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Low temperature rate coefficients of the H + CH\(^+\) → C\(^+\) + H\(_2\) reaction: New potential energy surface and time-independent quantum scattering

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The observed abundances of the methylidyne cation, CH\(^+\), in diffuse molecular clouds can be two orders of magnitude higher than the prediction of the standard gas-phase models which, in turn, predict rather well the abundances of neutral CH. It is therefore necessary to investigate all the possible formation and destruction processes of CH\(^+\) in the interstellar medium with the most abundant species H, H\(_2\), and e\(^-\). In this work, we address the destruction process of CH\(^+\) by hydrogen abstraction. We report a new calculation of the low temperature rate coefficients for the abstraction reaction, using accurate time-independent quantum scattering and a new high-level \textit{ab initio} global potential energy surface including a realistic model of the long-range interaction between the reactants H and CH\(^+\).

The calculated thermal rate coefficient is in good agreement with the experimental data in the range 50 K–800 K. However, at lower temperatures, the experimental rate coefficient takes exceedingly small values which are not reproduced by the calculated rate coefficient. Instead, the latter rate coefficient is close to the one given by the Langevin capture model, as expected for a reaction involving an ion and a neutral species. Several recent theoretical works have reported a seemingly good agreement with the experiment below 50 K, but an analysis of these works show that they are based on potential energy surfaces with incorrect long-range behavior. The experimental results were explained by a loss of reactivity of the lowest rotational states of the reactant; however, the quantum scattering calculations show the opposite, namely, a reactivity enhancement with rotational excitation. © 2015 AIP Publishing LLC.

I. INTRODUCTION

Since its first identification\(^1\) in the interstellar medium in 1941, the observed over-abundance of the methylidyne cation, CH\(^+\), is still a puzzling question. Its collision with H, which is the most abundant atom in interstellar media, leads to the formation of H\(_2\) by the H + CH\(^+\) → C\(^+\) + H\(_2\) abstraction reaction which is exothermic by 0.39 eV and accounts for its loss. The reverse process can then unlikely be considered as a possible mechanism of production of CH\(^+\) in interstellar conditions apart in high temperature shocked gas or in UV illuminated regions where H\(_2\) can be vibrationally excited.\(^2,3\) However, further works have shown that even the shock hypothesis is not fully conclusive when compared to observations.\(^4,5\) In any case, the accurate determination of the rate coefficient of this reaction is central in the modeling of the production and destruction mechanisms of the CH\(^+\) radical in the interstellar medium. In 2007, the first theoretical work\(^6\) on the reaction dynamics predicted a large rate coefficient, \(k = 2.4 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), independent of the temperature below 20 K, and then decreasing for higher temperatures, as a consequence of the opening of channels in the exchange reaction H' + CH\(^+\) → H + CH\(^+\) and in the inelastic process. This result was in agreement with the Langevin capture rate coefficient which is based on a \(-C_0/R^2\) isotropic interaction between an ion and a neutral species, and also with the experimental data available at that time, in the range 50 K–1000 K.

In 2011, a new measurement\(^7\) of the abstraction rate coefficient revealed an unexpected fall off by more than one order of magnitude when the temperature decreases from 60 K down to 10 K. This result suggested that there is a threshold in the translational energy dependence around 11 K. In an attempt to rationalize their findings, the authors investigated the dependence of the rate coefficient on the initial rotational state \(j\) of CH\(^+\) and assumed that the reactivity was low for the state \(j = 0\), and becoming larger with rotational excitation. The fall off could then be easily understood since the state \(j = 0\) is dominant in the thermal rotational population below \(-30\) K. However, the specific low reactivity of the state \(j = 0\) could not be explained. This question attracted further theoretical works.\(^8,10\) Grozdanov and McCarroll\(^9\) presented a statistical treatment in which the alignment of the reactants is controlled by the long-range induction interaction. The angular dependence of the adiabatic rotational states was investigated and it was found that the \(j = 0\) and \(j = 1\) states have a propensity to be aligned in the linear C–H–H configuration. By excluding the contribution
of the \( j = 0 \) state and partially of the \( j = 1 \) state, a good agreement with the experimental rate coefficient was obtained. However, this study is based on the induction interaction, which is a reliable potential energy model only for a separation of the reactants larger than at least \( 10 \, a_0 \), while the linear potential barriers occur at a separation of \( \sim 5 \, a_0 \). From 10 down to \( 5 \, a_0 \), the angular dependence of the potential energy surface (PES) changes considerably, as it will be shown below. Hence, the model of Grozdanov and Carroll neglects completely the reorientation effect by which the reactants will avoid the potential barriers and access easily to the principal potential well.

A new global PES was reported in 2011 by Warmbier and Schneider\(^a\) (hereinafter WS-PES). They calculated the thermal rate coefficients with both quasi-classical trajectories (QCTs) and time-independent quantum scattering approaches. For the abstraction reaction, they found a rate coefficient in agreement with the experimental data at 50 and 100 K, and decreasing for lower temperature. The low temperature fall off was not as steep as the experimental data, but the propensity was the same. Recently, Bovino \textit{et al.}\(^\text{1}\) have presented also a quantum scattering study of the abstraction reaction, using the WS-PES and reported a very similar rate coefficient. It can be shown that these seemingly good agreements with the experiment are actually the consequence of a PES model without long-range interaction. The largest separation of the reactants at which \textit{ab initio} energies were computed by Warmbier and Schneider is 12 \( a_0 \), and the functional form of the WS-PES is based on exponential functions of the internuclear distances. Consequently, the interaction energy given by the WS-PES is exponentially decreasing beyond the cutoff distance of 12 \( a_0 \), instead of the proper physical model that should involve the \( R^{-5} \) behavior accounting for the induction and dispersion interactions. Let us examine the effect of this shortcoming on the collision dynamics. In a first approximation, the rate coefficient is given by the product of the average relative speed of the reactants times the cross section. The cross section, in turn, is proportional to the square of the maximum impact parameter for the reaction. When the temperature drops, so does the speed of the reactants. If the interaction potential is zero beyond some cutoff distance, then the maximum impact parameter for the reaction cannot be larger than the cutoff distance. The decrease of the speed is not anymore compensated by the increase of the impact parameter, and therefore, the rate coefficient drops.

If we consider a \( -C_4/R^4 \) isotropic interaction potential, the impact parameter can be directly related to the collision energy.\(^\text{12}\) In the case of the title reaction, \( C_4 = a_{\text{H}}/2 \), where \( a_{\text{H}} \) is the polarizability of the hydrogen atom. For a 10 K collision energy, the calculated maximum impact parameter is 23 \( a_0 \), and for 50 K, we get 15.5 \( a_0 \). These numbers are significantly larger than the cutoff distance applied in the WS-PES, therefore implying that no reliable rate coefficient can be calculated with this PES below \( \sim 50 \) K. Another new global PES was reported recently by Li \textit{et al.}\(^\text{10}\) (hereinafter LZH-PES). With a cutoff length of 10 \( a_0 \) and an exponential decrease beyond this value, this PES is plagued by the same shortcoming of the WS-PES.

A realistic model of the long-range interaction is a basic prerequisite for a reliable calculation of the low temperature rate coefficients of an ionic collisional system. A proper consideration of all quantum effects, including interferences, resonances, and over-barrier reflections is also necessary. Only the time-independent quantum scattering approach is adequate for very low collision energy, since the QCT method is plagued by the zero point energy leakage and the time-dependent quantum scattering would require a wavepacket far too large in space and in time. The purpose of this work is to check if the experimental rate coefficients can be reproduced by using time-independent quantum scattering and a state-of-the-art new PES including the proper long-range interaction. The effect of the rotational excitation needs also to be investigated as it is essential for the interpretation of the experimental results. A single PES is used, therefore involving the neglect of the nonadiabatic couplings, as in the earlier studies on this system.

II. THE POTENTIAL ENERGY SURFACE

The ground state and the first excited state of the diatomic molecule CH\(^+\) are \( \Sigma^+ \) and \( \Pi \), respectively. The collision with H\((3S)\) yields the \( \Sigma^+ \) and \( \Pi \) states of linear CH\(^+\), which become two \( ^2\Lambda \) and one \( ^2\Lambda^\prime \) states for bent CH\(^+\). The collision forms also a \( ^4\Pi \) state which needs not to be considered here. The \( \Sigma^+ \) state of linear CH\(^+\) is repulsive and crosses the attractive \( ^2\Pi \) state, yielding a conical intersection. For a bent configuration of CH\(^+\), the crossing is avoided and the ground state is \( ^2\Lambda \). In this work, we consider only the ground state of the reactants, namely, CH\(^+(\Sigma^+\Sigma^+)\) + H\((3S)\), and only the \( ^2\Lambda \) ground state of CH\(^+\). There is no spin-orbit coupling because the electronic angular momentum is equal to zero.

A. \textit{Ab initio} calculations

The electronic energy has been calculated with the contracted multireference configuration interaction method including the so-called Davidson correction (MRCI + Q), and with molecular orbitals obtained from a complete active space self consistent field (CASSCF) calculation. The active space was developed over six molecular orbitals and five active electrons. The two core electrons were not correlated. The quintuple zeta quality basis set aug-cc-pvSZ was used. In the region of the two conical intersections located in the reactants channel, for the H–C–H and C–H–H linear configurations, the electronic wavefunction is better described by the mixture of the wavefunctions of the two crossing states. Therefore, the CASSCF wavefunction was averaged on the two lowest \( ^2\Lambda \) states and this procedure was applied to every calculation in order to gain the same level of description for the whole PES. With the same basis set, the coupled cluster with single and double and perturbative triple excitation (CCSD(T)) has been also used to check the quality of the MRCI + Q calculations in the long-range region of the H + CH\(^+\) arrangement.

All calculations were performed within the supermolecular approach. Therefore, the interaction energy is a difference between two electronic energies which can be very close in the long-range region and thus, computing meaningful long-range interaction energy needs precise calculations. To this end, the thresholds (in atomic units) for the calculations of the electronic wavefunction have been tightened to \( 10^{-9} \) for the energies, \( 10^{-13} \) for one- and two-electron integrals, and \( 10^{-15} \) for integrals prefactor.\(^\text{13}\)
A total of 11 235 \textit{ab initio} points have been used to determine the parameters of the functional form of the PES. These points span the region of the C\(^+\) + H\(_2\) arrangement within the limits 1.1 \(\leq R_1 \leq 1.9\) a\(_0\), 1.4 \(\leq \rho_1 \leq 50\) a\(_0\), and 0 \(\leq \varphi_1 \leq 90\); the region of the H + CH\(^+\) arrangement within the limits 1.8 \(\leq R_2 \leq 2.8\) a\(_0\), 1.4 \(\leq \rho_2 \leq 50\) a\(_0\), and 0 \(\leq \varphi_2 \leq 180\); and the region of the potential well within the limits 1.1 \(\leq R_2 \leq 1.9\) a\(_0\), 1.1 \(\leq R_3 \leq 1.9\) a\(_0\), and 0 \(\leq \theta_3 \leq 180\), with the restrictions \(R_3 \geq R_2\) and \(R_1 > 0.7\) a\(_0\). All \textit{ab initio} calculations have been carried out with the \textsc{molpro} suite of programs.\(^{13}\)

### B. Functional form of the PES

The potential energy is expanded as the sum of two-body \(V^{(2)}\) and three-body \(V^{(3)}\) terms,

\[
V(R_1, R_2, R_3) = V_{11}^{(2)}(R_1) + V_{12}^{(2)}(R_2) + V_{23}^{(2)}(R_3) + V_{31}^{(3)}(R_1, R_2, R_3),
\]

where \(R_1, R_2,\) and \(R_3\) are, respectively, the bond lengths of the diatomic fragments H–H, C–H, and C–H (see Fig. 1). The two-body potential functions are defined by

\[
V_{AB}^{(2)}(R) = \frac{b_{0AB}}{R} e^{-\alpha_{AB} R} + e^{-\beta_{AB} R} \sum_{i=1}^{N_{AB}} b_{i}^{AB} R^{i}.
\]

The three-body potential is the sum of the short-range potential \(V_{SR}\) and the long-range interaction energy \(V_{LR}\).

\[
V^{(3)}(R_1, R_2, R_3) = V_{SR}(R_1, R_2, R_3) + V_{LR}(R_1, R_2, R_3).
\]

This potential function must be symmetric under the exchange of the hydrogen nuclei, i.e., under the permutation of the \(R_2\) and \(R_3\) bond lengths. The short-range potential is the product of a 3-d polynomial and a damping function which tends towards zero when any of the bond lengths become large. We add also to this potential a contribution \(V_c\) necessary to represent the cusps resulting from the conical intersections,

\[
V_{SR}(R_1, R_2, R_3) = P(S_1, S_2, S_3)e^{-\gamma_1 R_1-\gamma_2 R_2+R_3} + V_c(R_1, R_2, R_3),
\]

where \(S_1, S_2,\) and \(S_3\) are the symmetry coordinates which transform like the irreducible representations of the symmetric group \(S_3\),

\[
\begin{align*}
S_1 &= \frac{1}{2}(R_2 + R_3), \\
S_2 &= \frac{1}{2}(R_2 - R_3), \\
S_3 &= R_1.
\end{align*}
\]

\textbf{FIG. 1.} Definition of the coordinate systems.

The symmetric 3-d polynomial can be written as

\[
P(S_1, S_2, S_3) = \sum_{i,j,k} C_{ijk} S_1^i S_2^j S_3^k,
\]

where the sum runs over all possible non-negative integer values for \(i, j,\) and \(k\) such that

\[
0 \leq i + j + k \leq N_p.
\]

The cusps induced by the conical intersections cannot be represented by polynomials functions which have continuous first derivatives. Therefore, we use local functions defined such that the potential barriers and the cusps obtained with the \textit{ab initio} calculations are reproduced at best. We have to take in account the conical intersections occurring for the C–H–H and the H–C–H linear configurations, as well as the hydrogen nuclei exchange symmetry,

\[
V_c(R_1, R_2, R_3) = F_1(R_2, R_3, \varphi_1) + F_1(R_2, R_3, \varphi_1)
\]

\[
+ F_2(R_1, R_2, \rho_2) + F_2(R_1, R_2, \rho_2),
\]

\[
F_n(R_i, \rho_i, \theta_i) = e^{-\alpha_i (\rho_i-\theta_i)} e^{-\rho_i R_{12}^{(0)}} G_n(R_i, \theta_i),
\]

\[
G_n(R_i, \theta_i) = g_{n1}(R_i) + g_{n2}(R_i)
\]

\[
- \sqrt{(g_{n1}(R_i) - g_{n2}(R_i))^2 + (2v \sin \theta_i)^2}
\]

\[
g_{nk}(R_i) = a_{nk} e^{-\theta_{nk} R_i}.
\]

The long-range interaction potential is defined as a sum over the three arrangements,

\[
V_{LR}(R_1, R_2, R_3) = \sum_{i=1}^{3} f_i(R_1, R_2, R_3) U_i(\rho_i(R_1, R_2, R_3), \varphi_i(R_1, R_2, R_3)),
\]

where \(f_i\) denotes a switching function which selects the \(i\)th arrangement and \(U_i\) the sum of the leading terms of electrostatic, induction, and dispersion interaction energies\(^{14}\) in the \(i\)-th arrangement,

\[
f_i(R_1, R_2, R_3) = \frac{1}{2} (1 - \tanh(\gamma_{i}^\prime (3\delta_i - \delta_j - \delta_k))),
\]

with \(\delta_i = R_i - R_i^\prime\), where \(R_i^\prime\) is the equilibrium bond length of the diatomic molecule of the \(i\)th arrangement. For the C\(^+\) + H\(_2\) arrangement, we can retain the charge-quadrupole, the charge-induced dipole, and charge-hexa pole, interactions,

\[
U_i(\rho_i, \varphi_i) = \sum_{n=3}^{5} C_{1n}(\varphi_i) \left(\frac{\chi(\rho_i)}{\rho_i}\right)^n,
\]

where \(\chi(\rho_i) = 1 - e^{-\alpha_i \rho_i^2}\) is a short-range damping function and the interaction coefficients \(C_{1n}\) are defined by

\[
C_{13}(\varphi_i) = \frac{Q_{H_2}}{2} (3\cos^2 \varphi_i - 1),
\]

\[
C_{1d}(\varphi_i) = -\frac{\alpha_{H_2}}{2} - \frac{1}{6} (\alpha_{H_2} - \alpha_{H_+}) (3\cos^2 \varphi_i - 1),
\]

\[
C_{1s}(\varphi_i) = \frac{Q_{H_2}}{8} (35\cos^4 \varphi_i - 30\cos^2 \varphi_i + 3).
\]

For the two arrangements H\(^+\) + CH\(^+\) and H + CH\(^+\), the leading terms retained are the charge-induced dipole, the
The global PES was fitted to the \textit{ab initio} data using the weighted linear least square method. Greater weights were assigned to the more relevant \textit{ab initio} points for the intended nuclear dynamics calculations. These are all the points with a potential energy smaller than 1 eV above the asymptotic potential of infinitely separated reactants. Furthermore, the weights associated to the points located in the long-range region of the H + CH\textsuperscript{+} arrangement were defined proportional to the square of the distance between reactants. The global root mean square (RMS) of the fitting error is 33 meV. In the region where the potential energy is less than 1 eV above the H + CH\textsuperscript{+} dissociation limit, the RMS is 25 meV. For \( \rho_{i} \geq 6 \, a_{0} \), \( i = 2 \) or 3, the RMS is 5 meV and for \( \rho_{i} \geq 10 \, a_{0} \), it is 0.2 meV. The numerical values of all coefficients and parameters of the fitted PES are gathered in Tables 1–7 of the supplementary material\textsuperscript{18}.

Table 1 compares the experimental spectroscopic parameters of the reactants and products with the values calculated with the fitted PES. A good agreement is shown, which means that the calculated rovibrational energies of the reactants and products are close to the experimental data. From the calculated dissociation energies \( D_{0} \), we can determine the exothermicity of the reaction, namely, 0.402 eV. This is close to the experimental value of 0.393 eV.

The long-range interaction energy in the H + CH\textsuperscript{+} arrangement has been calculated both with the CCSD(T) and MRCI + Q methods. In contrast with the former, the latter method is not size-consistent. This error is reduced by the Davidson correction, but the importance of the remaining error is unknown. In Fig. 2, we observe an excellent agreement between both \textit{ab initio} approaches, thus demonstrating that the size-consistency error is negligible in the long-range region. Furthermore, the fitted PES is compared to the \textit{ab initio} energy. At this large distance between the reactants, the interaction energy given by the fitted PES is almost equal to the sum of the induction and dispersion interactions given by Eqs. (18)-(21), and the good agreement with the \textit{ab initio} energy confirms that it is a reliable model. The same agreement between the \textit{ab initio} energies and the sum of dispersion and induction energies has been also observed for several values of \( \rho_{2} \) in the range 50 \( a_{0} \) down to 15 \( a_{0} \). No potential energy barrier has been found, except the short-range barriers induced by the conical intersections.

A comparison between the long-range interaction energy calculated with the WS-PES\textsuperscript{8}, the LZH-PES\textsuperscript{10}, and the present work is shown in Fig. 3. The present PES is dominated by the \( R^{-4} \) scaling, while the two other PES are attractive only for \( \rho_{2} \leq 12 \, a_{0} \) and show a zero energy plateau for a larger separation distance of the reactants. Consequently, the WS-PES and LZH-PES cannot yield the correct temperature dependence of the rate coefficients in the low temperature domain. As a matter of fact, for the \(- \frac{1}{2} \alpha_{H} R^{-4}\) isotropic interaction potential, if we want a maximum impact parameter smaller or equal to 12 \( a_{0} \), then the Langevin capture theory\textsuperscript{12} constrains the collision energy to be at least 137 K.

Table II collects the most recent calculated data and all the available experimental data on the characteristic properties of the global minimum of the ground state of CH\textsubscript{2}. Let us note that the data listed in the three first lines of this Table have been

\begin{table}[h]
\centering
\caption{Spectroscopic properties of the diatomic reactant and product.}
\begin{tabular}{lccccc}
\hline
\textbf{Property} & \textbf{CH}\textsuperscript{+} & \textbf{H}_2 \\
\hline
\textit{r}_e (\(a_0\)) & 2.135 & 2.137\textsuperscript{a} & 1.401 & 1.401\textsuperscript{a} \\
\textit{ω}_e (cm\textsuperscript{-1}) & 2851 & 2858\textsuperscript{b} & 4398 & 4401\textsuperscript{a} \\
\textit{ω}_{e,xc} (cm\textsuperscript{-1}) & 58 & 59\textsuperscript{b} & 118 & 121\textsuperscript{a} \\
\textit{D}_0 (eV) & 4.067 & 4.085\textsuperscript{c} & 4.470 & 4.478\textsuperscript{a} \\
\hline
\end{tabular}
\textsuperscript{a}Huber and Herzberg.\textsuperscript{15} \\
\textsuperscript{b}Carrington and Ramsay.\textsuperscript{16} \\
\textsuperscript{c}Hechtfischer et al.\textsuperscript{17}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Comparison of the \textit{ab initio} data and the PES in the H + CH\textsuperscript{+} arrangement, with \( \rho_2 = 20 \, a_{0} \) and \( R_2 = 2.135 \, a_{0} \).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Long-range interaction energy calculated with the Jacobi coordinates of the H + CH\textsuperscript{+} arrangement, with \( \varphi_2 = 130^\circ \) and \( R_2 \) equal to the equilibrium distance of the CH\textsuperscript{+} molecule, for the WS-PES,\textsuperscript{8} the LZH-PES,\textsuperscript{10} and the present PES.}
\end{figure}

\textsuperscript{a}Huber and Herzberg.\textsuperscript{15} \\
\textsuperscript{b}Carrington and Ramsay.\textsuperscript{16} \\
\textsuperscript{c}Hechtfischer et al.\textsuperscript{17}
TABLE II. Calculated and experimental equilibrium geometry, dissociation energy, and vibrational frequencies (harmonic or fundamental) for the C$_{2v}$ global minimum of CH$_2^+$ ($R_3 = R_2$).

<table>
<thead>
<tr>
<th>Method</th>
<th>$R_2$ (Å)</th>
<th>$\theta_1$ (deg)</th>
<th>$D_e$ (eV)</th>
<th>$\omega_1$ (cm$^{-1}$)</th>
<th>$\omega_2$ (cm$^{-1}$)</th>
<th>$\omega_3$ (cm$^{-1}$)</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$\nu_3$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MRCI+Q)/aug-cc-pV5Z$^{19}$</td>
<td>2.073</td>
<td>139.7</td>
<td>4.822</td>
<td>2963</td>
<td>1001</td>
<td>3298</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MRCI+Q)/aug-cc-pVQZ$^{20}$</td>
<td>2.075</td>
<td>137.3</td>
<td>4.861</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MRCI+Q)/aug-cc-pV6Z$^{10}$</td>
<td>2.067</td>
<td>141.0</td>
<td>4.813</td>
<td>2983</td>
<td>957</td>
<td>3283</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MRCI/aug-cc-pVQZ/SZ$^{21}$</td>
<td>2.088</td>
<td>139.8</td>
<td>4.811</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T)/aug-cc-pV5Z$^{22}$</td>
<td>2.066</td>
<td>140.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3260</td>
</tr>
<tr>
<td>CCSD(T)/CBS$^{23}$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2899</td>
<td>997</td>
<td>3132</td>
</tr>
<tr>
<td>Expt.$^{19,24,25}$</td>
<td>2.088</td>
<td>139.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>961</td>
</tr>
</tbody>
</table>

$^{19}$This work.

obtained by a global fit of the PES. Thus, the error includes both the error of the *ab initio* computations and the error of the fitting procedure. The experimental value of the bending fundamental frequency is taken from a preliminary work and needs to be confirmed.$^{19}$ The calculated bond length and bond angle of the present PES are in good agreement with the experimental data.

A contour plot of the fitted PES, based on the Jacobi coordinates of the H + CH$^+$ arrangement, is shown in Fig. 4. The potential barriers for both H–C–H and C–H–H collinear configurations are shown. It can also be observed that on a large angular range, namely, $\varphi_2 \in [30^\circ, 150^\circ]$, the global minimum is directly accessible from the reactants’ region through a continuously decreasing PES.

By comparison with the previously reported PES,$^{20}$ the present PES is improved in several ways. It is based on *ab initio* calculations using a larger basis set and about five times more points were computed, the RMS error of the fit is smaller, the exothermicity is closer to the experimental value, and the description of the long-range interaction is improved, both in the reactants and products arrangements.

III. QUANTUM SCATTERING CALCULATIONS

A. Methods and computational details

The time independent quantum scattering ABC code$^{26}$ was designed primarily for the study of direct reactions, i.e., reactions where the reactants and products are separated by a potential barrier. In the case of indirect reactions, i.e., reactions where the reactants and products are separated by a potential well involving a long-lived intermediate complex, the reliability of ABC might be questioned, owing to the use of the diatomic vibrational functions of the three arrangements to expand the surface functions. This can be seen as using a constant reference potential rather than the true triatomic potential for a given value of the hyperradius.$^{26}$ In the case of a shallow potential well, such as the quadruplet PES of OH$_2^+$, a good agreement between TDWP and ABC total reaction probability has been reported.$^{27}$ For deep potential wells, there is no comparison with an accurate calculation, but seemingly successful applications of ABC were reported.$^{28}$

The accuracy of the S-matrices computed by the ABC code is controlled by several parameters for which an optimal value must be selected. These parameters are the maximum hyperradius, the number of propagation sectors, the maximum rotational quantum number of any channel, and the maximum internal energy in any channel, denoted by $\rho_{\text{max}}$, $N_s$, $j_{\text{max}}$, and $E_{\text{max}}$, respectively. The last two parameters define the coupled channel basis set, where all the channels with a diatomic rovibrational energy less than or equal to $E_{\text{max}}$ and with a rotational quantum number less than or equal to $j_{\text{max}}$ are included. For a total angular momentum $J = 0$, many convergence tests were done. Due to the deep potential well, the cross sections show numerous overlapping and narrow resonances. It was found particularly difficult to achieve the convergence of such cross sections, especially versus the $E_{\text{max}}$ parameter. Our objective being to calculate the fully averaged thermal rate coefficients, therefore it was not necessary to converge all the details of the cross sections, but to obtain a sufficiently stabilized rate coefficients for each initial state of the reactants and furthermore to keep the calculations possible in a reasonable amount of time. While a good convergence of the rate coefficients against the $j_{\text{max}}$, $\rho_{\text{max}}$, and $N_s$ parameters was achieved, it was not possible to obtain a similar result with

FIG. 4. Contour plot of the PES for the arrangement H + CH$^+$ with $R_2 = 1.135$ Å. Contour levels are labeled by the energy in eV. The origin of coordinates corresponds to the center of mass of CH$^+$. Below $\sim$0.5 eV, the blue contour levels are spaced by 0.5 eV. The zero energy contour level is black. The red contour levels have positive energy, starting at 0.01 eV. Every next red contour energy is two times the energy of the previous one.
the \( E_{\text{max}} \) parameter. We selected the value of this parameter as the middle value of a range where the rate coefficients were slowly varying. The final values of these four parameters were \( f_{\text{max}} = 26, \rho_{\text{max}} = 30, N_{e} = 500, \) and \( E_{\text{max}} = 4 \) eV. Additional convergence tests were conducted for the helicity truncation parameter \( k_{\text{max}} \) with \( J > 0 \). Because this parameter can drastically increase the calculation time, we attempted to keep it at the lowest possible value and selected finally \( k_{\text{max}} = 4 \). It was found also that for \( J \geq 10 \), it was possible to reduce \( f_{\text{max}} \) to 10 without significant change of the rate coefficients.

The \( S \)-matrix was computed on a 100-points grid in collision energy ranging from 0.1 up to 200 meV, with an exponentially increasing step. This grid was selected such that the Maxwell-Boltzmann distribution of the collision energies for the temperature in the range 10 K–300 K could be integrated with a negligible error. In a thermal average at 300 K, the maximum value of the initial rotational quantum number \( j \) which corresponds to a non negligible population is 7. For each value of \( J \) between 0 and 7, which was used to define the total energy, the calculations were performed for the total angular momentum quantum number \( J \in \{ 0, 1, 2, 3, 4, 5, 10, 15, 20, 30 \} \). The initial vibrational number was always 0. For each value of \( j \) and \( J \), the \( S \)-matrix was calculated for all the allowed values of the inversion parity and of the identical nuclei permutation parity.\(^{26} \) The summation of the inversion parity-adapted \( S \)-matrices was done according to Skouteris et al.\(^{26} \) The summation over the permutation parity-adapted \( S \)-matrices involves the nuclear spin statistics. Indeed, the two hydrogen nuclei are indistinguishable and have spin \( \frac{1}{2} \). This implies that the total nuclear wavefunction, including the spin wavefunction, must be antisymmetric with respect to the permutation of these nuclei. This must be accounted for in the calculation of the physically observable cross sections and rate coefficients.

To this end, we used the postantisymmetrisation procedure proposed by Zhang and Miller.\(^{29} \) Then for each partial wave, the integrals necessary for computing the state-selected rate coefficients from the cross sections were performed with a simple trapezoidal rule. The sum over all partial waves was done using the uniform \( J \)-shifting (UIS) procedure,\(^{30} \) in the range \( J = 0–100 \). Finally, the thermal rate coefficient was obtained from the sum of the state-selected rate coefficients weighted according to the Boltzmann distribution.

Because the accuracy of the calculations performed with ABC can be questioned, due to the choice of moderate values for the input parameters and to the shortcoming arising from the constant reference potential, it is valuable to compare the rate coefficients calculated by ABC with those obtained from accurate quantum scattering calculations. For this purpose, we have used the fully Coriolis-coupled time-independent (CCTI) method based on body-frame hyperspherical democratic coordinates, originally developed by Launay.\(^{31} \) Details of this hyperspherical method can be found in Honvault and Launay\(^{32} \) and only a brief description is given here. This approach has already proved successful in describing the quantum dynamics of atom-diatom direct reactions,\(^{33} \) as well as complex-forming reactions,\(^{34,35} \) ultracold alkali-dialkali collisions\(^{36} \) and more recently the ortho-para conversion in the \( \text{H}^{+} + \text{H}_2 \) collision\(^{37} \) and the \( \text{O} + \text{O}_2 \) exchange reaction.\(^{38} \)

At each hyperradius \( \rho \), we determined a set of eigenfunctions (called surface states) of a fixed-hyperradius reference hamiltonian, which incorporates the total energy with the kinetic energy arising from deformation and rotation around the axis of least inertia, and the potential energy. At small hyperradius, in each sector, the adiabatic states, which are expanded on a basis of pseudo hyperspherical harmonics, span a large fraction of configuration space and allow for atom exchange. For a total angular momentum \( J = 0, 200 \) hyperspherical states have been considered. They dissociate at large hyperradius into the \( \text{CH}^+ \)\(^{34,31,28,24,20,15,6} \) and \( \text{H}_2(19,16,14,11,7) \) rovibrational sets (this notation indicates the largest rotational level \( j \) for each vibrational manifold \( v = 0 – 6 \) for \( \text{CH}^+ \) and \( v' = 0 – 4 \) for \( \text{H}_2 \)). We then perform a close-coupling expansion of the partial \( \text{CH}^+ \) wavefunction for given parity, permutation symmetry, and total angular momentum quantum numbers onto the surface states.

The hyperradial components satisfy a set of second-order coupled differential equations with couplings arising from the difference between the exact hamiltonian and the reference hamiltonian. The logarithmic derivative matrix is propagated inside each sector using the Johnson-Manolopoulos algorithm.\(^{39} \) Basis transformations are performed at the boundary between sectors and at large hyperradius, the numerically integrated wavefunction is matched onto a set of regular and irregular asymptotic functions expressed in the laboratory frame. The \( K \) and \( S \)-matrices are then extracted and state-to-state reaction probabilities are obtained from standard equations.

As mentioned above, the \( \text{CH}^+ \) system contains two identical nuclei that are indistinguishable. The specific symmetry properties of the nuclear wavefunction have been incorporated in a simple manner, through an appropriate choice of the hyperspherical harmonics that are built from products of simple analytical functions.\(^{31} \) Furthermore, the nuclear spin of the two identical hydrogen atoms has been taken into account through the procedure proposed by Zhang and Miller.\(^{29} \) The number of states \( nch \) (the size of the basis sets), the asymptotic matching distance \( \rho_{\text{max}} \), and the number of sectors \( nsec \) employed in the calculations are, respectively, 200, 30 \( \rho_{\text{0}} \), and 179. We carefully checked convergence with respect to these three parameters. To this end, separate calculations have been done with \( nch = 300, \rho_{\text{max}} = 40 \rho_{\text{0}}, \) and \( nsec = 280 \). In addition, the number of closed channels is also another important parameter. At the highest considered collision energy (0.2 eV), there are 6 closed vibrational manifolds in the \( \text{H} + \text{CH}^+ \) entrance arrangement and 4 in the exit arrangement \( \text{C}^+ + \text{H}_2 \), which is sufficient to ensure convergence. In this regards, we can note that the ABC code uses different basis functions which are the rovibrational functions of the arrangements, yielding a very large number of channels to get converged results. Another difference between the ABC and CCTI scattering calculations is that the CCTI calculations have included all the partial waves \( J \) which contribute to the integral cross sections and all allowed \( \Omega \) components (where \( \Omega \) is the projection of the total angular momentum \( J \) on the axis of least inertia) in the close-coupling expansion states, in order to obtain the most possible accurate integral cross sections. The maximum value \( J = 40 \) was found sufficient.
partial waves of the state-selected rate coefficient for the abstraction reaction with CH$^+ (j = 0)$, calculated with the ABC (solid lines) and CCTI (dashed lines) methods. The value of $J$ is indicated near each couple of corresponding curves. The state-selected rate coefficients summed over all partial waves are also shown.

B. Results and discussion

A comparison of the rate coefficients calculated with the ABC and CCTI methods is presented in Fig. 5. This comparison is done for the partial waves $J \in \{0, 5, 10, 15, 20, 30\}$ of the abstraction reaction with the initial state $j = 0$. The rate coefficients resulting from the sum of all partial waves are also shown. The approximate ABC calculations yield results which are close to the accurate CCTI results. The best agreement is obtained for the dominant partial waves, and consequently, the ABC-UJS rate coefficient is very close to the accurate CCTI rate coefficient. This figure shows also that the dominant partial waves are those for $J \in \{5, 15\}$ in the temperature range from 5 K up to 800 K. Above $J = 20$, the contributions of the partial waves drop rapidly.

The computational procedure combining ABC and UJS calculations being validated by comparison with the accurate results for $j = 0$; the same calculations have been performed also for $j \in \{1, 7\}$. The results are collected in Fig. 6. Let us note that the temperature considered in this figure is only the translational temperature. Although the range of collision energies was designed for the temperature range 10 K–300 K, we report the rate coefficients in Fig. 6 for the larger range 5 K–800 K. The contribution of the higher collision energies is lacking in the rate coefficient above 300 K, but it is only a small contribution, since all cross sections drop rapidly with the collision energy. Therefore, we assume that the calculated rate coefficients above 300 K are a reasonable approximation.

For the whole range of temperature shown in Fig. 6, the rate coefficient for $j = 0$ and $j = 1$ is close and the increase of the initial rotational excitation yields a monotonic decrease of the rate coefficients. This is clearly in contrast with the experimental hypothesis, which assumes that an energy barrier around 11 K hinders the reactivity of the lowest rotational states. Let us recall that the ab initio investigation of the long-range interaction did not disclose such a barrier. Furthermore, the quantum scattering results show that the anisotropy of the long-range interaction, which could induce rotational coupling, does not hinder the reactivity of the $j = 0$ or $j = 1$ rotational states. The weakening of the reactivity due to rotational excitation was also observed in the cross sections reported previously for the same abstraction reaction. This effect was rationalized on the basis of classical kinematic considerations. Increasing the rotation of CH$^+$ corresponds to increasing the rotational speed of the H atom around the C atom because the center of mass is close to the carbon. This is expected to amplify the probability of a close encounter between the two H atoms, and thus the probability of a non reactive process or an exchange reaction, thereby decreasing the probability of the abstraction reaction. This can be understood also in terms of quantum states. The increase of the initial rotational excitation is also an increase of the total energy, and consequently an increase of the number of open states in the three arrangements. Because the density of rovibrational states is larger for CH$^+$ than for H$_2$, the non reactive and exchange processes are favoured over the abstraction reaction.

The thermal rate coefficient for the abstraction reaction is shown in Fig. 7, along with the experimental data. Let us recall that the experimental rate coefficients were measured with all degrees of freedom in thermal equilibrium, except for the point at 12.2 K where the translational and rotational temperatures were slightly different. A good agreement is observed in the temperature range 50 K–800 K and a strong discrepancy in the range 12 K–40 K. The moderate decrease of the calculated thermal rate coefficient above 50 K is a consequence of the Boltzmann distribution. Increasing the temperature...
leads to an increase of the population of the less reactive rotationally excited initial states. Below 40 K, only the $j = 0$ and $j = 1$ states, which have close reactivity, contribute to the thermal rate coefficient and below 10 K, only the $j = 0$ state. Thus, the thermal average is assumed to have no effect below 40 K. Furthermore, according to the Langevin capture model, the rate coefficient is expected to be independent of the temperature. Instead of being constant below 40 K, the calculated rate coefficient is slightly decreasing. This is probably because the contributions of the cross sections at collision energies below 0.1 meV are lacking. Indeed, while the energies below 0.1 meV have a negligible contribution to the Maxwell-Boltzmann distributions around 10 K, the fact that the cross sections are very large makes this contribution to the rate coefficients not completely negligible.

IV. CONCLUSION

An accurate quantum scattering calculation of the low temperature rate coefficients of the H + CH$^+$ abstraction reaction has been performed. For this purpose, a new PES was developed, based on high-level ab initio calculations and a careful analysis of the long-range interaction of the H + CH$^+$ reactants. No energy barrier was found in the long-range region. Therefore, the reactants are subject to a continuously attractive interaction, from the very long-range region until the formation of the strongly bound intermediate complex CH$_2$. Moreover, at low temperature, reorientation effect allows the reactant to avoid the short-range barriers induced by conical intersections in the linear configurations. Owing to the shape of the PES, at low temperature and low $j$, when the reactants are largely separated, the CH$^+$ molecule will tend to be oriented in the direction of the H atom. Then, when the reactants are approaching, CH$^+$ will progressively tend to be about perpendicular to the direction of the H atom. With rotational excitation, the reorientation effect is hindered and consequently, the abstraction rate coefficient decreases. The comparison with the experimental rate coefficients shows a strong discrepancy below 50 K and a good agreement above. Owing to the nature of the long-range interaction between an ion and a neutral species, a rate coefficient independent of the temperature is expected below 40 K. This is what is observed in the calculated rate coefficient, in contrast to the experimental one.

To our knowledge, this work reports the first comparison between ABC and an accurate quantum method for a complex-forming reaction with a deep potential well. While ABC cannot bring different results at low temperature than the present work because the lowest points of the crossing seams are around 0.1 eV. It is rather at high temperature, or high rovibrational excitation that these two conical intersections could have an effect on the dynamics. A third conical intersection is located in the C + H$_2$ arrangement, and a large part of the crossing seam is significantly below the H + CH$^+$ dissociation limit. The effect of this crossing on the PES is visible in the Fig. 4, for $\varphi_2$ around 120° and $\mu_2$ around 2 $\mu_0$. This crossing will certainly have an effect on the dynamics, probably by increasing the lifetime of the intermediate complex and the redistribution of energy on all modes of motion. The Renner-Teller coupling should also produce a similar effect on the dynamics. However, it is difficult to see how the third conical intersection and the Renner-Teller coupling could have a drastic effect on the reactivity in a very small range of the total energy.

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