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Bond-Selective and Mode-Specific Dissociation of CH_3D and CH_2D_2 on Pt(111)

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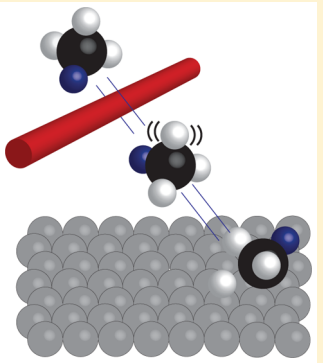
ABSTRACT: Infrared laser excitation of partially deuterated methanes (CH_3D and CH_2D_2) in a molecular beam is used to control their dissociative chemisorption on a Pt(111) single crystal and to determine the quantum state-resolved dissociation probabilities. The exclusive detection of C−H cleavage products adsorbed on the Pt(111) surface by infrared absorption reflection spectroscopy indicates strong bond selectivity for both methane isotopologues upon C−H stretch excitation. Furthermore, the dissociative chemisorption of both methane isotopologues is observed to be mode-specific. Excitation of symmetric C−H stretch modes produces a stronger reactivity increase than excitation of the antisymmetric C−H stretch modes, whereas bend overtone excitation has a weaker effect on reactivity. The observed mode specificity and bond selectivity are rationalized by the sudden vector projection model in terms of the overlap of the reactant's normal mode vectors with the reaction coordinate at the transition state.



INTRODUCTION

Ever since the invention of the laser in 1960, chemists have strived toward laser control of chemical reactions. Starting in 1990, the groups of Crim and Zare[1,2] reported a number of bond-selective bimolecular reactions in the gas phase demonstrating that bond selectivity can be achieved via selective vibrational reactant excitation. In addition to realizing the 30 year old dream of laser controlled reactions, the investigation of vibrational control of reaction probabilities (mode specificity) and branching ratios (bond selectivity) provides detailed insight into the microscopic dynamics of a chemical reaction. More recently it was demonstrated that mode specificity and bond selectivity are not limited to gas-phase reactions but can be observed also in gas−surface reactions.[3,4] The dissociative chemisorption of methane on transition metal surfaces has become a prototype system to investigate mode selectivity and bond specificity in gas−surface reactions in both experiment and theory.[5] A detailed understanding of methane chemisorption is of great practical interest because this reaction is known to be the rate-limiting step in the steam reforming process for industrial hydrogen production.[6]

Partially deuterated species are particularly well suited to explore mode- and bond-selective reactivity. A first case of bond selectivity in a bimolecular gas-phase reaction was reported by Crim and co-workers[7] for HOD where a strong preference for the cleavage of the O−H bond was observed in the hydrogen abstraction reaction by H atoms when the O−H bond was vibrationally excited to a localized O−H stretch overtone.

For a reaction to be mode-specific, the reaction probability does not simply depend on the total vibrational energy content but on the specific vibrational quantum state of the reactant. Two iso-energetic reactant states can lead therefore to rather different reaction probabilities. One example of a mode-specific gas-phase reaction is the H-abstraction reaction of CH_3D by a chlorine atom, reported by Yoon et al.[8,9] The authors used their state-resolved reactivity data to calculate state-specific reaction cross sections for the ν_1, ν_4, and $2\nu_5$ normal modes of CH_3D. They find the symmetric stretch vibration (ν_1) to be 7 times more reactive than the antisymmetric stretch (ν_4) whereas the bending overtone ($2\nu_5$) had no detectable influence on the reactivity. Furthermore, the reaction of vibrationally excited CH_3D with chlorine was reported to be bond-selective.[10] The reaction of vibrationally excited CH_2D_2 with chlorine atoms was also reported to be bond- and mode-selective.[11,12] The group of Richard Zare[11,12] showed that upon excitation of the first C−H stretch overtone in CH_2D_2 a C−H bond breaks preferentially whereas upon C−D stretch excitation a C−D bond breaks preferentially. In addition, they found that excitation of the $|20\rangle$ C−H stretching mode of CH_2D_2 shows different rotational distributions, vibrational distributions, and scattering angles of the reaction products than excitation of the $|11\rangle$ mode.

Despite their larger complexity, experiments performed on gas−surface reactions show many parallels to the findings obtained in bimolecular gas-phase reactions. In 2003 vibrational mode-specific reactivity of doubly deuterated methane on a nickel single-crystal surface was reported[13] and several studies

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of mode-specific methane/transition metal surface reactions followed.[14−17]

In 2008 the first example of vibrational bond selectivity on surfaces was reported in the dissociative chemisorption of CHD_3 on Ni(111).[3] Recently, our laboratory at EPFL presented a study[4] where reflection−absorption infrared spectroscopy (RAIRS) was used to directly detect the nascent products of methane dissociation on Pt(111). The dissociation of all three partially deuterated methane isotopologues (CH_3D (ν_4), CH_2D_2 (ν_6), and CHD_3 (ν_1)) was discovered to be highly bond-selective for C−H stretch excitation. The experimentally observed bond selectivity on Ni(111) was simulated by using quasi-classical trajectories on a global potential energy surface (PES),[18] and the simulation results are consistent with the experiment.[19]

In this article, we present experimental data that show that the dissociative chemisorption of CH_3D and CH_2D_2 on Pt(111) is highly bond-selective for excitation of different vibrational eigenstates. Furthermore, we used RAIRS to measure state-resolved sticking coefficients of the three mentioned vibrational states and thereby demonstrate that the reactions are mode-specific. To rationalize the experimental findings, we have used the recently proposed sudden vector projection (SVP) model, which assumes the reaction occurs in the sudden limit and attributes the vibrational enhancement of reactivity to the coupling of the reactant mode with the reaction coordinate at the transition state.[20,21]

EXPERIMENTAL SECTION

The experiments reported here were performed in a molecular beam/surface science apparatus that is described in more detail elsewhere.[22] Therefore, we only briefly summarize its most important features and the experimental procedure used here. A triply differentially pumped molecular beam source is coupled to a UHV camber containing a single crystal surface mounted on a home-built four-axis manipulator. The sample mounting allows for heating to 1300 K and cooling to 78 K. During the experiments reported here, the temperature was stabilized to 150 ± 0.1 K. Adsorbed products of the dissociative chemisorption of methane are detected by reflection absorption infrared spectroscopy (RAIRS) using a Fourier transform infrared spectrometer (FTIR) (Bruker Vertex 70v) with an external InSb detector. RAIRS provides a noninvasive method for the online detection of the adsorbed methyl (CH_xD_y $x + y = 3$) species produced by the dissociative chemisorption of incident methane on the cold Pt(111) surface. Auger electron spectroscopy (AES) was used to calibrate the RAIRS signals for the different methyl isotopologous in terms of surface coverage θ.[22]

A continuous molecular beam of either singly and doubly deuterated methane (99% isotopic purity) was formed by expanding 3% CH_3D or CH_2D_2 seeded in helium (3 bar, 300 K) through a 50 μm diameter nozzle and a 2 mm diameter skimmer. Velocity distributions of the molecular beam were measured by an on-axis quadrupole mass spectrometer in combination with a fast chopper wheel. At a nozzle temperature of 300 K the average translational energy of CH_3D and CH_2D_2 was determined to be 24 ± 4.5 kJ/mol.

The methane isotopologues were prepared in specific ro-vibrational eigenstates by intersecting the molecular beam between nozzle and skimmer with infrared radiation from a tunable continuous wave single mode optical parametric oscillator (cw-IR OPO). The OPO idler output was frequency stabilized to ±1 MHz by locking to a Doppler-free saturation hole (Lamb-dip) detected in a static gas cell. Excitation of the molecular beam occurred by rapid adiabatic passage using a cylindrical lens (f = +25 cm) to gently focus the IR beam into the interaction region with the molecular beam. The focusing creates curved wavefronts that lead to a Doppler frequency tuning effect as the reactant molecules pass through the divergent IR beam. Under suitable conditions the frequency chirp will invert the reactant population from the ground state to a ro-vibrationally excited state by rapid adiabatic passage (RAP).[23] Three different ro-vibrational eigenstates of CH_3D and two eigenstates of CH_2D_2 were prepared in the molecular beam by excitation of the $R_0(1)$ transitions originating from J = 1, K = 0 of the symmetric top molecule CH_3D and $R_{01}(1)$ transitions of the asymmetric top molecule CH_2D_2. The incident flux of CH_3D or CH_2D_2 was monitored by measuring the partial pressure of the respective gas in the UHV chamber with a quadrupole mass spectrometer. A room temperature pyroelectric detector that could be translated into the molecular beam to measure its vibrational energy content was used to determine the fractions of state prepared CH_3D or CH_2D_2 in the molecular beam. The measured flux of excited molecules incident on the surface was used with the resulting methyl product coverage on the surface obtained from the calibrated RAIRS detection to determine the absolute reaction probabilities and branching ratios for C−H and C−D cleavage.

RESULTS

State-Resolved Dissociation of CH_3D. Comparison of the five RAIR spectra shown in Figure 1 demonstrates the bond-selective and mode-specific character of the dissociation for C−H stretch excited CH_3D. In the laser-off spectrum (a) taken with a nozzle temperature of 700 K, we observe RAIRS peaks due to both CH_3(ads) and CH_2D(ads), produced via C−D and C−H bond cleavage, respectively. The laser-off branching ratio determined from calibrated RAIRS signals is 22% C−D cleavage and 78% C−H cleavage, close to the

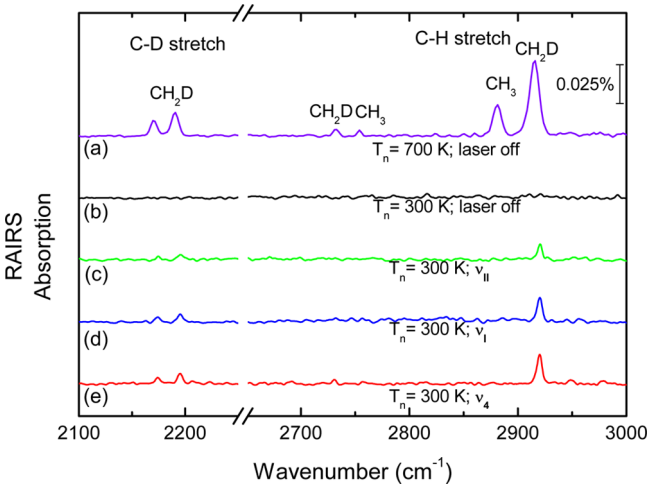

Figure 1. RAIR spectra of CH_3D dissociation products on a Pt(111) surface at a surface temperature of 150 K. The peak assignments are given in spectrum a recorded for deposition from a hot nozzle (700 K, E_t = 49 kJ/mol) resulting in both C−H and C−D bond cleavage. With the nozzle 300 K and E_t = 24 ± 4.5 kJ/mol, dissociation is only observed for the laser excited molecular beam. The three vibrational quantum states probed all lead to bond-selective C−H cleavage.

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statistical limit of 1:3.[4] Figure 1b shows a laser-off RAIR spectrum for T_n = 300 K, indicating that no dissociation occurs at this lower nozzle temperature without vibrational excitation via IR excitation. Figure1c,d,e shows three RAIRS spectra for incident CH_3D prepared in three different vibrational states, labeled as ν_I, ν_{II}, and ν_4. In all three laser-on experiments, we observed exclusively the CH_2D(ads) dissociation products and no evidence for C−D cleavage, indicating strong bond selectivity for C−H cleavage. Hence, excitation of CH_3D with one quantum of either the antisymmetric stretch (ν_4) or the symmetric stretch/bend overtone mixed eigenstates (ν_I and ν_{II}) activates only the C−H cleavage reaction channel. The fact that the CH_2D absorption peak heights are different in Figure1c,d,e for identical depositions (incident dose 95 ML of state prepared CH_3D) indicates mode-specific reactivity for the three states probed here. The CH_2D peaks in (c)−(e) are smaller than those in (a) because spectrum (a) was taken after saturation of the surface.

Figure 2 shows the state-resolved uptake curves of the C−H cleavage product CH_2D(ads) measured by RAIRS during a

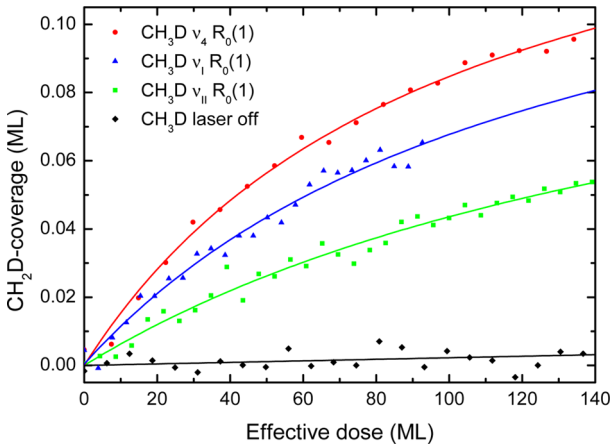

Figure 2. State-resolved uptake curves θ(D) for CH_2D(ads) on Pt(111) at T_s = 150 K. The state-resolved initial sticking coefficient S_0 is determined from the initial slopes of the uptake curves θ(D) fitted to the data (see text). The effective dose measures the incident flux for each quantum state prepared by IR pumping, as determined by a pyroeletric detector inserted into the molecular beam.

deposition experiment on Pt(111). The state-resolved reactivity is proportional to the slope of the uptake curve. We fit an analytical uptake model to the data based on the Langmuir form

$$\theta(D) = A \cdot \frac{B \cdot D}{1 + B \cdot D}$$

where D is the incident dose, A is the saturation coverage, and B is a fitting constant. The coverage dependent sticking coefficient $S(\theta)$ is given by $\partial\theta/\partial D$, the derivative of the fitted uptake curve $\theta(D)$ with respect to the dose D. The initial slope (for D = 0) corresponds to the initial sticking coefficient S_0 on the clean Pt(111) surface and is given by $A{\cdot}B$. The analysis of the state-resolved uptake data show in Figure 2 yields different initial sticking coefficients for the three different quantum states of CH_3D prepared by IR pumping as indicated by their different initial slope (see Table 1).

It should be noted that we also observe a variation in the saturation coverage for the three vibrational states, where the

Table 1. Sticking Coefficients and Saturation Coverages for Three Different Ro-vibrationally Excited Eigenstates of CH_3D (E_t = 24 ± 4.5 kJ/mol, T_s = 150 K)

eigenstate	S_0	saturation coverage θ
ν_I	(1.3 ± 0.4) × 10^{-3}	0.13 ± 0.01
ν_{II}	(0.7 ± 0.3) × 10^{-3}	0.13 ± 0.02
ν_4	(1.7 ± 0.5) × 10^{-3}	0.17 ± 0.01

state with the largest reactivity results in the largest saturation coverage. A recent combined experiment/theory study reported such an increase in CH_2D saturation coverage with increasing reactivity and found it to be due to a coverage dependent reaction barrier.[24]

Due to a strong Fermi resonance between the normal modes ν_1 (symmetric C−H stretch) and $2\nu_5$ (C−H bending overtone) of CH_3D, the vibrational eigenstates $|\nu_I\rangle$ and $|\nu_{II}\rangle$ prepared by IR pumping with a single mode laser correspond to a mixture of the ν_1 and $2\nu_5$ modes with different relative contributions. Wang et al. have developed an ab initio potential energy surface for CH_3D and calculated its vibrational states up to 9000 cm^{-1}. Their calculations[25,26] identify the CH_3D eigenstates $|\nu_I\rangle$ at 2969.5 cm^{-1} and $|\nu_{II}\rangle$ at 2910 cm^{-1} in terms of a normal mode expansion with the leading terms given by $|\nu_I\rangle$ = 0.77 ν_1 + 0.63 $2\nu_5$ and $|\nu_{II}\rangle$ = 0.63 ν_1 + 077 $2\nu_5$, indicating that these contain 60% stretch and 40% bending motion and vice versa. The third state at 3016 cm^{-1}, in contrast, is a nearly pure antisymmetric C−H stretch normal mode ν_4 (96%). To further analyze the mode-specific behavior of the reactions, we calculate the hypothetical reactivities of the zero-order vibrational states ν_1 and $2\nu_5$. Simply inserting the measured $|\nu_I\rangle$ and $|\nu_{II}\rangle$ reactivities and solving the system of equations resulted in a small but negative reactivity for the pure $2\nu_5$ state. We decided to rather follow the analysis of Yoon et al., who measured the relative reactivity CH_3D prepared in the same three eigenstates $|\nu_I\rangle$ $|\nu_{II}\rangle$ and ν_4 for the bimolecular collision with a chlorine atom.[8] Yoon at al. made the implicit assumption that the reactivities of the mixed eigenstates can be described as linear combinations of the reactivities of the zero-order states if they are scaled by the respective mixing factors (60% and 40%).

Because a hydrogen atom abstraction reaction is considered (in both this work and ref 8), it is plausible to assume that bending vibration $2\nu_5$ does not promote reactivity. Thus, the reactivities will be proportional to the content of reactive zero-order stretching state in the excited eigenstate. Hence we can write the ratio of measured reactivities as

$$\frac{S_0^{|\nu_I\rangle}}{S_0^{|\nu_4\rangle}} = \frac{(1.3 \pm 0.4) \times 10^{-3}}{(1.7 \pm 0.5) \times 10^{-3}} = \frac{0.5929 \cdot S_0^{\nu_1}}{0.96 \cdot S_0^{\nu_4}}$$

Therefore, we can find the ratio of the sticking coefficients for the zero-order symmetric stretch excitation to antisymmetric stretch to be

$$\frac{S_0^{\nu_1}}{S_0^{\nu_4}} = 1.23 \pm 0.4$$

The consistency of this analysis can be tested by using the measured sticking coefficient for the $|\nu_I\rangle$ eigenstate to predict that of the $|\nu_{II}\rangle$ eigenstate.

$$\frac{S_0^{|\nu_I\rangle}}{S_0^{|\nu_{II}\rangle}} = \frac{0.5929}{0.3969} = 1.5$$

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So the predicted $|\nu_{II}\rangle$ reactivity of $S_0^{|\nu_{II}\rangle-calc} = (0.9 \pm 0.3) \times 10^{-3}$, which is in good agreement with the experimental result of $S_0^{|\nu_{II}\rangle} = (0.7 \pm 0.3) \times 10^{-3}$. The fact that the predicted reactivity is larger than the measured one, indicates that this analysis does not underestimate the $2\nu_5$ reactivity. Therefore, the analysis is consistent and the initial assumption of a nonreactive bending overtone is justified. The deduced zero-order reactivities are summarized with the CH_2D_2 reactivities in Table 2.

Table 2. Eigenstate-Resolved Reactivities on Pt(111) at T_s = 150 K and Translational Energies of 24 ± 4.5 kJ/mol

molecule	zero-order state	S_0
CH_3D	ν_1	$(2.2 \pm 0.5) \times 10^{-3}$
CH_3D	ν_4	$(1.8 \pm 0.2) \times 10^{-3}$
CH_2D_2	ν_1	$(2.02 \pm 0.09) \times 10^{-3}$
CH_2D_2	ν_6	$(1.47 \pm 0.07) \times 10^{-3}$

Despite the fact that this analysis yields consistent results, one has to be aware of the considerable simplifications that are introduced by assuming zero reactivity for the $2\nu_5$ mode. It has been shown previously for CH_4 dissociation on Pt(110)-(1×2) that the efficacies of different vibrations cannot be simply added to calculate the efficacies of combination bands.[16] Therefore, the reactivities of the zero-order states in $|\nu_I\rangle$ and $|\nu_{II}\rangle$ might influence each other differently for the different mixing ratios. In addition, calculations suggest that bending vibrations can increase reactivity, for example, for CH_4 on Ni(111).[27] Nevertheless, the consistency of the analysis shows that the initial approximations are justifiable.

State-Resolved Dissociation of CH_2D_2 on Pt(111). The dissociation of C−H stretch excited CH_2D_2 was also found to be bond-selective both for excitation of the antisymmetric (ν_6) and for the symmetric C−H stretch (ν_1). The RAIRS spectra of the products of CH_2D_2 dissociation on Pt(111) are shown in Figure 3. Spectrum (a) at the top was obtained for deposition from a hot nozzle (T_n = 700 K) with a translational energy of 49 kJ/mol.[4] Both C−H and C−D cleavage products are observed in this case with a branching ratio of 55% CH cleavage and 45% CD cleavage, close to the statistical limit of 1:1. The laser-off spectrum recorded at a nozzle temperature of 300 K did not show any reactivity on the time scale of the experiment (≈1 h). With IR pumping of either the symmetric C−H stretch (ν_1) or the antisymmetric C−H stretch mode ν_6 we detect only the C−H cleavage product CHD_2(ads), indicating strong bond selectivity upon C−H stretch excitation.

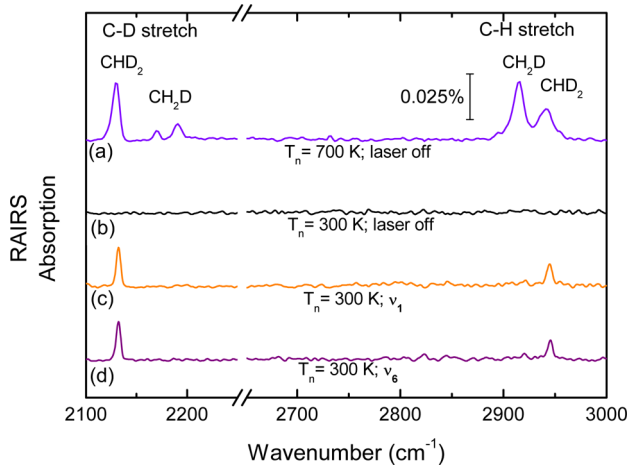

Figure 3. RAIR spectra of CH_2D_2 dissociation products on a Pt(111) surface at a surface temperature of 150 K. The peak assignments are given in spectrum a recorded for deposition from a hot nozzle (700 K, E_t = 49 kJ/mol) resulting in both CH and CD bond cleavage With the nozzle 300 K and E_t = 24 ± 4.5 kJ/mol, dissociation is only observed for the laser excited molecular beam. The two quantum states probed all lead to bond-selective CH cleavage.

Figure 4 shows uptake curves of CHD_2 that were obtained by monitoring the RAIRS absorption peak height of the C−H stretch peak of CHD_2. The steeper initial slope of the uptake curve for the ν_1-excited CH_2D_2 indicates that the ν_1-excited molecules are 1.4 times more reactive than the ν_6-excited molecules.

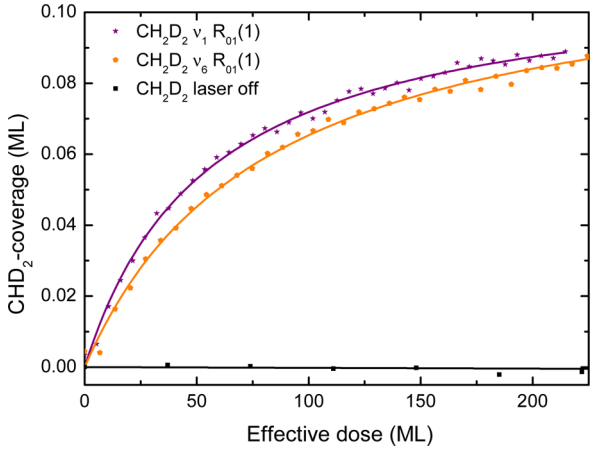

Figure 4. Uptake curves of CHD_2 on Pt(111) as CH_2D_2 dissociation product. The steeper initial slope of the ν_1 curve indicates a higher initial sticking coefficient S_0 by a factor 1.4.

DISCUSSION

Our observation that both CH_3D and CH_2D_2 dissociate bond selectively if excited to vibrational eigenstates comprising C−H stretch and bend amplitude indicates that any intramolecular vibrational redistribution (IVR) that might occur between the laser preparation and the dissociation of the molecule is absent or at least incomplete. No IVR can occur during the typically 100 μs flight time between laser preparation region and the approach to the surface in our apparatus because excitation by the cw-IR OPO (line width <1 MHz) prepares a single ro-vibrational eigenstate of the reactant molecule that has no time dependence and cannot undergo IVR. Once the reactant molecule enters the range of any molecule/surface interactions (d < 1 nm), surface-induced IVR[28] may start to occur during the remaining time needed for the molecule to reach the transition state. At the incident speed used in the experiments described here, this flight time within range of molecule/surface interactions is less than 500 fs. Apparently, the time window available for surface-induced IVR is too short or the interactions too weak to allow for vibrational energy transfer between the C−H and C−D oscillators leading to bond-selective dissociation upon C−H stretch and bend excitation.

The experimentally observed bond selectivity is in disagreement with the prediction of statistical models for the dissociation of methane on Pt(111).[29,30] These models assume randomization of the initial vibrational energy due to rapid

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intramolecular energy transfer within a short-lived complex formed with surface atoms before the C−H bond breaks and therefore exclude mode-specific and bond-selective dissociation of methane.

Both CH_2D_2 and CH_3D show mode-specific dissociation where the symmetric stretching vibration is more reactive than the antisymmetric C−H stretching. Yoon et al.[8] who studied the reaction of CH_3D with chlorine atoms in the gas phase performed ab initio calculations to rationalize the difference in reactivity observed for reactant preparation in the ν_4 and ν_1 modes. They calculated the evolution of the vibrational frequencies as the CH_3D molecule approached the Cl atom and found that the vibrational frequency of the ν_1 mode was reduced significantly, leading to a reduction in dissociation barrier height whereas the frequency of the ν_4 mode stayed nearly constant throughout the approach of the reactants. Furthermore, for the ν_1 vibration, the vibrational amplitude of three C−H stretch oscillators became localized in the reactive C−H bond pointing toward the Cl atom. In contrast, the vibrational amplitude of the ν_4 vibration remained quarantined in the two C−H oscillators pointing away from the reaction partner.

Similarly, for molecule−surface reactions, the interaction of the incident molecule with a metal surface can lead to surface-induced intramolecular vibration redistribution (IVR), which could lead to vibrational mode specificity due to differences in the localization of vibrational energy for different initial vibrational states. Halonen et al.[31] proposed a simple model for this process, which calculates the evolution of the C−H stretch modes as a nonrotating CH_4 approaches a metal surface with a single C−H bond pointing toward the surface. The model predicts that the symmetric stretch (ν_1) of CH_4 transforms adiabatically into excitation of the single C−H oscillator pointing toward the metal surface. The antisymmetric CH_4 stretch mode ν_3, however, is predicted to evolve adiabatically to the excitation of the methyl group, pointing away from the surface. On the basis of the different localization of the vibrational energy for the two initial states, Halonen et al. predicted a larger effect of ν_1 excitation on the CH_4 reactivity compared to the effect of the initial ν_3 excitation. State-resolved reactivity measurements[15,32] for $CH_4(\nu_1)$ and $CH_4(\nu_3)$ later confirmed the prediction of this simple model.

More recently, Bret Jackson developed a dynamical model for CH_4 chemisorption on transition metals,[33,34] which includes all internal modes of methane as well as rotation and surface atom motion. Jackson's reaction path Hamiltonian model[33,34] predicts higher reactivity for initial excitation of the symmetric C−H stretch mode ν_1 due to stronger mode softening and lowering the vibrational adiabatic dissociation barrier for ν_1 than for the other normal modes. In addition, vibrationally nonadiabatic transitions to the vibrational state of lower energy can convert vibrational energy into translational motion along the reaction coordinate, leading to mode-specific enhancement of the reactivity. Such mode-specific surface-induced IVR is also possible for the reaction of CH_3D and CH_2D_2 with a Pt(111) surface if the initially prepared states evolve differently during the reactant's approach to the surface, leading to different degrees of vibrational amplitude localization and different reactivities.

Alternatively, the so-called sudden vector projection model (SVP) was recently proposed by some of the current authors[20,21] to explain and predict vibrational mode specificity and bond selectivity both in bimolecular gas-phase and in gas−surface reactions. The SVP model assumes that IVR within the reactants is much slower than the time scale of the reactive collision and therefore treats the reaction as sudden; i.e., it neglects the surface-induced IVR processes that are calculated in Jackson's RPH model. The SVP model simply calculates the overlap of the reactant's normal mode vectors with the corresponding reaction coordinate at the appropriate transition state.[18,19] The application of this model to various gas-phase[20] and gas−surface reactions[35] has generally been successful. In particular, it predicted successfully the observed strong bond selectivity in the chemisorption of deuterated methanes on Ni(111).[19]

In Table 3, the SVP values have been computed for the dissociation of CH_3D and CH_2D_2 on Pt(111), using the protocol described in ref 36, directly from density functional theory calculations implemented in Vienna ab initio simulation package (VASP).[37,38] Briefly, the Pt(111) surface was modeled with a five-layer slab and the methane molecule was placed above a 3 × 3 (1/9 ML coverage) surface unit cell. The interaction between the ionic cores and electrons was described with the projector-augmented wave (PAW) method,[39] and the Kohn−Sham valence electronic wave function was expanded in a plane-wave basis set[40] with a cutoff at 350 eV. The Brillouin zone was sampled with a 4 × 4 × 1 γ-centered k-points grid. The generalized gradient approximation (GGA) was used to treat the electron exchange−correlation effects with the Perdew−Burke−Ernzerhof (PBE)[41] functional. The top three layers were relaxed during optimization and the transition state was found by the climbing-image nudged elastic band method,[42] followed by the normal-mode analysis to confirm a single imaginary frequency. The reactant geometry was obtained by separating the molecule and the surface in the direction of the surface normal, and then optimizing the transition state geometry to the equilibrium geometry of methane with little reorientation. The SVP values were then determined as the overlaps between reactant vibrational normal mode vectors and the vector of reaction coordinate at transition state corresponding to the imaginary frequency.

Table 3. Sudden Vector Projections of the Reactant Vibrational and Translational Modes onto the Reaction Coordinate at the Transition State[a]

	CH_3D	CH_2D_2
mode	H + CH_2D/D + CH_3	H + CHD_2/D + CH_2D
ν_1	0.44/0.04	0.57/0.04
ν_2	0.04/0.71	0.06/0.48
ν_3	0.29/0.05	0.30/0.09
ν_4	0.38/0.01	0.03/0.32
ν_5	0.24/0.15	0.36/0.31
ν_6	0.14/0.24	0.48/0.02
ν_7		0.12/0.31
ν_8		0.02/0.53
ν_9		0.31/0.07
trans X	0.006/0.02	0.005/0.01
trans Y	0.003/0.01	0.005/0.005
trans Z	0.32/0.39	0.32/0.40

[a]C−H and C−D cleavage channels are identified by the corresponding C−H or C−D bond elongated at the transition state.

It is clear from the table that the SVP model is in general agreement with the mode specificity and bond selectivity observed in the experiment. For CH_3D dissociation, for

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example, the observation that the excitation of CH_3D in C−H stretch modes (ν_1 and ν_4) only promotes the CH cleavage reaction channel is in agreement with the much larger SVP values for this channel over the CD cleavage channel. In addition, the SVP for ν_1 is slightly larger than for ν_4, again corresponding well to the slightly higher reactivity of symmetric C−H stretch mode ν_1 compared to that of the antisymmetric C−H stretch mode ν_4. It is also predicted that the excitation of C−D stretch modes would substantially activate the CD cleavage channel without promotion of the CH cleavage channel, similar to the highly bond-selective behavior due to the C−H stretch excitation in CHD_3 dissociative chemisorption.[3,4,43] Furthermore, for the CH_2D_2 molecule, the SVP model successfully reproduces the strongly bond-selective CH cleavage due to the excitation of C−H stretch modes ν_1 and ν_6, and the slight reactivity preference of ν_1 over ν_6. It is also suggested that the excitation of C−D stretch modes ν_2 and ν_8 would selectively enhance the C−D cleavage channel. However, the prediction of the SVP model to the bending modes could be less reliable, and the influence of bending overtones (e.g., the $2\nu_5$ state in CH_3D and the $2\nu_3$ state in CH_2D_2) may be better investigated by dynamical calculations on a global potential energy surface.

CONCLUSIONS

We measured the reaction probabilities for the dissociative chemisorption of CH_3D and CH_2D_2 on a clean Pt(111) surface for several vibrational eigenstates. For vibrational excitation comprising C−H stretch excitation, the reactions are observed to be both mode-specific and bond-selective. Calculation of the normal mode reaction probabilities from the measured reactivities of the mixed eigenstates of CH_3D $|\nu_I\rangle$ and $|\nu_{II}\rangle$ shows that the pure symmetric stretching vibration promotes reactivity more than the pure antisymmetric stretch. Analogous results were observed in the case of CH_2D_2. These results show that surface-induced IVR between C−H and C−D stretch modes is absent or incomplete on the time scale of the molecule/surface collision, leading to bond-specific dissociation.

To understand the origin of the observed mode specificity and bond selectivity, we have relied on the recently proposed SVP model. Assuming the collision time to be much shorter than the time needed for IVR, the SVP model attributes the ability of a reactant mode for enhancing the reactivity into a particular product channel to its overlap with the reaction coordinate of the corresponding transition state. The SVP model correctly predicted the experimental trends, revealing the different coupling strengths of the various vibrational modes of these two deuterated methane molecules with the reaction coordinate of the respective transition states.

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Notes

The authors declare no competing financial interest.

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