On the Cl*($^2P_{1/2}$) Reactivity and the Effect of Bend Excitation in the Cl + CH_4/CD_4 Reactions[†]

Jingang Zhou,[‡] Jim J. Lin,[‡,§] Bailin Zhang,[‡] and Kopin Liu*,[‡,#]

Institute of Atomic and Molecular Sciences (IAMS), Academia Sinica, P.O. Box 23-166, Taipei, Taiwan 106,
Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 300, and
Department of Chemistry, National Taiwan University, Taipei, Taiwan 106

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The reaction of atomic chlorine with methane was studied in crossed-beam experiments at a collisional energy of $E_c \approx 4.7$ kcal/mol. Using a time-sliced product imaging technique, several outstanding issues about this reaction were addressed in this work. It was found that the reactivity of the spin−orbit excited Cl*($^2P_{1/2}$) atom toward methane is negligibly small, in agreement with the assertion of recent studies. The excitation of methane bending/torsional modes exhibits only modest enhancement in reactivity, in contrast to the previous experiments. The product angular distributions are mainly backscattered for Cl + CD_4, and sideways scattered for Cl + CH_4. The shapes of the distributions from the ground state and the bend-excited methane are remarkably similar.

I. Introduction

The reaction of Cl + CH_4 → HCl + CH_3 has an important role in the ozone production/depletion cycle in the stratosphere.[1] As a result, it has been under extensive investigations, both experimentally[2−5] and theoretically,[6−14] over the past decades. The reaction is endothermic by 1.21 kcal/mol and has a rate of 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K. Kinetics experiments show non-Arrhenius behavior with a temperature-dependent activation energy of 2.4−3.2 kcal/mol and an approximate pre-exponential factor of $A \approx 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is ~30 times smaller than the hard-sphere collision rate at room temperature.[2−5] Such a small value of A is often indicative of tight steric hindrance for surmounting the barrier to reaction.

Non-Arrhenius behavior generally is not unusual and can be attributed to many factors. For the activated Cl + CH_4 reaction, H-atom transfer is involved in chemical rearrangement. At low temperatures, tunneling must occur and its contribution to the deviation from linear Arrhenius plot cannot be neglected. In addition, Ravishakara and Wine[5] ascribed the non-Arrhenius behavior to differential reactivity of the spin−orbit excited Cl*($^2P_{1/2}$) reactants that are accessible under thermal conditions. This hypothesis is counter-intuitive. Hence, since then, numerous kinetics studies have been devoted to solving this intriguing proposition.[15−19] However, because the measured quenching rate constants are typically ~300 times faster than the rate of the ground-state Cl($^2P_{3/2}$) reaction, the collision of Cl*($^2P_{1/2}$) + CH_4 is simply overwhelmed by the physical quenching process, yielding Cl($^2P_{3/2}$) + CH_4. Therefore, these kinetics studies cannot decipher the relative reactivities of Cl*($^2P_{1/2}$) and Cl($^2P_{3/2}$).

By analyzing the speed-dependent spatial anisotropy of the CH_3 product in a PHOTOLOC experiment, Kandel and Zare[20] concluded that the Cl* + CH_4 reaction is not significant in the collision energy range of 3−6.7 kcal/mol. They instead suggested the dominant role of the Cl($^2P_{3/2}$) + CH_4 (v_2 or $v_4 = 1$) reaction in contributing to the non-Arrhenius behavior. A reinvestigation by Kim et al.,[21] using BrCl near 420 nm as the photolysis Cl-atom source (which gives a Cl* yield of ~50%) confirmed the two conclusions mentioned previously. The estimated vibrational enhancement factor in the rate from these studies, which is ~200 (or 80) times faster for one quantum excitation of v_2(torsion) or v_4(bend) mode of CH_4 (or CD_4), compared to the vibrational ground-state reaction,[20,21] is, however, substantially larger than the enhancement factor of 30 ± 15 that has been observed for the asymmetric stretching mode excited ($v_3 = 1$) CH_4 reaction.[22,23] This is in sharp contrast to the earlier, rather indirect experiments in which no enhancement was found for either bending or torsional excited CH_4 reaction.[24,25] In a very recent study of this reaction using the PHOTOLOC approach coupled with velocity-map ion imaging, Bass et al. found that the estimated rate enhancements for bend-/torsion-excited methanes are heavily dependent on how one treats the experimental resolution in fitting the data.[26] With proper accounting for the speed distribution of the photolyzed Cl reactant, a satisfactory simulation of the product image can be obtained without invoking the contribution from the vibrational excited methanes; otherwise, a significant enhancement factor will be concluded.

Theoretical investigations predicted, at most, only modest enhancement factors for the v_2- and v_4-mode excited reactants.[12−14] Very recently, Michelsen and Simpson[27,28] modeled the non-Arrhenius behavior of this reaction from the viewpoints of both the kinetics and dynamics. They concluded that the curvature in the Arrhenius plot at temperatures above room temperature can be explained by the rate enhancement from the symmetric (v_1) or asymmetric stretch (v_3) excited CH_4. Non-Arrhenius behavior at lower temperatures is taken into consideration by both tunneling and a modest rate enhancement from bending or torsional excited CH_4.

The purpose of the present study is to clarify the aforementioned uncertainty or discrepancy on the vibrational enhancement

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* Author to whom correspondence should be addressed. E-mail: kpliu@gate.sinica.edu.tw.

[‡] Academica Sinica.

[§] National Chiao Tung University.

[#] National Taiwan University.

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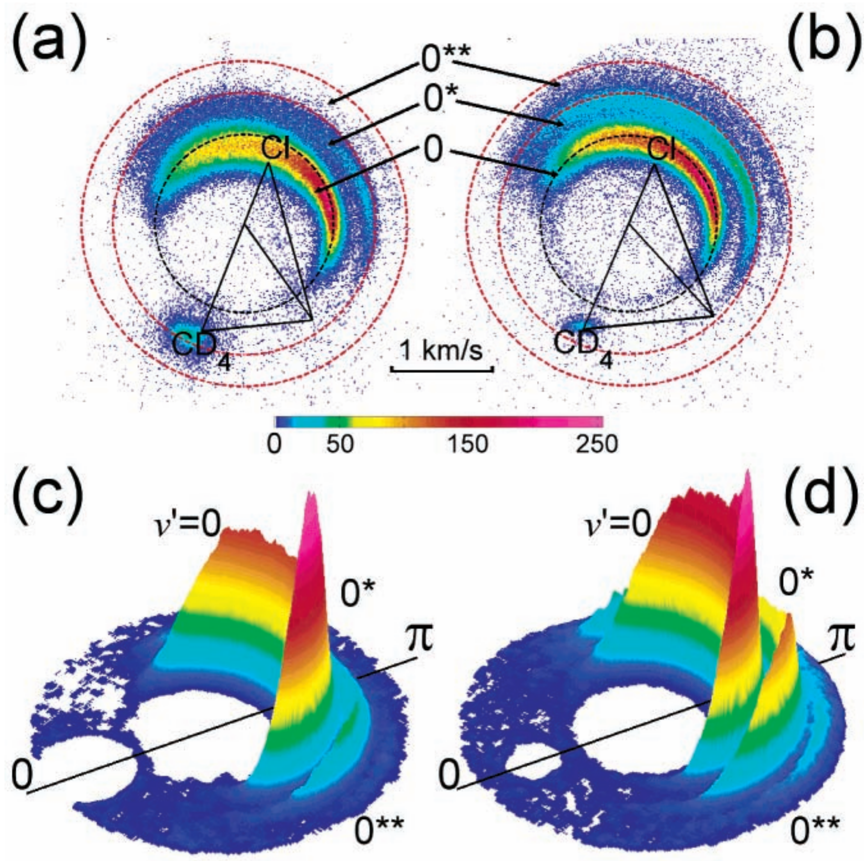

Figure 1. Two raw images of the $CD_3(v = 0)$ products from the Cl + CD_4 reaction at the same collision energy ($E_c = 4.78$ kcal/mol) but under different source temperatures of the CD_4 beam ((a) 340 and (b) 463 K). Overlaid on the images are the Newton diagrams. The dashed circles, labeled as 0, 0^*, and 0^{**}, represent the anticipated $CD_3(v' = 0)$ product speeds from the $v = 0$, $v_4 = 1$, and $v_4 = 2$ states of the CD_4 reactants, respectively. In panels c and d, the corresponding product velocity−flux contour maps are displayed. The obvious background in the forward direction, which was caused by the collision of CD_4 with the metastable He^* in the discharged Cl beam, was discarded.

factor for bending and/or torsional excited CH_4. For experimental reasons, most of experiments were performed for the Cl + CD_4 reaction.

II. Experiment

The experiments were conducted with the crossed-beam apparatus that has been described in detail previously.[29] In brief, a dc high-voltage discharge source was used to generate the Cl-atom beam (3.5% Cl_2 in helium, at 6 atm.).[30,31] To prolong the stability of the discharge beam, a scheme of pulsed high voltage with a pre-ionization pulse was adapted.[29,32−34] The amounts of $Cl(^2P_{3/2})$ and $Cl^*(^2P_{1/2})$ were not determined in this study. The previous investigation, using a slightly different discharge scheme, indicated that the relative yield of $Cl^*(^2P_{1/2})$ can be quite significant.[30] A neat CH_4 or CD_4 beam was delivered from a heatable, pulsed valve (an Evan-Lavie valve) at 6 atm. Two source temperatures—340 and 463 K, from the thermocouple measurement—were used to vary the initial populations of v_2- and v_4-mode excited CD_4. Their speeds—1.1 and 1.29 km/s, respectively—were measured using two fast ionization gauges. To isolate the effects of the initial vibration excitation, the intersection angles of the two molecular beams were adjusted accordingly, so that the experiments under different source temperatures yield approximately the same collision (translation) energy of $E_c = 4.78 \pm 0.03$ kcal/mol. The reaction product CD_3 (or CH_3) was interrogated by (2 + 1) resonance-enhanced multiphoton ionization (REMPI), using the time-sliced ion velocity imaging technique.[29,32−34] The laser frequency of the probe was fixed at the peak of the $X^2A_2 \longrightarrow 3p_z^2A_2\ 0_0^0$ Q-head for better image resolution. Consequently, only the low N-states of the vibrational ground state of methyl radicals were sampled.[32] REMPI spectra, nonetheless, indicate that they represent a very significant fraction of total reactivity.

III. Results and Discussion

A. Identification of Product Images. Figures 1a and 1b present the two raw images of CD_3 products at 340 and 463 K, respectively. After the density-to-flux correction,[29] the corresponding product velocity−flux contour maps, $d^2\sigma/d\mu d(\cos\theta)$, are displayed in Figures 1c and 1d. Both images feature three backscattered, ring-like structures. The reaction of Cl + CD_4 → CD_3 + DCl is endothermic by 2.34 kcal/mol. Using the conservations of energy and momentum, the most intense ring can readily be assigned to the ground-state reaction, $Cl(^2P_{3/2}) + CD_4(v = 0) \rightarrow CD_3(v = 0) + DCl(v' = 0)$. The two outer rings, labeled 0^* and 0^{**}, with faster recoil speeds, must then orginate from internally excited reactants. The possible candidate from the Cl beam is the spin−orbit excited $Cl^*(^2P_{1/2})$ state that lies 882 cm^{-1} (2.52 kcal/mol) above the ground $Cl(^2P_{3/2})$ state. The dramatic increase of the 0^* and 0^{**} signals that is observed when the secondary beam source is heated (see Figure 1d versus Figure 1c), however, implicates the vibrationally excited CD_4 reactants as the major contributors. Among them, the excitations of the two low-frequency modes v_2 (1092 cm^{-1} or 3.12 kcal/mol, double degeneracy) and v_4 (998 cm^{-1} or 2.85 kcal/mol, triple degeneracy) of CD_4 are the prime candidates. The outermost ring has a maximal kinetic energy of ~7.6 kcal/mol, as seen below. Hence, it is most likely from the $Cl(^2P_{3/2})$ +

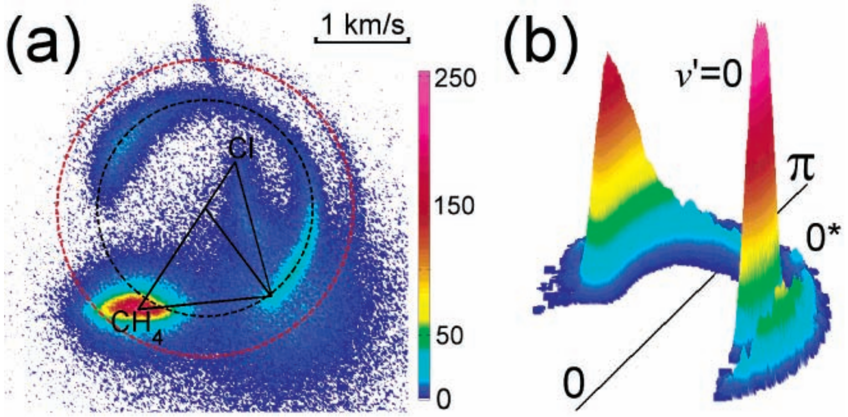

Figure 2. Similar to Figures 1b and 1d, except the reaction is Cl + CH_4 at $E_c = 4.60$ kcal/mol. Obviously, the background problem is more severe when m/e = 15 was detected. In addition to the two localized beam-related backgrounds, there is a widespread background centered around the laboratory origin, which was caused by the interactions of the UV laser with the pump-oil background. These backgrounds were subtracted, and the resultant contour map is shown in panel b.

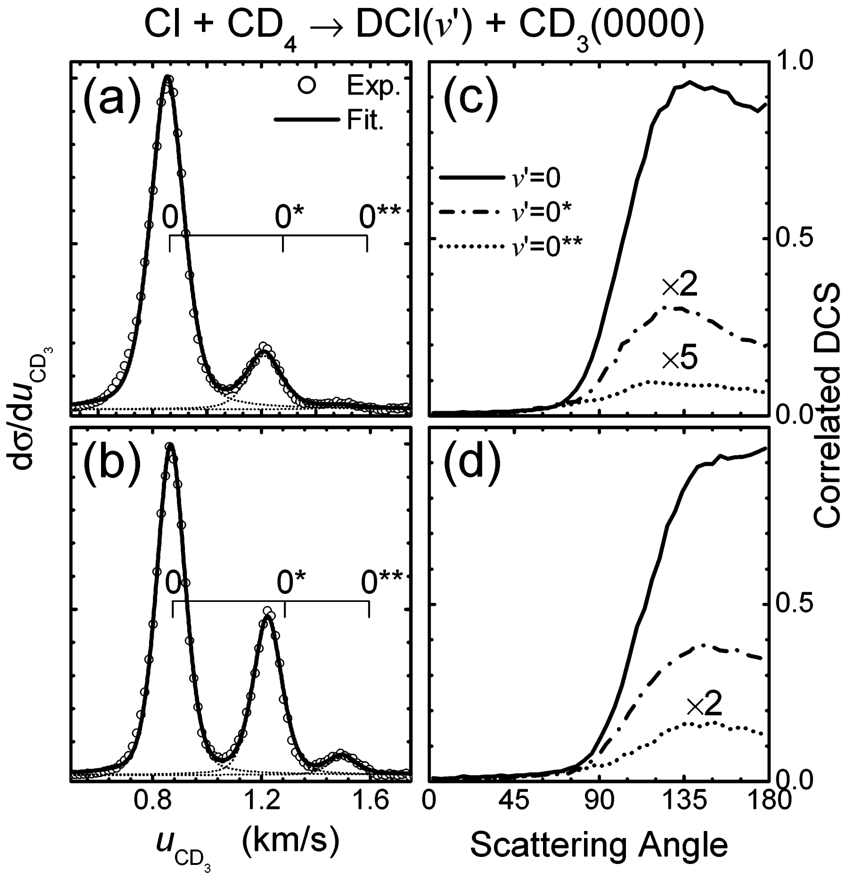

Figure 3. CD_3 product speed distributions for the two source temperatures (a) 340 and (b) 463 K. The labels are the same as those in Figure 1. The small shift of the peaks from the labeled marks reflect the rotational excitations of the two product rotors. The corresponding angular distributions are shown in panels c and d. The slight difference in shapes between panels c and d for the same labeled reaction could be the experimental uncertainty and/or could result from the slight variations of the CD_4 beam characteristics. (Note that the peaks in panel b are slightly narrower than those shown in panel a.)

$CD_4(v_4 = 2) \rightarrow CD_3(v = 0) + DCl(v' = 0)$ reaction, although some minor contributions from the other excited states of CD_4 such as $v_2 = 2$, v_1 and/or $v_3 = 1$ cannot be ruled out. The origin of the middle ring, peaking at an average kinetic energy release of 4.8 kcal/mol, is somewhat ambiguous, because of the proximity of the energetics between $Cl^*(^2P_{1/2})$ and $CD_4(v_4$ or $v_2 = 1)$, which is beyond our energy resolution.

To differentiate the aforementioned two possibilities, the image of the Cl + CH_4 reaction was acquired and shown in Figure 2a. To enhance the signals from the hot-band reaction, the source temperature of the CH_4 beam was raised to 465 K, for which a beam speed of 1.42 km/s was measured. Despite the background interferences, two clear rings in the sideways/backward direction are observed. After subtracting the background and performing the density-to-flux correction, the product velocity−flux contour map is shown in Figure 2b. Energetically, the inner feature corresponds to the $Cl(^2P_{3/2}) + CH_4(v = 0) \rightarrow CH_3(v = 0) + HCl(v' = 0)$ ground-state reaction. The outer ring is separated from the inner one by ~3.5 kcal/mol, which is consistent with the energetics of 3.75 kcal/mol

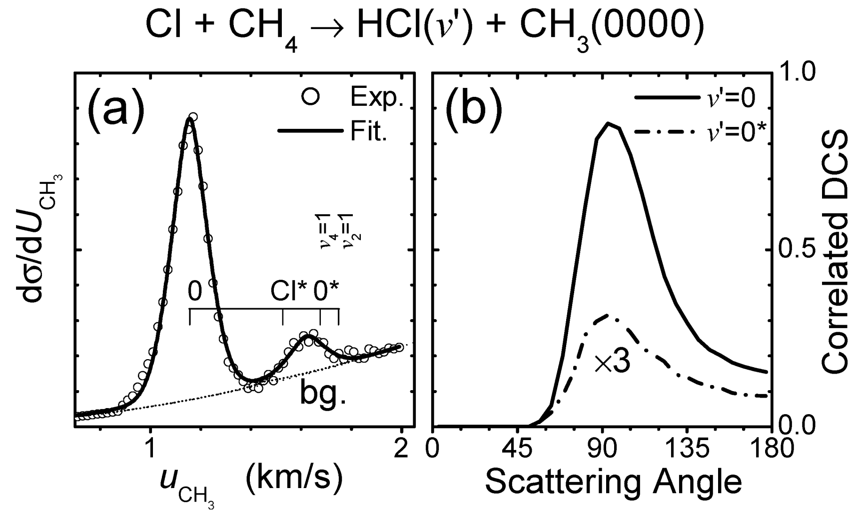

Figure 4. Similar to Figure 3, except the reaction is Cl + CH_4. The residual background was removed when partitioning the peaks in the speed distribution. Note the absence of any significant signals at the location anticipated for the $Cl^*(^2P_{1/2}) + CH_4(v = 0)$ reaction. The hot band feature is more consistent with the assignment of $v_4 = 1$ than $v_2 = 1$.

TABLE 1: Vibrational Enhancement Factors in the $Cl(^2P_{3/2}) + CD_4(v_2/v_4)$ Reaction[a]

	S^*/S_0	S^{**}/S_0	$n_{v_4=1}/n_0$	$n_{v_4=2}/n_0$	$n_{v_2=1}/n_0$	$n_{v_2=2}/n_0$
340 K	0.161	0.0061	0.044	7.1×10^{-4}	0.02	2.1×10^{-4}
463 K	0.474	0.053	0.137	6.6×10^{-3}	0.068	2.3×10^{-3}
ratio(463 K/340 K)	2.94	8.7	3.1	9.3	3.4	11
σ^*/σ_0 or σ^{**}/σ_0	3 ± 1	7.5 ± 2				

[a] Note: The relative cross sections are deduced from $S = n\sigma$.

from the $Cl(^2P_{3/2}) + CH_4(v_4 = 1) \rightarrow CH_3(v = 0) + HCl(v' = 0)$ reaction. Nothing obvious, as will be shown below, is present at the energy anticipated for $Cl^*(^2P_{1/2}) + CH_4(v = 0)$, clearly demonstrating the insignificance of its contribution or reactivity, which confirms the previous assertion by Zare's group.[20,21] Analogously, we conclude thqat the assignment of the middle ring for the CD_3 product predominantly originates from the $Cl(^2P_{3/2}) + CD_4(v_4 = 1)$ reaction.

B. Reactivity Enhancement of Bend-Excited Methane. Analysis of the product images provides more-quantitative determination of the relative reactivity. Integrating the contour map over the scattering angles, weighted by sin θ to account for the solid angle factor, yields the product speed distribution. The results for the CD_3 products under the two source temperatures are presented in Figure 3a. Three peaks are clearly resolved and can be assigned as noted previously. The integrated area of each peak then yields the respective contribution, $S = n\sigma$, from the process of interest. The results from the speed distributions are summarized in Table 1. Also indicated in the table are the anticipated Boltzmann populations of the excited v_2 and v_4 modes (the ground-state population is set as one), assuming that the vibrational populations in our beam are similar to source thermal values. As is observed, both the ratios of S^*/S_0 and S^{**}/S_0 of the two temperatures are, within 10%, in accord with the thermal population enhancement factors of the v_4 mode, e.g., $(S^*/S_0)_{463K}/(S^*/S_0)_{340K} \approx (n_{v_4=1}/n_0)_{463K}/(n_{v_4=1}/n_0)_{340K}$, and the agreement is slightly less so for the v_2 mode. This comparison suggests little vibrational cooling in our $CD_4(CH_4)$ beam, despite rather strong supersonic expansion that yields cold rotational and translational distributions.

Based on this information, we can now estimate the vibrational enhancements in reactivity (σ^*/σ_0 and σ^{**}/σ_0, as shown in Table 1). The range of values is dependent on if we consider the v_4 mode solely or both the v_4 and v_2 modes (with equal reactivity). Roughly speaking, each quantum excitation results in an ~3-fold enhancement in cross section. Similar analysis can be performed for the Cl + CH_4 reaction, as shown in Figure 4. Assuming that the vibrational population of the CH_4 beam is equilibrated at the source temperature of 465 K—in analogy to the CD_4 beam—and with $S^*/S_0 \approx 0.13$, we deduce a reactivity enhancement factor of 2−4 (depending on if $v_2 = 1$ is active or not) for bend-excited CH_4 at $E_c = 4.60$ kcal/mol. These factors are significantly smaller than the factor of ~80 for Cl + CD_4 and ~200 for Cl + CH_4 that were obtained by Zare's group[20,21] but are more consistent with the suggestion by Michelsen and Simpson.[27,28]

It is instructive to compare the vibrational enhancement factor to the reagent translational factor. The excitation function for the ground-state Cl + CD_4 reaction has recently been measured in this laboratory. The unpublished results indicate that, with equivalent amounts of additional energy in the translational degrees of freedom, the enhancement factors in the reaction cross sections become ~3.5 and 4.3 times larger in the order of increasing E_c. Hence, the vibrational enhancement from the v_4 (and/or v_2)-mode excitation is not much different from the reagent translational energy, and, thus, is not mode-specific. This comparison should have a strong bearing in future modeling, such as the Michelsen's approach,[27,28] of the kinetic behaviors of this reaction.

A recent theoretical investigation indicated that the v_4 mode of CH_4 is intimately coupled to the reaction coordinate and adiabatically correlated to the v_2 (umbrella) mode of the CH_3 product.[14] This analysis corroborates the classical intuition of the geometric change from the pyramidal structure of the CH_3 moiety in the transition state to the planar methyl radical product. Yet, the observed enhancement factor of the vibrationally *nonadiabatic* product channel of the ground-state CH_3 does not seem to be mode-specific. Further work on the formation of the v_2-mode excited products, which will be the adiabatically correlated channel, is planned.

We note that the effect of bend excitation of CH_4 on the product HCl rotational distribution has also been investigated theoretically.[35] A cold unimodal rotational distribution of HCl was found with ground-state reaction of CH_4,[35a] and a unimodal, although slightly hotter, distribution was found for the bend fundamental.[35b] These results are in accord with the present experiment and the previous observation.[22] The calculations also predicted a bimodal HCl rotational distribution for the second bend-excited CH_4. If this prediction also holds for CD_4, this would not be supported by the experiments on $CD_4(\nu_4 = 2)$, judging from the clear separation and the shape of our $d\sigma/d\mu$ distributions (Figures 3a, 3b, and 4a). Further theoretical studies are warranted.

C. Product Angular Distributions. Figures 3c and 3d show that the product angular distribution from the ground-state reaction of Cl + CD_4 is backward scattered and has a sharp cutoff toward the forward hemisphere. This is in qualitative agreement, although quantitative discrepancies are discernible, with the previous measurements[20,21] and with the theoretical expectation that the transition state is highly collinear along the Cl−D−*C* axis. The observed angular distribution is very similar to that found for the $Cl(^2P_{3/2}) + H_2$ reaction[36] but significantly different from the F + CD_4 reaction and its isotopic variants.[32−34]

Although the product angular distribution for the Cl + CH_4 ground-state reaction also indicates an abrupt cutoff, it exhibits a distinct sideways-scattered peak (see Figure 4b). The origin of the striking difference between the two isotopic reactions, probably reflecting the difference in the cones of acceptance of the two reactions, is currently under investigation. The present study also shows that the angular distribution for the bend-excited methane reaction is predominantly backward or sideways scattered with a shape similar to the respective ground-state reaction. This is to be contrasted with the previous finding when one quantum of asymmetric CH stretch ($v_3 = 1$) of CH_4 was excited, for which a significant change in product angular distributions was noted.[22,23]

IV. Conclusions

To summarize, many important issues about the Cl + CH_4 reaction have been addressed in this work, from which several conclusions can be drawn.

(1) The reactivity of $Cl^*(^2P_{1/2})$ toward CH_4/CD_4 seems negligibly small, which is in sharp contrast to the previous, still controversial, finding for the analogous $Cl/Cl^* + H_2/D_2/HD$ reactions.[30,31,36−39]

(2) The supersonic expansion is not efficient in cooling the vibrational degrees of freedom of the CD_4/CH_4 reactants.

(3) At variance with previous experiments,[20,21] the vibrational enhancement factor with v_4- and/or v_2-mode excitation of CH_4/CD_4 in forming the ground-state CH_3/CD_3 is quite modest (∼3 times per quantum excitation), which is not much different from the translational enhancement factor with equivalent amounts of energy.

(4) The DCl/HCl product rotational distributions are cold and unimodal, which is in accordance (or at variance) with a recent theoretical prediction for the ground-state (or the bend-excited) CH_4 reaction.

(5) Both the ground and bending/torsional excited methane reactants yield predominantly backscattered (for reaction with CD_4) or sideways scattered (for CH_4) products, and their angular distributions are remarkably similar.

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