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Crossed Beam Experiment on the Validity of Born-Oppenheimer Approximation in $\text{Cl}(^2\text{P})+\text{D}_2\rightarrow\text{DCI}+\text{D}$ Reaction[†]

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The reaction of chlorine atom $\text{Cl}(^2\text{P})$ ($\text{Cl}(^2\text{P}_{3/2})$ and $\text{Cl}^*(^2\text{P}_{1/2})$) with D_2 was investigated at collision energy from 4.5 kcal/mol to 6.5 kcal/mol with a high-resolution crossed molecular beam apparatus using the technique of D-atom Rydberg tagging detection. The contribution from the spin-orbit excited reaction $\text{Cl}^*(^2\text{P}_{1/2})+\text{D}_2$, which is prohibited by Born-Oppenheimer (BO) approximation, was observed. Collision-energy dependence of differential cross sections (DCSs) near the backward scattering direction was measured. The BO-forbidden reaction Cl^*+D_2 was found to be dominant at lower collision energy. As collision energy increases, reactivity of BO-allowed reaction $\text{Cl}+\text{D}_2$ increases much faster than that of BO-forbidden reaction and becomes dominant at higher collision energy. Our experiment indicates that the additional energy of spin-orbit excitation in Cl^* facilitates BO-forbidden reaction to pass through the barrier at lower collision energy, while BO approximation is still valid at collision energy near and above the reaction barrier. This tendency of reactivity of $\text{Cl}/\text{Cl}^*+\text{D}_2$ is similar to the isotopic reaction of $\text{Cl}/\text{Cl}^*+\text{H}_2$.

Key words: Spin-orbit state, Born-Oppenheimer approximation, Crossed beam experiment

I. INTRODUCTION

Born-Oppenheimer (BO) approximation is one of the basic concepts underlying the description of the quantum states of molecules. It was proposed by Max Born and Robert Oppenheimer in 1927, based on the fact that the mass of a nucleus in a molecule is much larger than that of an electron, as a consequence, the electron moves much faster than the nucleus. In a dynamical sense, the electron can be considered as a particle that instantaneously follows the nuclear motion [1]. Thanks to BO approximation, the motion of nuclei and electrons in a molecule are separable, so the molecule can be treated as a set of nuclei moving over a potential energy surface (PES) provided by electrons, leading to a great acceleration on calculation of molecular wavefunction. However, there are cases where the nuclear and electronic motion are coupled, and the assumption of separable motion no longer holds, and then BO ap-

proximation loses validity. The breakdown of BO approximation is particularly common in the photochemistry of polyatomic molecules, where there are a large number of electronic states that are close in energy and many nuclear degrees of freedom [2, 3]. The validity of BO approximation in chemical reactions has also been widely studied experimentally and theoretically [4–7].

In past decades, the reaction of $\text{Cl}(^2\text{P})+\text{H}_2\rightarrow\text{HCl}+\text{H}$ and its isotopic variants have been a very important test ground for the validity of BO approximation in chemical reactions. Cl is an open-shell atom with ^2P as the electronically ground state, which splits into $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$. Spin-orbit (SO) excited $\text{Cl}^*(^2\text{P}_{1/2})$ lies at 881 cm^{-1} (or 2.52 kcal/mol) above the SO ground $\text{Cl}(^2\text{P}_{3/2})$ state [8]. As shown in FIG. 1, in the adiabatic picture, Cl^* does not correlate adiabatically with the ground electronic state of reaction products. If the reaction proceeds adiabatically on a single PES, as predicted by BO approximation, Cl^* does not react. However, this reaction has a considerably high barrier (about 5 kcal/mol), so the additional energy of 2.52 kcal/mol of SO excitation might play a non-ignorable role in helping the reaction to overcome the reaction barrier, especially when the available energy of BO-allowed reaction is significantly lower than the barrier. Thus, the valid-

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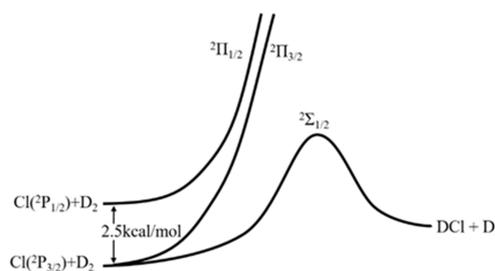


FIG. 1 Schematic plot of the energetics of the $\text{Cl}(^2\text{P})+\text{D}_2$ reaction. At collision energies reported in this work, if the reaction proceeds adiabatically on a single PES, as predicted by BO approximation, the $^2\Sigma_{1/2}$ pathway of $\text{Cl}(^2\text{P}_{3/2})+\text{D}_2$ is the only accessible pathway, and $\text{Cl}(^2\text{P}_{1/2})$ would not react.

ity of BO approximation in $\text{Cl}(^2\text{P})+\text{H}_2$ and its isotopic variants has been a subject of both experimental and theoretical interest.

In 1996, an investigation combined crossed beam experiment and theoretical calculation on $\text{Cl}+\text{H}_2/\text{D}_2$ carried out by Casavecchia and coworkers found that product angular and velocity distributions could be fitted without considering the contribution from Cl^* at several collision energies starting from 4.75 kcal/mol, implying SO excited state can be neglected [9]. Later Skouteri and Werner compared the experimental results with theory and found that the sideways scattered intensity was consistently underestimated in both $\text{Cl}+\text{H}_2/\text{D}_2$ reactions, especially at low collision energy, which was supposed to be originated from the participation of SO excited Cl^* in the reactions [10]. Later, in a crossed beam experiment of $\text{Cl}(^2\text{P})$ with H_2/D_2 by exploiting two different Cl-beam sources, Liu and coworkers found that Cl^* exhibits higher reactivity than Cl at high collision energies [11–13]. These results evoked great attention from both experimental and theoretical sides, since it is quite unexpected, indicating the breakdown of BO approximation in this benchmark reaction, especially when available energy of BO-allowed reaction is enough to overcome the reaction barrier. But later, Neumark and co-workers' photodetachment experiments on ClH_2^- and ClD_2^- anion found minor contribution from Cl^* , which was supported by theory [14, 15]. Wang and coworkers carried out a high-resolution crossed beam experiment with H-atom Rydberg tagging detection and concluded that only at low collision energy BO-forbidden reaction Cl^*+H_2 exhibits higher reactivity than BO-allowed reaction $\text{Cl}+\text{H}_2$ [16].

The $\text{Cl}(^2\text{P})+\text{H}_2\rightarrow\text{HCl}+\text{H}$ reaction and its isotopic variants have long been central reactions in the understanding of kinetic isotope effects, which provide an efficient probe of the same PES in a different dynamical view [17, 18]. The inclusion of spin-orbit coupling and the validity of BO approximation in $\text{Cl}+\text{H}_2$ reaction have been tested in previous crossed experiment and photodetachment experiment [14, 16]. As a direct

comparison with $\text{Cl}/\text{Cl}^*+\text{H}_2$ reaction, in this work, we investigated the validity of BO approximation in the isotopic reaction of $\text{Cl}(^2\text{P})+\text{D}_2\rightarrow\text{DCl}+\text{D}$, by measuring the collision-energy dependence of reactivity in a high-resolution crossed beam experiment.

II. EXPERIMENTS

The $\text{Cl}(^2\text{P})+\text{D}_2$ reaction was carried out in a crossed molecular beam apparatus with D-atom Rydberg tagging detection as described before [16, 19]. The D_2 molecular beam was generated by expanding pure normal- D_2 through a fixed pulsed valve (Parker-Hannifin Corporation, General valve, serial 9) at a stagnation pressure of about 30 psi. The pulsed valve was modified and cooled down to the liquid nitrogen temperature (~ 78 K). After supersonic expansion, most D_2 molecules were populated in the lowest two rovibrational states ($v=0, j=0, 1$), with a ratio of $\text{D}_2(v=0, j=0)$: $\text{D}_2(v=0, j=1)$ equal to 2:1, which is determined by the ratio of ortho- D_2 and para- D_2 in normal- D_2 at room temperature. The velocity of D_2 beam was measured to be 1.03 km/s with a speed ratio ($v/\Delta v$) of about 25. Doubly skimmed $\text{Cl}(^2\text{P})$ beam was produced by a double-stage discharge of Cl_2 (5% Cl_2 seeded in 95% He) at room temperature [20]. The density ratio of $\text{Cl}:\text{Cl}^*$ was determined to be 3.3:1 in a previous work [16]. The $\text{Cl}(^2\text{P})$ atom beam was rotatable around the crossing point in order to change the crossing angle between two reactant beams from 80° to 120° with an interval of 5° , so the collision energy could be tuned from 4.5 kcal/mol to 6.5 kcal/mol, correspondingly.

The D atoms produced from the reaction of $\text{Cl}(^2\text{P})+\text{D}_2\rightarrow\text{DCl}+\text{D}$ were excited to a high Rydberg state (with main quantum number $n\approx 50$) by two lasers at the wavelengths of 121.6 and 365 nm, respectively [21]. The 121.6 nm radiation was generated by four-wave mixing of 212 and 845 nm in a Kr/Ar gas cell. The 365 nm laser was produced from frequency doubling of a 730 nm dye laser. 121.6 and 365 nm laser pulses were overlapped in both time and space at the crossing region. After excitation to the high Rydberg state, the electrically neutral Rydberg D atoms flew 318 mm and then were field-ionized before reaching a microchannel plate (MCP) detector [20]. Since most of backgrounds were generated by discharge of Cl_2 , the Cl_2 pulsed valve, the detecting lasers and the data acquisition system ran at 26 Hz, while D_2 pulsed valve was operated at 13 Hz, in order to accumulate the signal and background on a shot-to-shot basis. At different collision energies, time-of-flight (TOF) spectra of D-atom products were obtained at detecting angles corresponding to 170° in the center of mass (CM) frame for 4000 laser shots each time. Each TOF spectrum was consecutively accumulated back and forth for 30 rounds to reduce experimental errors.

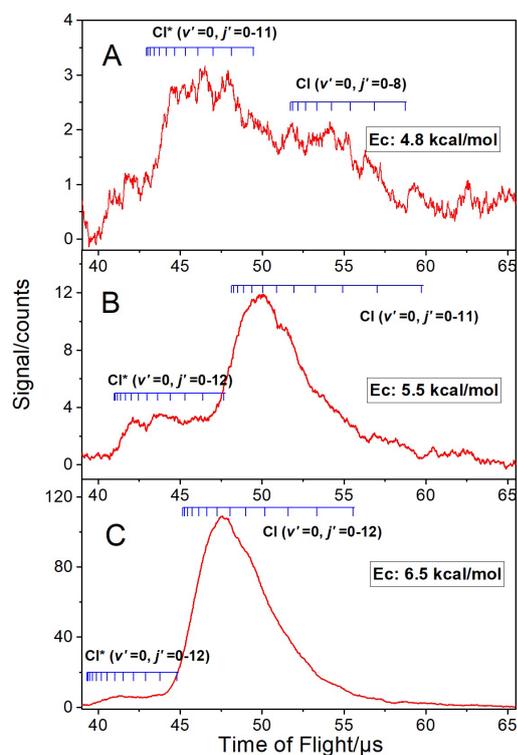


FIG. 2 Time-of-flight spectra of D atom product from $\text{Cl}(^2\text{P})+\text{D}_2\rightarrow\text{DCl}+\text{D}$ reaction at three different collision energies: (A) 4.8 kcal/mol, (B) 5.5 kcal/mol, and (C) 6.5 kcal/mol, with background removed. For better signal-to-noise ratio, (A) and (B) were accumulated twice the time than (C) and then divided by a factor of two. Each Time-of-flight spectrum corresponds to $\text{DCl}(v'=0)$ produced from Cl^*+D_2 near the backward direction (roughly 170°) in the center-of-mass frame respectively. Contributions from different ro-vibrational state are indicated by blue lines.

III. RESULTS AND DISCUSSION

The TOF spectra of D atom were obtained by subtracting the D_2 -valve-off TOF spectra from the corresponding D_2 -valve-on TOF spectra. FIG. 2 exhibits three typical TOF spectra corresponding to 170° in CM frame at collision energies of 4.8, 5.5, and 6.5 kcal/mol, respectively. Based on the conservation of energy and momentum, the main structure in the TOF spectra could be assigned to DCl products in $v'=0$ vibrational state, as indicated in the figure. As the signal is quite small at low collision energy, TOF spectra shown in FIG. 2 (A) and (B) were accumulated twice the time as FIG. 2(C), and then divided by a factor of two. The “bumps” in FIG. 2(A) originated from worse signal-to-noise ratio due to the extremely small signal at the lowest collision energy, instead of rotational states of DCl products. We found the signal at low collision energy is mainly contributed from Cl^*+D_2 reaction, indicating additional electronic energy available in Cl^*+D_2 reaction can facilitate the pass through the reaction barrier,

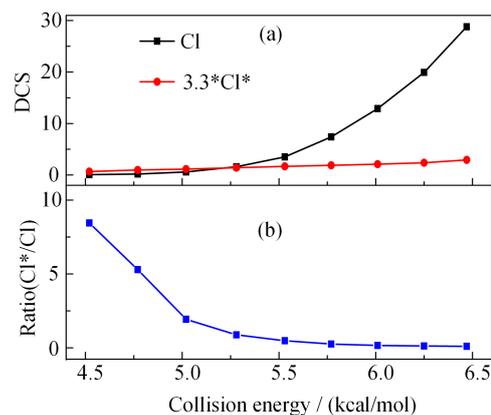


FIG. 3 (a) Collision-energy dependence of the relative reactive differential cross sections, summed over product vibrational and rotational levels, near the backward direction (170°) for $\text{Cl}/\text{Cl}^*+\text{D}_2$ at collision energy from 4.5 kcal/mol to 6.5 kcal/mol, with black and red lines representing relative reactivity of Cl and Cl^* , respectively. Due to the concentration of Cl and Cl^* in the discharge beam source is 3.3:1, a factor of 3.3 is used for correction of the reactivity of Cl^*+D_2 reaction. (b) The ratio of reactivity of Cl^*/Cl is showed in (a).

implying the breakdown of BO approximation. Both Cl^* and Cl become more and more reactive as the collision energy increases, while the reactivity of Cl increases much faster. At higher collision energy, products were predominantly contributed from SO ground state Cl atom, and only a small portion of products can be attributed to SO excited reaction, indicating the validity of BO approximation.

In this work, normal- D_2 gas was used to generate D_2 molecular beam at liquid nitrogen temperature. About one-third of D_2 molecules were populated in $\text{D}_2(v=0, j=1)$, which lies at 60 cm^{-1} above $\text{D}_2(v=0, j=0)$. According to previous works, the rotational excitation to $j=1$ of D_2 has little effects on reactivity [13], so it is ignored in current experiment. D atoms in the backward scattering direction in CM frame were close to the discharging $\text{Cl}(^2\text{P})$ beam, from which intense backgrounds were produced. Thus, it is difficult to accumulate TOF spectra in the exact backward scattering direction in CM frame. Because $\text{Cl}(^2\text{P})+\text{D}_2$ is a typical direct abstraction reaction with strongly backscattered products [10, 17], we used TOF spectra obtained corresponding to 170° in CM frame to be a reasonable approximation to the backward scattering signal for evaluating the reactivity of both Cl/ Cl^* . By adding signal of DCl in all rovibrational states produced from Cl or Cl^* in each TOF spectrum, the relative reactivity of Cl and Cl^* with D_2 was determined approximately at collision energies ranging from 4.5 kcal/mol to 6.5 kcal/mol. The curve for Cl^*+D_2 was scaled after inclusion of the Cl: Cl^* ratio of 3.3:1. As shown in FIG. 3, Cl^* is more reactive than Cl at lower collision energy, implying the breakdown of BO approximation at lower collision energy.

Both Cl and Cl* become more and more reactive as the collision energy increases, while the reactivity of Cl increases much more rapidly than Cl*. At collision energy near 5.2 kcal/mol, Cl* and Cl exhibit the same reactivity. At collision energy greater than 5.2 kcal/mol, the contribution from BO-allowed reaction of Cl quickly becomes dominant, demonstrating the validity of BO approximation at higher collision energy.

This work shows that the tendency of reactivity of Cl/Cl*+D₂→DCl+D is similar to the isotopic reaction of Cl/Cl*+H₂→HCl+H. At lower collision energy, where the BO-allowed reaction of Cl+D₂ does not have adequate energy to overcome the reaction barrier, the BO-forbidden reaction of Cl*+D₂ is more likely to pass through the reaction barrier due to the additional SO excitation energy. As collision energy increases, the reactivity of BO-allowed reaction increases much faster than BO-forbidden reaction and becomes predominant at collision energy greater than 5.2 kcal/mol, indicating the validity of BO approximation at higher collision energy. Compared with non-BO coupling in Cl/Cl*+H₂ reaction, isotopic substitution does not introduce obvious differences in Cl/Cl*+D₂ reaction.

IV. CONCLUSION

We have carried out a high resolution crossed molecular beam study on the Cl(²P)+D₂→DCl+D reaction with D atom Rydberg tagging detection. Relative DCSs near the backward scattering direction were measured at collision energies from 4.5 kcal/mol to 6.5 kcal/mol. The BO-forbidden reaction Cl*+D₂ is more reactive at lower collision energy, implying the breakdown of BO approximation. While BO-allowed reaction Cl+D₂ becomes predominant at collision energy greater than 5.2 kcal/mol, suggesting the validity of BO approximation when the reaction have enough energy to overcome the reaction barrier. This work demonstrated BO approximation is broken at lower collision energy, but still valid at collision energy close to and higher than reaction barrier, similar to the isotopic reaction of Cl/Cl*+H₂.

V. ACKNOWLEDGMENTS

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