereas empty circles correspond to the Monte-Carlo version. In addition to three $j = 12$ states, we included four $j = 18$ states: 18_0^+ , 18_6^+ , 18_{12}^+ and 18_{18}^+ . For these we carried out only the Monte-Carlo calculations with 100 trajectories, since regular calculations would be much more expensive. Computational speed up of the Monte-Carlo sampling gives significant advantage for the initial states with large values of angular momentum j and at higher collision energies U , since in these cases the “volume” of sampling space is much larger, due to wide ranges of variations of the quantum numbers m and l . For example, for the initial state $j = 18$ the computational speed up of Monte-Carlo, relative to the regular calculations, is by a factor of about fifteen at $U = 100 \text{ cm}^{-1}$, and it is by a factor of close to forty at $U = 1000 \text{ cm}^{-1}$.

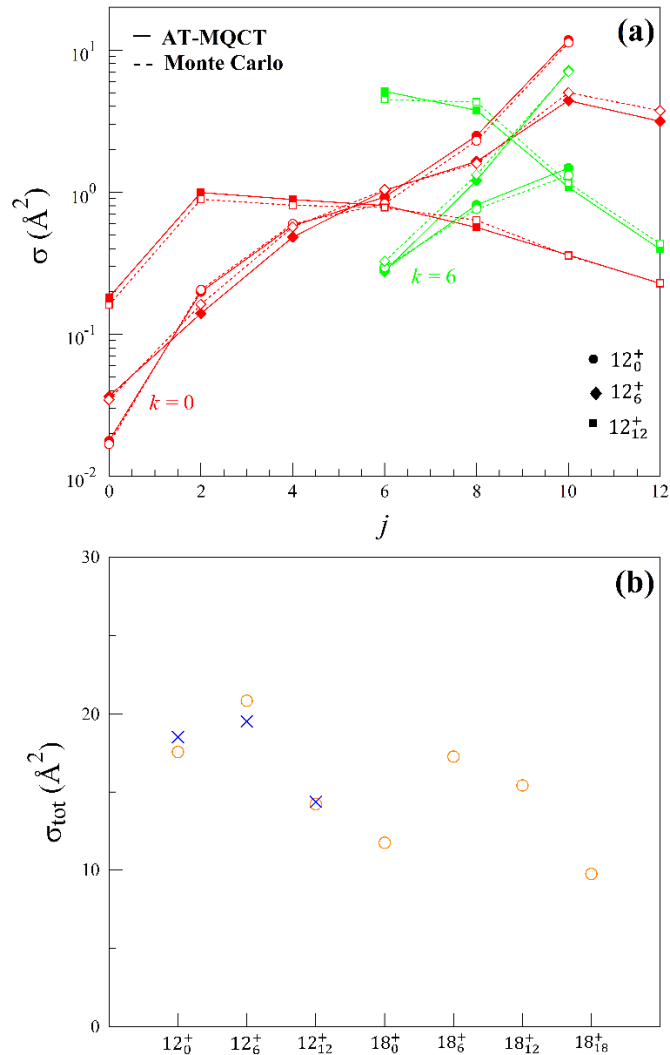


Figure 7: Individual state-to-state (a) and the total (b) quenching cross sections for several initial states of C_6H_6 collided with He atom at kinetic energy 100 cm^{-1} . The results of Monte-Carlo sampling are shown by empty symbols.

CONCLUSIONS

In this work we devised and tested a computationally affordable methodology to calculate cross sections and rate coefficients for collisional quenching and excitation of large interstellar molecules, such as PAHs. Our approach is based on the mixed quantum/classical theory of inelastic scattering, in which quantum state-to-state transitions between rotational states of the

molecule are described using time-dependent Schrodinger equation, while scattering of collision partners is described classically, using the mean-field trajectory approach. Two more developments were undertaken to boost numerical efficiency of the method. One is the decoupling scheme, named adiabatic trajectory approximation, that permits to propagate equations for evolution of classical and quantum degrees of freedom separately, which is much faster. The second trick is a multi-dimensional Monte-Carlo sampling, which permits to reduce dramatically the number of trajectories needed for numerical convergence, without sacrificing the physical rigor.

In this form, our method was applied to compute cross sections for collisional excitation and quenching of benzene molecule C_6H_6 by He atom in a broad range of collision energies. Although benzene is the smallest member of the PAH family, these are the first ever calculations of rotational state-to-state transitions for benzene, and for any other PAH molecule, to our best knowledge. For C_6H_6 a very large basis set of close to 180 rotational eigenstates is needed (up to $j = 60$), which results in almost one million non-zero matrix elements for state-to-state transitions. Moreover, the system is characterized by a long-range interaction, which requires to start trajectories at a distance of ~ 50 Bohr. But, using our methodology and code, these huge calculations are still affordable. Overall, the accuracy of adiabatic trajectory approximation was found to be acceptable, with errors within 5% of cross section values for significant cross sections. Comparison of cross sections for excitation and quenching shows that some of them violate the principle of microscopic reversibility, but not significantly. Therefore, the state-to-state cross section matrix can be symmetrized *a posteriori*.

Success of our decoupling scheme (adiabatic trajectory version of MQCT) can be easily explained using figures 3 and 5 above. They show that in the $C_6H_6 + He$ system the elastic scattering cross section is at least an order of magnitude larger than any inelastic cross section, through wide range of collision energies. This property is rather general, so, AT-MQCT is expected to be reasonably accurate for many other molecular systems. Elastic cross section is governed by isotropic part of the molecule-quencher interaction potential, while inelastic state-to-state transitions are driven by anisotropic part of the PES. Therefore, one may expect that the worst-case scenario for our decoupling scheme would correspond to the molecules with highly anisotropic potentials, such as long carbon chains. This topic will be explored elsewhere.

All these findings are quite encouraging, which permits us to cautiously state that our method can be employed to generate a database of quenching rate coefficients, useful in the astrophysical modelling of C_6H_6 abundance in the interstellar media. Such calculations will be carried out soon, and the data will be deposited in the relevant databases such as BASECOL⁴³ and/or LAMDA⁴⁴. New features of the mixed quantum/classical theory developed and tested here will be made available to the community in new release of the MQCT suite of programs, planned for 2022.

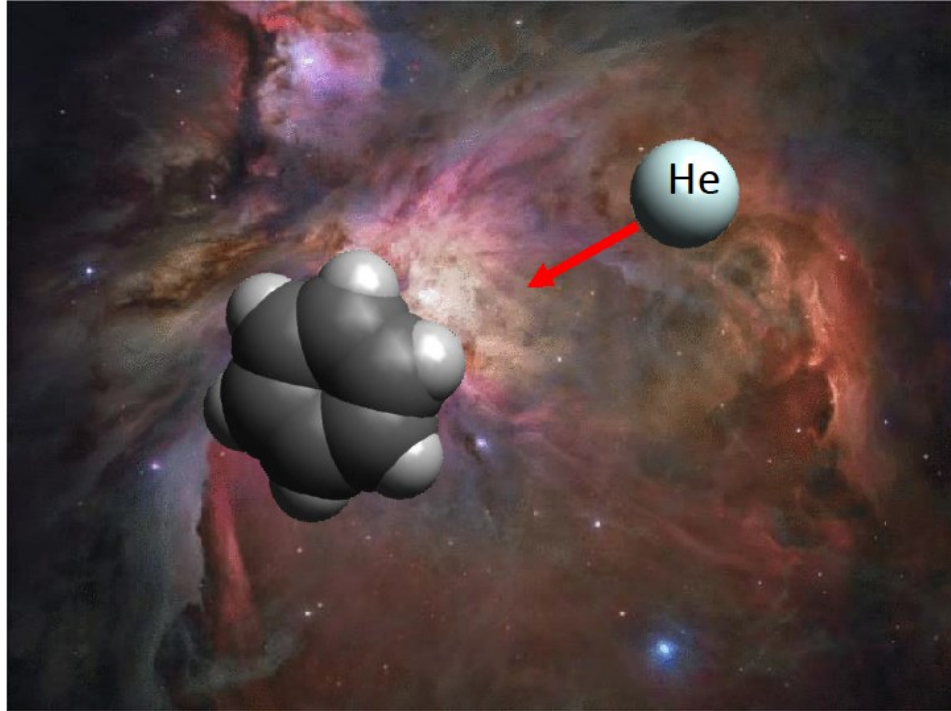
ACKNOWLEDGEMENTS

This research was supported in part by NASA Astrophysics Program, grant number NNX17AH16G, and in part by NSF Chemistry program, grant number CHE-2102465. B. Mandal acknowledges support of Eisch Fellowship at Marquette. We used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-5CH11231.

SUPPORTING INFORMATION

Comparison of results of the approximate AT-MQCT method against the full-coupled CC-MQCT calculations for $C_6H_6 + He$ as in figures 3 and 4, but at collision energy of 1000 cm^{-1} ; Test of the Monte-Carlo sampling for the individual state-to-state and for the total quenching cross sections for several initial states of C_6H_6 collided with He atom, as in figure 7 but for kinetic energy 1000 cm^{-1} .

TOC GRAPHIC



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