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Crossed Molecular Beam Study of H+CH₄ and H+CD₄ Reactions: Vibrationally Excited CH₃/CD₃ Product Channels†

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We study the H+CH₄/CD₄→H₂/HD+CH₃/CD₃ reactions using the time sliced velocity map ion imaging technique. Ion images of the CH₃/CD₃ products were measured by the (2+1) resonance enhanced multi-photon ionization (REMPI) detection method. Besides the CH₃/CD₃ products in the ground state, ion images of the vibrationally excited CH₃/CD₃ products were also observed at two collision energies of 0.72 and 1.06 eV. It is shown that the angular distribution of the products CH₃/CD₃ in vibrationally excited states gradually vary from backward scattering to sideways scattering as the collision energy increases. Compared to the CH₃/CD₃ products in the ground state, the CH₃/CD₃ products in vibrationally excited states tend to be more sideways scattered, indicating that larger impact parameters play a more important role in the vibrationally excited product channels.

Key words: Velocity map ion imaging, Crossed molecular beam, Angular distribution, Vibrationally excited state

I. INTRODUCTION

The H+CH₄ reaction and its isotopic variants play an important role in combustion chemistry, interstellar chemistry and organic chemistry. As the prototype of polyatomic reactions, these reactions are of fundamental importance in the study of reaction dynamics. Over the past decades, the H+CH₄/CD₄ reactions have been studied in both bulk and jet cooled environment [1–14]. The kinetics and dynamics of these reactions were investigated using various experimental [4–14] and theoretical [11–23] methods. In particular, in 2010, in a combined experimental and theoretical study presented by Zhang et al. [11], it was found that when the collision energy is just above the reaction barrier (about 0.5 eV), the integral cross section increases as the collision energy raises: when the collision energy becomes far beyond the barrier (about 1.2 eV), the integral cross section starts to decrease as the collision energy raises. Unprecedented agreement was achieved between the experiments and theory. The theory suggests that the observed behavior is due to the effect through the tug-of-war between the H atom and the non-reacting CD₃. The angular distribution of CD₃ changes with collision energies as well. At low collision energy, this angular distribution tends to be backward scattering; when the collision energy increases, the angular distribution becomes less backward scattering and more sideways scattering. Recently, Pan et al. further studied the H+CH₄ reaction [8]. The isotope effect of the reaction was observed. While previous experiments mainly focused on the CH₃/CD₃ products in the ground state, the vibrationally excited CH₃/CD₃ product channels have not been clearly investigated. Since the integral cross sections of the H+CH₃/CD₃ reactions are very small (about 0.1 A² at the collision energy of 1 eV), it is therefore very difficult to study these reactions in scattering experiments. As a result, detecting the products in excited states is in general very challenging.

With improved molecular beam setup, we reinvestigated the H+CH₄/CD₄→H₂/HD+CH₃/CD₃ reactions. Besides the CH₃/CD₃ products in the ground state, the vibrationally excited CD₃/CH₃ channels (v=1, 2) were clearly observed and identified. The results could shed light on the reaction dynamics on more product chann-
els of the H+CH₄/CD₄ reactions.

II. EXPERIMENTS

The H+CH₄/CD₄→H₂/HD+CH₃/CD₃ reactions were investigated by using the time-sliced velocity map ion imaging technique. The main setup of the apparatus has been described previously [24–26]. In brief, the H atom beam was generated by the photodissociation of HI molecules. A general valve (Parker Series 9) was set in a fixed source chamber to produce the HI molecular beam by supersonic expansion at a stagnation pressure of 1 atm. The operating pressure in the fixed source chamber was 6×10⁻⁶ mbar while the background pressure was 8×10⁻⁸ mbar. The pulsed valve that generating the HI beam was mounted vertically upward, 10 mm downstream from the nozzle of the pulsed valve, the HI molecular beam crossed with the photolysis laser beam. The HI molecules were dissociated, which produce H and I atoms. There are two spin-orbit product channels in the HI photodissociation. At each photolysis wavelength, H atoms with two different speeds are produced. Since the angular distributions of the two channels are different, we can choose the H atoms at one out of the two channels by changing the polarization of the photolysis laser beam. In the current experiments, the dissociated H atom beam in the slower speed channel was selected. After passing through a skimmer with 2 mm orifice, the horizontally travelled H atom beam then came into the reaction zone in the detection chamber and collided with the CH₄ or CD₄ beam. Laser beams at 248 nm emitted from a excimer laser (COHERENT, Compex pro 50F) and 266 nm from the forth harmonic generation of the output of a Nd:YAG laser(continuum PL 9020 DLS) were used in the photodissociation process. The CH₄/CD₄ molecular beams were generated in a rotatable source chamber by the supersonic expansion too. Compared to previous setup, the intensity of the CH₄/CD₄ molecular beams were improved by using an Even-Lavie pulsed valve at the stagnation pressure of 20 atm. A skimmer with 2 mm orifice was used to collimate the CH₄/CD₄ molecular beam. The operating pressure of the rotatable chamber and the detection chamber were 1.8×10⁻⁶ and 1.4×10⁻⁷ mbar, respectively, while the background pressures were 9×10⁻⁹ and 1.5×10⁻⁸ mbar. As a result, the collision energies were set at 1.06 and 0.72 eV, respectively. The entire path of the photolysis laser in the detection chamber was shielded by a stainless steel tube to prevent the stray light.

The CH₃/CD₃ products were detected by the (2+1) resonance enhanced multi-photon ionization (REMPI) scheme. Six different wavelengths of the detection laser beam were set to ionize the ground state and two excited states of these two channels: namely, 333.56 nm for CH₃ in the (0⁰) transition, 329.49 nm for CH₃ in the (2¹) transition, 340.89 nm for CH₃ in the (2⁰) transition, 333.91 nm for CD₃ in the (0⁰) transition, 330.52 nm for CD₃ in the (2¹) transition, 339.36 nm for CD₃ in the (2⁰) transition. The symbols in the bracket represent the vibrational state of the species. The front number represents the vibrational mode of the products, for instance, 0 corresponds to the ground state and 2 corresponds to the umbrella vibrational mode. The numbers in the bottom right are the vibrational state quantum number of the products while the numbers in the top right are the vibrational state quantum number of the intermediates at excited electronic state in the process of REMPI.

The products were ionized in the crossing region which is in the center of the ion optics. After passing through the 650 mm long time-of-flight tube, the ionized products were detected by a 70 mm-diameter micro-channel plate (MCP) coupled with a phosphor screen (P43). The resulting two-dimensional images on the phosphor screen were recorded by a CCD camera (Imager pro plus 2M, LaVision). The time-sliced ion image of the product’s Newton sphere was acquired by applying a gate pulse to the MCP. A real time event counting method was performed during the data acquisition process. The velocity calibration was performed by measuring the O⁺ images from multiphoton dissociation/ionization process of the O₂ molecules.

III. RESULTS AND DISCUSSION

For the H+CH₄/CD₄→H₂/HD+CH₃/CD₃ reactions, ion images of the CH₃ and CD₃ products in the ground state (υ=0) and vibrationally excited states (υ≥1) at the collision energies of 1.06 and 0.72 eV are displayed in FIG. 1. For the products in the ground state and vibrationally excited states, a double concentric rings structure can be observed in the image of the CD₃ products at the collision energy of 1.06 eV, which represents two different kinetic energy release distributions of the CD₃ products. Due to the laws of conservation of energy and momentum in a scattering process, products with higher internal energy have smaller kinetic energy. Therefore, the two rings in the image of CD₃ products at 1.06 eV correspond to the HD co-products in the ground state and vibrationally excited states. On the other hand, only one product ring was observed in the image of the CD₃ products at the collision energy of 0.72 eV and of CH₃ products at both collision energies (including CH₃/CD₃ products both in the ground state and vibrationally excited states). This result shows that the vibrational state distributions of the HD and H₂ co-products are relatively cooler. The isotope effect is in good agreement with previous study by Pan et al. In addition, the width of the ring is smaller at the lower collision energy than that at the higher collision energy, which may indicate a hotter rotational distribution of the HD and H₂ co-products at higher collision energy.
rameter of the reaction may lead to more sideways scattering.

As shown in FIG. 2, the products in vibrationally excited states are more sideways scattered than those in the ground state. However, no significant differences were observed in the angular distribution of the vibrational state v2=1 and v2=2. Compared with the distributions of CH3/CD3 product channels in the ground state, the angular distributions of CH3/CD3 product channels in excited state descend more gently when the angle decreases. But the angular distribution in sideways scattering show little difference between the products in the ground state and vibrationally excited states. Apparently, the products in vibrationally excited states are more sideways scattered. As the angular distribution is related to the impact parameter, to certain extent, the vibrational excited state channel is more likely to correlate with larger impact parameters.

Moreover, the isotope effect can be found both in the ground state and vibrationally excited states. At the same collision energies and product states, the angular distribution of the H+CH4→CH3+H2 reaction tends to be more sideways scattering than that of the H+CD4→CD3+H2 reaction. Previous work has found this isotope effect in ground state [8, 10]. We discover that this isotope effect is also shown in vibrationally excited states.

It is worth to mention that only the results at scattering angle larger than 40° are shown in FIG. 2 (a, c) and larger than 60° in (b, d). The improvement of the intensity of the CH4/CD4 molecular beam has enabled the observation of the vibrationally excited product channel in this reaction which has very small reactive cross sections. On the other hand, the more intense CH4/CD4 molecular beam also increases the background in the forward direction. An alternative detection method using the VUV light source might be beneficial.

The total kinetic energy release distributions were derived by integrating the intensity of the CH3/CD3 signal at the same translational energy in the center of mass frame and then converting the translational energy of CH3/CD3 to the total kinetic energy according to the conservation of momentum between the CH3/CD3 and H2/HD. As shown in FIG. 3, the peak shifts towards the lower kinetic energy when the products populate in the higher vibrationally excited states. When comparing the same products between different collision energies, the peaks tend to be wider as the collision energy becomes higher, which could be caused by the rotational state population of the H2/HD. When the collision energy is higher, the rotational excitation of the H2/HD becomes hotter, which makes the peaks wider than those at low collision energy. At the low collision energy, the H2/HD only populated in ground state, corresponding to the one peak in the FIG. 3. As the collision energy increases, the channel in relation to the vibrationally excited HD product opens, lead-

FIG. 1 Ion images of the products CH3/CD3 from the reaction H+CH4/CD4→H2/HD+ CH3/CD3. (a) The images of the products CH3 in ground state and vibrationally excited state (v2=1, 2) respectively at the collision energy of 1.06 eV. (b) The images of the products CH3 in ground state and vibrationally excited state (v2=1, 2) respectively at the collision energy of 0.72 eV. (c) The images of the products CD3 in ground state and vibrationally excited state (v2=1, 2) respectively at the collision energy of 1.06 eV. (d) The images of products CD3 in ground state and vibrationally excited state (v2=1, 2) respectively at the collision energy of 0.72 eV.

The angular distributions of the CH3/CD3 product are derived by integrating the images of product ions along the radial direction after the density-to-flux corrections. The scattering angle is defined relative to the direction of the relative velocity between the two reactants in the center of mass frame. The CH3/CD3 products are mainly backward scattered with respect to the incoming H atom beam. The angular distributions of the CH2/CD2 products in the ground state change gradually from backward scattering to sideways scattering as the collision energy increases. This behavior is in good agreement with the previous studies [8, 11]. Furthermore, the sideways scattering of the CH3/CD3 in excited vibrational state (v2=1, 2) channels has a higher proportion at larger collision energy which suggests that the angular distribution is also closely related to the larger impact parameters in the vibrational excited product channels. The feature could be understood that when the collision energy is just above the potential energy barrier, only the collision with relative small collision parameters contribute to the reaction. As the collision energy increases, the larger impact pa-
FIG. 2 Angular distributions of the products CH$_3$/CD$_3$ from the H+CH$_4$→H$_2$+CH$_3$ and the H+CD$_4$→HD+CD$_3$ reactions at two collision energies. (a) H+CH$_4$, 1.06 eV, (b) H+CH$_4$, 0.72 eV, (c) H+CD$_4$, 1.06 eV and (d) H+CD$_4$, 0.72 eV. For clarity in the comparison, the maximum intensities of the data at different states have been set to 1.

FIG. 3 Total kinetic energy release distributions of CH$_3$/CD$_3$ products from the reaction H+CH$_4$/CD$_4$→H$_2$/HD+CH$_3$/CD$_3$ at two collision energies. (a) Products CH$_3$ at the collision energy of 1.06 eV, (b) products CH$_3$ at the collision energy of 0.72 eV, (c) products CD$_3$ at the collision energy of 1.06 eV, (d) products CD$_3$ at the collision energy of 0.72 eV.

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ing to two peaks shown in the figure, corresponding to the two rings in the images shown in FIG. 1. It is also found that in this experiment, the H$_2$ products in vibrationally excited state are negligible in the reaction H+CH$_4$; whereas for the vibrationally excited CD$_3$ channels, the correlated HD products in vibrationally excited states were clearly captured at the collision energy of 1.06 eV. The behavior is similar to the results found for products in the ground state.

**IV. CONCLUSION**

The H+CH$_4$/CD$_4$→H$_2$/HD+CH$_3$/CD$_3$ reactions were investigated with the time sliced velocity map ion imaging method. The isotope effect between the CH$_3$ and CD$_3$ product channels was observed. In particular, the vibrationally excited CH$_3$/CD$_3$ products were measured using the (2+1) REMPI scheme. The analysis of the images shows that, as the collision energy increases, the angular distribution of the products CH$_4$/CD$_3$ at vibrationally excited states gradually vary from backward scattering to sideways scattering as the collision energy increases. Compared to the CH$_3$/CD$_3$ products in the ground state, the angular distributions of the vibrationally excited CH$_3$/CD$_3$ products are more sideways scattering than those in the ground state, and it suggests that collisions at larger collision parameters play a more important role in the vibrationally excited product channels.

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