

Quantum dynamics of the Cl+H₂ reaction at ultracold temperatures[#]

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Abstract. Quantum calculations are reported for the reaction between vibrationally excited H₂ molecules and Cl atoms at energies ranging from the ultracold to thermal regimes. It is found that chemical reaction leading to vibrationally excited HCl molecules dominates over non-reactive vibrational quenching. The product HCl molecule is found to be formed predominantly in the $v = 1$ vibrational level with appreciable rotational excitation. A spin-orbit uncorrected value of $1.86 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is predicted for the rate coefficient in the zero-temperature limit, which is about two orders of magnitude larger than the thermal rate coefficient of the Cl+H₂ reaction at 300 K.

Keywords. Ultracold molecules; ultracold chemistry; reactive scattering; quantum dynamics.

1. Introduction

The dramatic advances in recent years in cooling, trapping and manipulating ensembles of atoms and molecules have opened up the possibility of studying molecular interactions and chemical reactions at temperatures close to absolute zero.^{1,2} In this regime, molecular collisions are dominated by quantum effects and tiny perturbations in the interaction potential can dramatically influence the collisional outcome. At collision energies lower than one Kelvin, perturbations introduced by external electric and magnetic fields become significant and they can be used as tools to control and manipulate reaction outcomes.¹ Furthermore, due to long de Broglie wavelengths associated with ultralow energy collisions, ultracold collisions sample regions of potential energy surface (PES) that are far removed from the strong interaction region. Thus, effects of long-range tail of the interaction potential are much more significant in ultracold collisions than thermal energy collisions. Indeed, ultracold collisional studies can be used as sensitive tests to determine accuracy of intermolecular PESs. In recent years, there has been much interest in understanding the effect of van der Waals forces on reactivity.^{3–5} In particular, quasibound states of the van der Waals complexes may enhance reactivity at low energies. This is particularly important for tunnelling dominated reactions which are characterized by an energy barrier between the reactants and the products.

The rapid progress at the experimental fronts in cooling and trapping of molecules led to several collisional studies of cold and ultracold systems in recent years. This includes both non-reactive and reactive systems.^{6–14} Methods based on buffer gas cooling and Stark deceleration techniques have enabled cooling and trapping of OH^{8–10} and NH^{11–14} radicals at milliKelvin temperatures. Experimental studies of rotational energy transfer in Stark decelerated OH radicals in collisions with argon atoms have recently been reported.¹⁰ Elastic and inelastic collisions in N+NH systems have also been reported based on buffer gas cooling techniques.¹⁴ On the reactive front, the recent experiments on K+KRb and KRb+KRb systems^{6,7} have shown that external electric and magnetic fields and spin states of the molecules can be used to control reaction outcomes.

Unlike thermal energy collisions, an accurate description of cold and ultracold collisions requires a quantum mechanical treatment. A large number of calculations of both nonreactive and reactive collisions have been reported in recent years.^{4,5} Many of the initial studies of cold and ultracold collisions have focused on vibrational and rotational energy transfer in atom–diatom systems.^{4,5,15–22} The non-reactive calculations explored efficiency of vibrational and rotational quenching and quantum threshold behaviour of inelastic collisions in atom–diatom systems at temperatures close to absolute zero. These studies were recently extended to rovibrational energy transfer in molecule–molecule systems.^{23–26} The calculations revealed that cold and ultracold collisions are particularly constrained by internal energy and internal rotational angular momentum

[#]Dedicated to Prof. N Sathyamurthy on his 60th birthday

conservation effects. Quasi-resonant vibration-rotation (QRVR) transfer in atom-diatom systems¹⁶ and quasi-resonant rotation-rotation (QRRR) and quasi-resonant vibration-vibration (QRVV) transfers in molecule-molecule systems^{23–26} have recently been found to occur with high efficiency at low energies. The QRRR and QRVV processes conserve the total internal rotational angular momentum of the molecules and nearly conserve the internal energy making the process highly efficient. The most interesting aspect of these mechanisms is that their rate coefficients are largely insensitive to fine details of the interaction potential even in the limit of zero temperature.

Ultracold calculations of many reactive systems have also been reported in recent years. Studies of the benchmark $F+H_2 \rightarrow HF+H$ reaction on its electronically adiabatic ground state PES showed that it may occur with a rate coefficient of about $1.25 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ in the limit of zero temperature.²⁷ Calculations of $F+HD$ ²⁸ and $F+D_2$ ^{29,30} systems indicated that deuterated systems react less efficiently than their H_2 counterpart, due to the less efficient tunnelling of the D atom compared to the H atom. Calculations of $Cl+HD(v=1, j=0) \rightarrow HCl+H$ system revealed that the reaction is dominated by tunnelling at low energies and that chemical reaction dominates over non-reactive vibrational quenching in the ultracold limit.³

In this paper, we present quantum dynamics of the $Cl+H_2(v=1, j=0) \rightarrow HCl(v', j')+H$ reaction at cold and ultracold temperatures. The reaction is slightly endoergic ($\Delta E=0.0252 \text{ eV}$ estimated from the BW2 PES³¹ for the ClH_2 system employed in this study) with rovibrationally ground state H_2 molecules but becomes exoergic with vibrationally excited H_2 . The energy barrier for the reaction (without zero-point energy correction) involving ground state reagents is about 0.366 eV (includes spin-orbit correction)³¹ and the reaction occurs by tunnelling at low energies. The corresponding zero-point energy corrected barrier height is about 0.239 eV .³² The $Cl+H_2$ system has been the topic of a large number of theoretical and experimental studies^{31–52} in recent years and it has been considered as a benchmark system for exploring electronically non-adiabatic and spin-orbit effects in atom-diatom reactions involving open-shell atoms. Recent experiments^{38,49} and rigorous quantum calculations^{34,36} have indicated that the reactivity of the excited spin-orbit state of the Cl atom is small compared to that of the ground state Cl atoms, except at very low energies where spin-orbit interaction between the ground state $Cl(^2P_{3/2})$ and excited $Cl(^2P_{1/2})$ atoms contribute to reactivity. Quantum Calculations of Mahapatra³⁵ and Ghosal and Mahapatra³⁹ within a three-state

model indicated that spin-orbit interaction essentially quenches electronic coupling in this system. Alexander *et al.*^{34,36} reported explicit multi-surface quantum calculations within a six-state model, that incorporates electronically diabatic, coriolis and spin-orbit couplings. Their calculations yielded nearly identical results as that of a two-state model that includes solely the spin-orbit interaction, indicating that electronically non-adiabatic and coriolis couplings are not significant in $Cl+H_2$ reaction. These findings have been further confirmed by recent photoelectron imaging experiments of ClH_2^- and ClD_2^- anionic species which sample the reactant van der Waals wells of $Cl \cdots H_2$ and $Cl \cdots D_2$ complexes.³⁷

Most studies of $Cl+H_2$ reaction have focused on the ground vibrational level of the H_2 molecule. Ghosal and Mahapatra⁴⁰ had reported reaction probabilities for $Cl+H_2(v=0-3)$ using the time-dependent wave packet method and the PES of Capecchi and Werner.³² González-Sánchez *et al.*³³ recently reported a detailed analysis of both non-reactive and reactive scattering in $Cl+H_2(v=0, 1)$ collisions in the total energy range of $0.5\text{--}1.5 \text{ eV}$. Their calculations indicated that while inelastic (non-reactive) scattering is dominated by large impact parameter collisions, reactive scattering is driven primarily by collisions with small impact parameters. However, no calculations of $Cl+H_2(v)$ collisions have been reported at cold and ultracold temperatures. In particular, we shall explore the branching between reactive scattering and non-reactive vibrational quenching at collision energies below 1 K . We shall also explore the effects of van der Waals forces on reactivity and analyse quasibound states of the $Cl \cdots H_2(v, j)$ complexes that influence reactivity at low temperatures. This paper is organized as follows: In section 2 we provide a brief description of the methodology. Results and discussions are presented in section 3 and a summary and conclusions of our study are given in section 4.

2. Methodology

The quantum scattering calculations are carried out using the ABC reactive scattering code of Skouteris *et al.*⁵³ The ABC code solves the time-independent Schrödinger equation in Delves hyperspherical coordinates in all the three arrangement channels of the $A+BC$ system. Schrödinger equation has been solved using the log derivative method of Manolopoulos by discretizing the hyperradius ρ into M_{ir} equally spaced sectors between ρ_{min} and ρ_{max} . Special considerations are needed in ultralow energy calculations. The coupled

channel equations must be propagated to sufficiently large ρ_{max} so that the interaction potential is negligibly small compared to the collision energy. This required propagation to $\rho_{max} = 200$ a.u. at the lowest energy reported in this work. Furthermore, the number of sectors had to be much larger than that is typically used in thermal energy calculations. For the lowest energy calculations we have used $M_{tr} = 20,000$. For the higher energy calculations reported here we used $\rho_{max} = 25$ a.u. and $M_{tr} = 5,000$. These are stringent parameters compared to typical values of $\rho_{max} = 10 - 15$ a.u. and $M_{tr} = 100 - 500$ employed in thermal energy calculations. A cut-off energy of 1.9 eV and a maximum rotational quantum number $j_{max} = 15$ are adopted for the H₂ and HCl molecules. This led to a total of 102 rovibrational basis functions in the calculations. Cross sections are computed on a fine grid of 1800 collision energies ranging from 10^{-9} eV to 1.10 eV. To keep the computational efforts reasonable results are reported only for the total angular momentum quantum number $J = 0$ and initial vibrational level $v = 1$ and rotational level $j = 0$ of the H₂ molecule. The BW2 PES developed for the Cl+H₂ system by Bian and Werner³¹ is adopted for the calculations. Though a more recent surface by Capecchi and Werner³² that includes spin-orbit and non-adiabatic interaction is available we have used the spin-orbit uncorrected BW2 PES to enable comparisons with earlier calculations of Cl+HD($v = 1, j = 0$) reaction at low energies using the same PES.

3. Results and discussion

In figure 1 we present cross sections for vibrational quenching and chemical reaction as functions of the

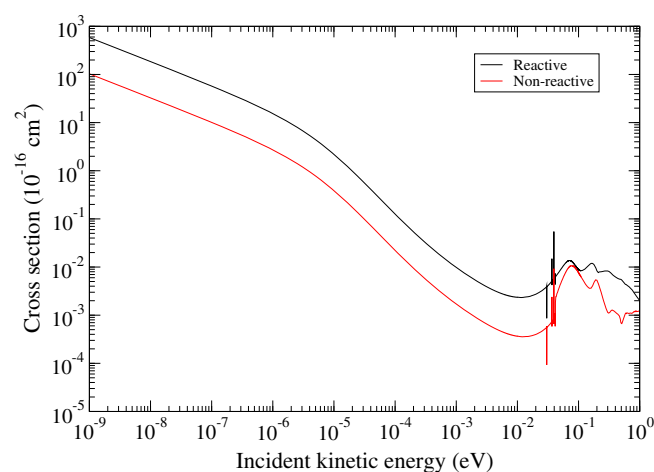


Figure 1. Cross sections for non-reactive vibrational quenching leading to Cl+H₂($v = 0$) and chemical reaction leading to HCl+H channels in Cl+H₂($v = 1, j = 0$) collisions as functions of the incident kinetic energy.

incident kinetic energy. It is seen that chemical reaction dominates over vibrational quenching for energies below 0.1 eV. The reaction occurs primarily through tunnelling. The sharp resonances that occur in the narrow energy range of 0.03–0.05 eV correspond to quasibound states of the Cl···H₂ van der Waals complexes formed during the collision. They occur in both the reactive and non-reactive cross sections indicating that they correspond to features in the entrance channel of the Cl–H₂ system. Reaction probabilities (not shown) from our calculations are in close agreement with those reported by Ghosal and Mahapatra⁴⁰ despite the differences in the PESs employed in the two calculations.

To further analyse the resonances, in figure 2 we show the cross sections as a function of the total energy in the vicinity of the resonances. The energy is measured relative to the bottom of the H₂ potential in the Cl+H₂ channel. The thresholds of the $v = 1, j = 0$ and $v = 1, j = 2$ channels correspond to energies of 0.787414 eV and 0.829187 eV, respectively. It is seen that all four resonance features appear at energies below the $v = 1, j = 2$ threshold and their origin is attributed to the decay of the quasibound states of the Cl···H₂($v = 1, j = 2$) complexes. The quasibound states are identified by computing both adiabatic and diabatic potentials that correlate with the Cl+H₂(v, j) levels. First, the diabatic potential matrix is constructed by evaluating matrix elements of interaction potential between rovibrational wavefunctions of the H₂ molecule. Diagonal elements of the potential matrix at large values of the hyperradius correlate with different rovibrational levels of the H₂ molecule. Diagonalization of the diabatic potential matrix yields adiabatic energy levels that also correlate with the rovibrational levels of

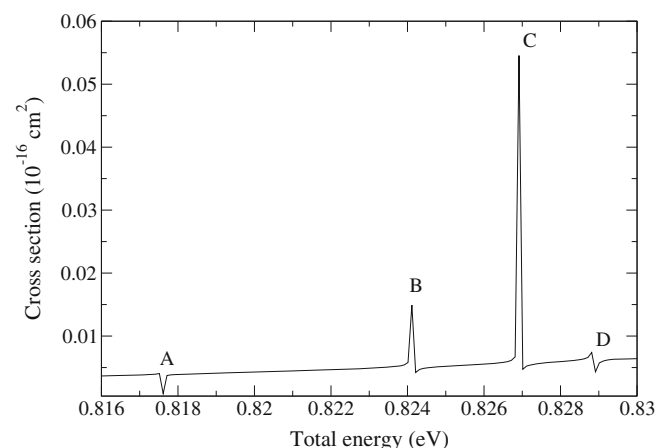


Figure 2. Cross sections for chemical reaction leading to HCl+H channel in Cl+H₂($v = 1, j = 0$) collisions as functions of the total energy.

the H_2 molecule at large ρ values. Quasibound states of both the diabatic and adiabatic potentials are computed using the Fourier grid Hamiltonian method.⁵⁴ The adiabatic and diabatic potentials that correlate with the $v = 1, j = 2$ level of the $\text{Cl} + \text{H}_2$ system are found to support four quasibound states with nearly identical energies as the resonances in figure 2. The resonances A-D are located at 0.8176, 0.8241, 0.8269, and 0.8289 eV. The corresponding adiabatic (diabatic) energies are, 0.8170 (0.8169), 0.8237 (0.8236), 0.8266 (0.8266), and 0.8287 (0.8287) eV, respectively. The agreement between the resonance positions in the cross section and bound state calculations confirms that the resonances are associated with decay of $\text{Cl} \cdots \text{H}_2(v = 1, j = 2)$ complexes.

Figure 3 shows the reaction cross sections resolved into individual vibrational levels v' of the product HCl molecule in the same energy range as in figure 1. It is seen that although both $v' = 0$ and $v' = 1$ levels of the HCl molecule are open in this energy range, the reaction preferentially populates the $v' = 1$ level. The population of $v' = 1$ relative to $v' = 0$ is largely unchanged in the energy range of 10^{-2} – 10^{-9} eV, spanning seven orders of magnitude, though the cross section varies by about five orders of magnitude in this energy range. This is partly due to the smaller energy gap for the formation of $\text{HCl}(v' = 1)$ product compared to the $\text{HCl}(v' = 0)$ product.

Figure 4 depicts the rotational level resolved cross sections for the $v' = 1$ vibrational level of the HCl molecule. It is seen that the cross sections are dominated by $j' = 1 - 3$ of the product molecule with $j' = 2$ being the most populated rotational level. This indicates that although s -wave (orbital angular momentum $l = 0$) scattering dominates in the incident channel, the outgoing channel includes a range of partial waves

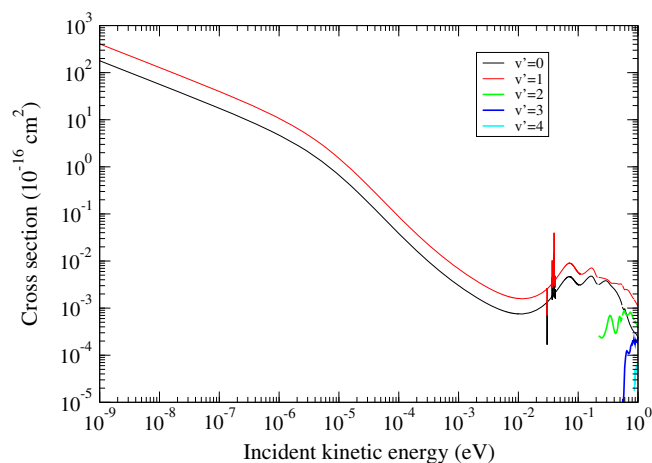


Figure 3. Cross sections for chemical reaction leading to $\text{HCl}(v') + \text{H}$ in $\text{Cl} + \text{H}_2(v = 1, j = 0)$ collisions as functions of the incident kinetic energy.

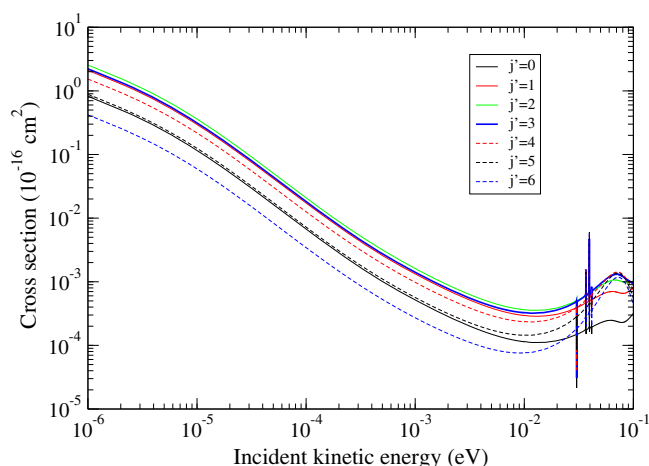


Figure 4. Rotationally resolved cross sections for $\text{Cl} + \text{H}_2(v = 1, j = 0) \rightarrow \text{HCl}(v' = 1, j')$ collisions as functions of the incident kinetic energy.

with dominant contributions from $l = 1 - 3$. The rotational excitation of the product HCl molecule is governed by a combination of internal energy and angular momentum conservation effects. Conservation of internal energy requires that the HCl molecule be formed in the highest energetically accessible rotational level with energy closest to that of the $v = 1, j = 0$ level of the H_2 molecule. However, this entails large changes in orbital angular momentum which is not possible in slow collisions of Cl and H_2 . Conservation of the rotational angular momentum of the H_2 molecule requires that the product HCl be formed in the $j' = 0$ rotational level. However, this involves the largest internal energy gap. Thus, a compromise between conservation of internal energy and rotational angular momentum of the molecule leading to a modest rotational excitation of the HCl molecule occurs in cold and ultracold collisions. The rotational population changes for collision energies above 0.02 eV and increased population of higher rotational levels occurs as the energy is increased.

Figure 5 shows energy-dependent rate coefficients for reactive and nonreactive collisions obtained as the product of the relative velocity and the corresponding cross sections. It is seen that the rate coefficients attain constant values in the limit of zero-temperature in accordance with Wigner threshold law.^{15,55} This is a consequence of the inverse velocity dependence of the corresponding cross sections. The limiting values of the reactive and vibrational quenching rate coefficients are 1.86×10^{-12} and $3.28 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Thus, chemical reactivity appears to be a factor of 6 larger than the non-reactive scattering at ultralow energies. In comparison, measured value of the thermal rate coefficient for the $\text{Cl} + \text{H}_2$ reaction is $1.83 \pm$

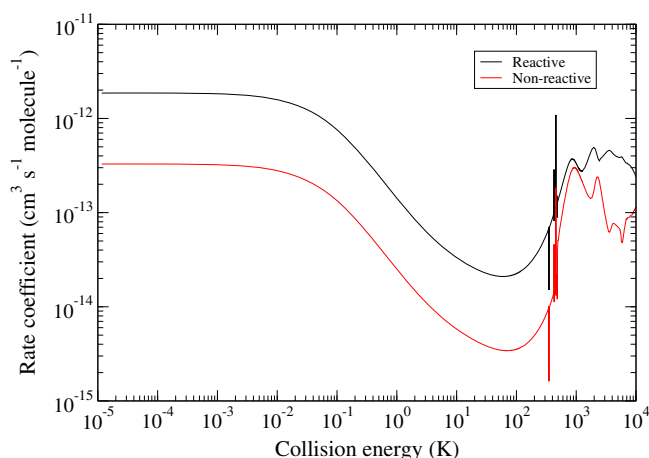


Figure 5. Energy-dependent rate coefficients obtained as cross sections \times relative velocity for reactive and non-reactive scattering in Cl+H₂($v = 1, j = 0$) collisions as functions of the incident kinetic energy in Kelvin.

$0.27 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K.⁵⁶ It would also be instructive to compare our results with a previous study of the Cl+HD($v = 1, j = 0$) reaction on the BW2 PES.³ Zero temperature rate coefficients of 1.7×10^{-13} , 7.1×10^{-16} , and $7.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were reported, respectively, for the HCl+D, DCl+H, and Cl+HD($v = 0$) nonreactive channels. Thus, it appears that the Cl+H₂($v = 1, j = 0$) system is about an order of magnitude more reactive than the Cl+HD($v = 1, j = 0$) reaction. It should, however, be emphasized that the present calculations do not account for the spin-orbit coupling in the Cl atom. Inclusion of spin-orbit coupling will raise the energy barrier for the reaction by about a third of the spin-orbit splitting energy ($\Delta E_{so} = 0.1093 \text{ eV}$) and may decrease the reactivity of the ground state chlorine atoms at ultralow energies.

4. Conclusions

We have carried out quantum scattering calculations of Cl+H₂($v = 1, j = 0$) \rightarrow HCl(v', j')+H reaction at cold and ultracold temperatures. It has been found that in the ultracold limit reactive scattering dominates over non-reactive vibrational quenching despite a substantial energy barrier for the reaction in the entrance channel. The reaction occurs primarily through tunnelling at low energies. The van der Waals interaction potential is found to support a number of quasibound states which preferentially undergo pre-reaction over pre-dissociation. Decay of the quasibound levels appears as Feshbach resonances in the energy dependence of the reaction cross section. Specifically, the resonances are attributed to the decay of Cl \cdots H₂($v = 1, j = 2$)

van der Waals complexes. The zero-temperature limiting value of the Cl+H₂($v = 1, j = 0$) reaction rate coefficient is predicted to be 1.86×10^{-12} on the BW2 potential. This value does not account for the effect of spin-orbit coupling which is not included in the BW2 potential energy surface. Inclusion of spin-orbit coupling will increase the effective energy barrier for the reaction by about a third of the spin-orbit splitting energy and may lower the reactivity of the ground state chlorine atoms at ultralow energies. However, at ultralow energies, contributions from excited spin-orbit state of the chlorine atoms may become important and could result in higher reactivity due to its smaller energy barrier for the reaction. Thus, an accurate prediction of rate coefficients at ultralow energies should include spin-orbit coupling, and to a lesser extent, non-adiabatic effects. Such calculations are in progress.

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