

# Chemical dynamics of vibrationally excited molecules: Controlling reactions in gases and on surfaces

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Experimental studies of the chemical reaction dynamics of vibrationally excited molecules reveal the ability of different vibrations to control the course of a reaction. This Perspective describes those studies for the prototypical reaction of vibrationally excited methane and its isotopologues in gases and on surfaces and looks to the prospects of similar studies in liquids. The influences of vibrational excitation on the C—H bond cleavage in a single collision reaction with Cl and in dissociative adsorption on a Ni surface bear some striking similarities. Both reactions are bond-selective processes in which the initial preparation of a molecular eigenstate containing a large component of C—H stretching results in preferential cleavage of that bond. It is possible to cleave either the C—H bond or C—D bond in the reaction of Cl with CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, or CHD<sub>3</sub> and, similarly, to use initial excitation of the C—H stretch to promote dissociation of CHD<sub>3</sub> to CD<sub>3</sub> and H on a Ni surface. Different vibrational modes, such as the symmetric and antisymmetric stretches in CH<sub>3</sub>D or CH<sub>4</sub>, lead to very different reactivities, and molecules with the symmetric stretching vibration excited can be as much as 10 times more reactive than ones with the antisymmetric stretch excited. The origin of this behavior lies in the change in the vibrational motion induced by the interaction with the atomic reaction partner or the surface.

The essence of chemistry is converting reactants into products by rearranging the connectivity of the atoms, and excitations that promote that rearrangement potentially influence the course of a reaction profoundly. A powerful experimental approach for discovering the details of a reaction is studying single collisions, where molecules have only one chance to react, to minimize the averaging over the initial distributions of collision energies and internal states. By controlling the direction of approach of the reactants and observing the direction of recoil of the products in a scattering experiment, it is possible to learn even more from the angular distribution of the products. The additional possibility of using laser excitation to prepare reactants in individual quantum states and laser spectroscopic techniques to identify the final states of the products has produced a rich history of experimental studies that connect with comparably detailed theoretical descriptions (1, 2). The interplay of theory and experiment in chemical reaction dynamics incisively tests models and calculations (3), and theory and experiment together often yield robust descriptions of chemical reactions at the most fundamental level.

Preparing molecules in a selected initial state and measuring populations of different final states can answer several questions about the role of internal energy in chemical reactions. The first question concerns energy flow between molecules and within a molecule, a central aspect of chemical reactions. Intermolecular energy transfer in collisions is the means by which molecules acquire enough energy to react, and intramolecular energy transfer is the means by which energy in a molecule finds its way

into motion along the reaction coordinate. Thus, for both fundamental and practical reasons, the first use of a new state preparation or analysis technique is often studying energy transfer. The second question concerns the fate of the energy available to the products of a reaction. One can ask about the partitioning of the available energy between internal excitation and relative translation of the products or about the relative populations of the different states of the products. The third question concerns the influence that different types of excitation have on the probability of reaction and on the disposal of energy in the products. For example, one can inquire as to the relative efficiency of vibrational energy in promoting a reaction compared with translational energy, or one can ask which internal states best accelerate a reaction.

Combining notions of energy consumption with those about energy disposal leads to the idea that an initial excitation might correlate with particular product excitations and, thus, to the possibility of state-to-state chemistry. A closely related aspect is the influence that different initial excitations have on the course of a reaction. In the simplest terms, initial excitation of a motion that has a large component along the reaction coordinate should accelerate the reaction. Because the passage from reactants to products rearranges the nuclei, vibrational excitation is a likely means of moving a system along a selected reaction coordinate, and indeed, there are experimental examples of bond-selected reactions in which different vibrations preferentially promote cleavage of one bond over another (4). These ideas about consumption and disposal of energy and about driving reac-

tions toward selected products are not fundamentally limited to single collisions in gases (5). They should also apply to reactions in liquids, on surfaces, and in more exotic environments such as clusters or superfluid helium droplets. For example, discovering the influence that the interaction of a few molecules bound in a van der Waals cluster or in a hydrogen-bonded oligomer has on a reaction is a step toward understanding chemical dynamics in a crowded environment such as a liquid.

Chemistry at interfaces presents the same questions about energy- and state-resolved processes. Scattering a molecular beam from a surface also removes much of the averaging present in a thermal reaction, and such experiments have observed the recoil direction and speed of reaction products and have determined the internal states of the scattered molecules (6). There are also examples of scattering molecules with carefully controlled translational energy (7) or in selected vibrational states (8–19) to determine their influence on reactivity. Pioneering experiments on liquid surfaces (20, 21) and on self-assembled monolayers (22) have taken a similar point of view, controlling the translational energy of the incoming particles and measuring the recoil velocities of the products to differentiate direct reactions from those in which molecules remain on the surface and exchange energy. These experiments on

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interfaces have followed the pattern of studying energy accommodation first and then moving on to reactions, and spectroscopic probes are now providing information about the internal states of molecules scattered from liquid surfaces (23, 24).

The theme of removing averaging to uncover the details of a reaction is equally appealing in liquids, but the meaning of a single collision is more complicated in an environment where the interactions between the molecules are nearly continuous (5). Thus, the distinction between intramolecular and intermolecular energy transfer is less obvious, and the frequency of encounters in a liquid, corresponding to a collision interval of  $\approx 100$  fs in a comparably dense gas, demands better time resolution with correspondingly reduced spectral resolution. Following the historical pattern in studying gas phase chemical reaction dynamics, energy transfer in liquids (25) has been a target of ultrafast spectroscopy, followed by studies of excited state isomerization and photodissociation (26). However, there are examples of time-resolved studies of bimolecular reactions in solution (27–30) that are the first steps toward addressing the full array of chemical dynamics questions in the complex environment of a liquid.

The goal of this Perspective is to illustrate the scope of state-resolved studies of molecular dynamics in gases and on surfaces and to look toward the prospects of extracting similar insights about reactions in liquids. Reviewing a significant portion of the work in all of those areas is beyond the scope of this article, but the contributions to this Special Feature of the Proceedings illustrate advances in many different aspects of chemical reaction dynamics. Here, we consider reactions of methane and its isotopologues as illustrations of state-resolved chemical dynamics in gases and on surfaces with a particular focus on the role of vibrational energy. Methane has become a touchstone for studying the dynamics of polyatomic molecules for both fundamental and practical reasons. It has well characterized spectroscopy, is amenable to vibrational excitation, and is simple enough for sophisticated theoretical calculations. The following discussion progresses from single collision studies in gases, to scattering experiments on surfaces, and finally comments briefly on the prospects in liquids.

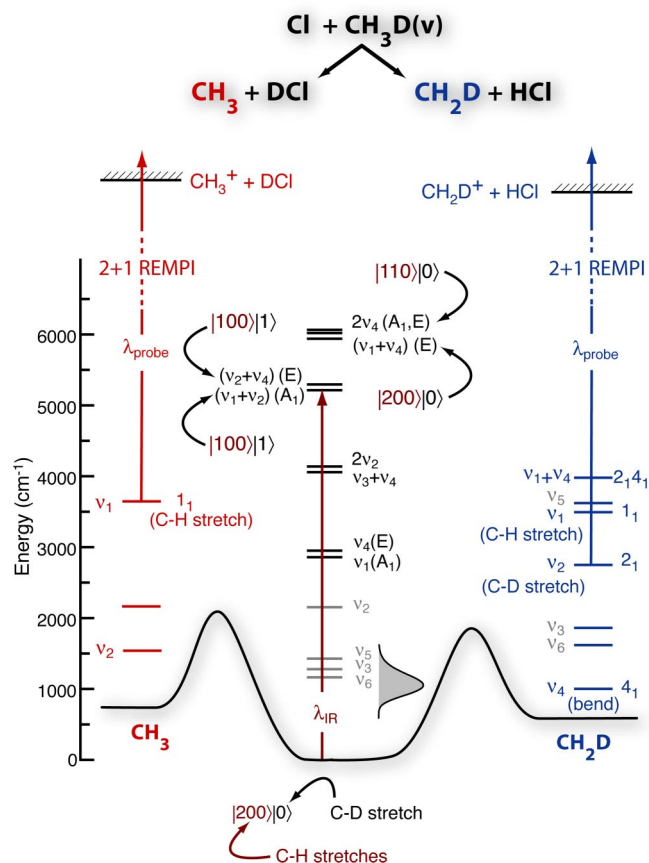
### Gas Phase Dynamics: Bimolecular Reactions of Methane with Chlorine

The abstraction of a hydrogen atom from methane by a chlorine atom,



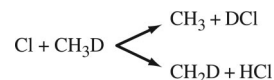
is endothermic by 7 kJ/mol ( $600 \text{ cm}^{-1}$ ) with a calculated barrier of  $\approx 20$  kJ/mol ( $1,800 \text{ cm}^{-1}$ ) (31, 32). The  $\approx 3,000\text{-cm}^{-1}$  C—H stretching vibration of methane provides enough energy to overcome the barrier, and, because the calculated transition state has a linear arrangement of C—H—Cl (33), stretching excitation in the C—H bond should contain motion along the hydrogen atom transfer coordinate. Because one of the goals is understanding the influence of vibrational excitation on bond cleavage, experiments often use partially deuterated methane isotopologues,  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ , or  $\text{CHD}_3$ , which have both C—H and C—D stretching vibrations that can promote transfer of the hydrogen atom or the deuterium atom, respectively.

Fig. 1 is a sketch of the reaction coordinate for  $\text{CH}_3\text{D}$  that shows the two reaction channels along with the vibra-



**Fig. 1.** Sketch along the reaction coordinates for the reaction of Cl with  $\text{CH}_3\text{D}$ . The energy levels marked in the center of the figure are the vibrational levels of  $\text{CH}_3\text{D}$ , and the black lines indicate the ones used for bond-selected reactions. There are both normal-mode notation and local-mode notation designations for the higher levels. In local-mode notation, the first three quantum numbers designate the excitation of a C—H stretching vibration, and the fourth quantum number gives the excitation of the C—D stretching vibration. The left side of the figure shows some of the vibrations of the  $\text{CH}_3$  product detected by (2 + 1) REMPI, and the right side gives the same information for the  $\text{CH}_2\text{D}$  product. The vertical arrows are examples of the vibrational excitation and probe transitions in the experiment.

tional levels of the reactant and of the two different methyl radical products,  $\text{CH}_3$  and  $\text{CH}_2\text{D}$ . The former comes from abstraction of the D atom and the latter from abstraction of one of the H atoms with the corresponding formation of DCl or HCl, respectively.



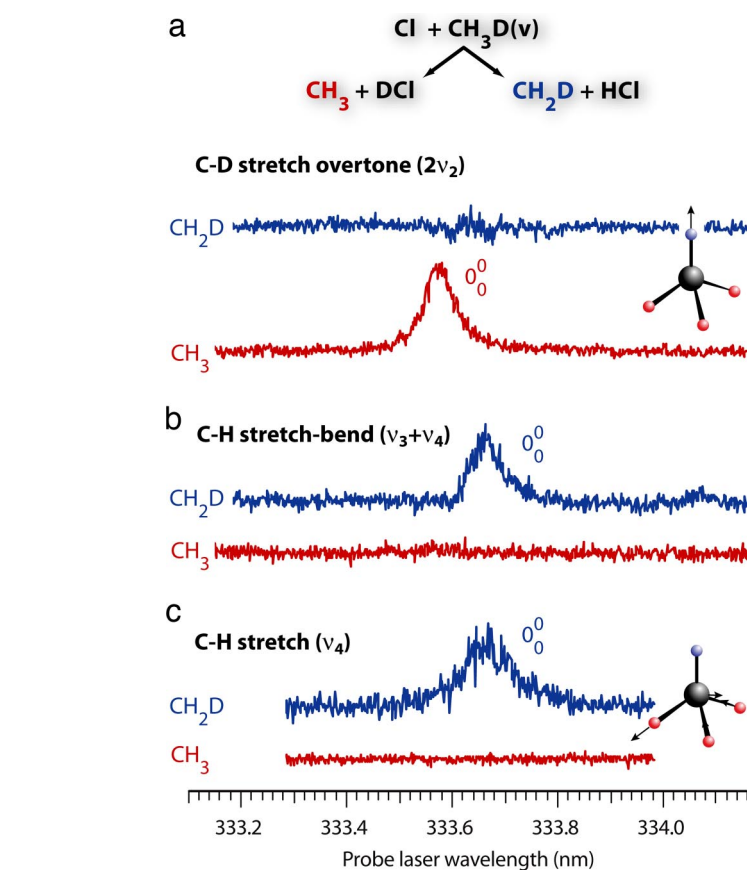
Either translational or vibrational energy is useful for overcoming the barrier, and experiments that control both of them can explore their relative efficacy (34). Studies of molecules with different initially excited vibrations can determine their ability to promote and direct the reaction, measurements of angular distributions can reveal the mechanism, and determination of product state populations can determine the fate of the energy initially deposited in

the system. The reaction of chlorine with methane is a system for which there are now answers to many of the questions of chemical reaction dynamics.

The minimum requirements for studying state-to-state reactions of vibrationally excited methane with chlorine are a source of Cl atoms, a means of preparing vibrationally excited methane, and a method of state-resolved detection of at least one of the reaction products. Further information on the angular distribution or differential cross-section requires controlling the direction of the relative velocity of the collision and determining the recoil direction of the products. Laser photolysis of Cl<sub>2</sub> is a convenient means of producing Cl atoms, particularly in experiments that use a single molecular beam containing a mixture of molecular chlorine and methane. The excess energy in the photolysis provides translational energy to the Cl atoms, and the polarization of the photolysis light imparts a laboratory direction to the recoiling Cl atoms, which permits extraction of angular distributions and differential cross-sections in favorable cases (35). Vibrational excitation of the methane reactant uses infrared laser light generated by a nonlinear mixing scheme, and state-resolved product detection relies on laser spectroscopy as well. State-specific detection of either the HCl or CH<sub>3</sub> products of the reaction of chlorine with methane is possible by using resonance enhanced multiphoton ionization (REMPI), and in the most advanced experiments, ion imaging provides the angle and speed distributions of the product. With sufficient translational energy resolution, these approaches allow the inference of the internal energy content of the unobserved product (36).

**Bond-Selected Reactions.** The preferential cleavage of a selected bond is one of the most intuitively appealing aspects of vibrational state-controlled chemistry. The simple conceptual basis for bond-selected chemistry is placing energy in a vibration that moves the system along a selected reaction coordinate to break one bond in preference to another.

Here, we consider molecular eigenstates of methane (or of an isotopologue) that meet that criterion. For example, in the CH<sub>3</sub>D system shown in Fig. 1, exciting a C—H stretching eigenstate should carry the system over the barrier to cleave the C—H bond to form the CH<sub>2</sub>D product, but exciting a C—D stretching eigenstate should promote formation of the CH<sub>3</sub> product. Indeed, measurements find exactly that behavior in all of the substituted isotopologues, CH<sub>3</sub>D (37–40), CH<sub>2</sub>D<sub>2</sub> (41,



**Fig. 2.** REMPI spectra of the CH<sub>2</sub>D (blue) and CH<sub>3</sub> (red) products of the reaction of CH<sub>3</sub>D in different vibrational levels with Cl atoms. (a) Spectrum obtained after excitation of the first overtone of the C—D stretch ( $2\nu_2$ ) of CH<sub>3</sub>D. (b) Spectrum obtained after excitation of a combination of the antisymmetric C—H stretch and a bending vibration ( $\nu_3 + \nu_4$ ). (c) Spectrum obtained after excitation of a combination of the antisymmetric C—H stretch ( $\nu_4$ ). In all cases, preparation of a state containing C—H or C—D stretching excitation leads to cleavage of the excited bond.

42), and CHD<sub>3</sub> (41, 43), as illustrated by the results for CH<sub>3</sub>D shown in Fig. 2. The traces are (2 + 1) REMPI signals from products of the reaction of the vibrationally excited CH<sub>3</sub>D obtained by monitoring parent ions of either the CH<sub>2</sub>D product (blue) or the CH<sub>3</sub> product (red) as a function of the ionization laser wavelength. As Fig. 2a shows, exciting the first overtone transition of the C—D stretch ( $2\nu_2$ ), which prepares an eigenstate that contains primarily C—D stretching excitation, yields predominantly CH<sub>3</sub> radicals from cleaving the C—D bond.

The data in Fig. 2c show the opposite behavior, in which excitation of the antisymmetric C—H stretching eigenstate ( $\nu_4$ ) leads solely to the CH<sub>2</sub>D product from cleaving the C—H bond. As shown in Fig. 2b, the ability of the initially excited vibration to promote cleavage of a selected bond survives even for excitation of the combination state containing both the C—H stretching and bending motions ( $\nu_3 + \nu_4$ ), which provides essentially the same energy as excitation of

the C—D stretching overtone. Data on all of the isotopologues suggest a simple picture in which excitation of a C—H or C—D stretching vibration accelerates the reaction compared with that for unexcited molecules and favors cleavage of the vibrationally excited bond.

**Mode-Selected Reactions and State-to-State Chemistry.** The observation that adding vibrational energy steers the reaction along one path raises questions about the influence of different vibrations and about the relative efficiency of translation compared with vibration. Measurements comparing the reactivity of CH<sub>3</sub>D molecules with the symmetric C—H stretching state ( $\nu_1$ ) excited to that of molecules with the antisymmetric C—H stretching state ( $\nu_4$ ) excited show that the symmetric stretch accelerates the reaction approximately seven times more efficiently than the antisymmetric stretch (38). This striking, and perhaps nonintuitive, difference is consistent with predictions about the reactivity of vibrationally excited water (44) and



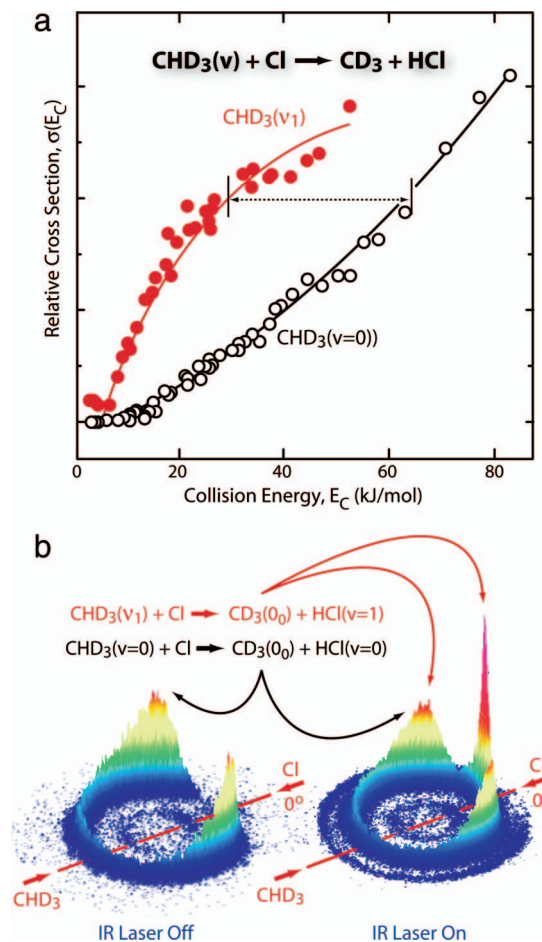
about the reactivity of vibrationally excited methane on Ni surfaces (45). Electronic structure calculations of the energies of the vibrations in  $\text{CH}_3\text{D}$  with Cl located at different distances along a C—H bond (38) bear out this analysis and confirm that the essential feature is the evolution of the vibrations in the target molecule as the Cl approaches.

The perturbation by the incoming Cl atom changes the initially excited symmetric stretching vibration into motion of the C—H bond pointing toward the incoming atom. However it changes the anti-symmetric stretching vibration into motion of the two C—H bonds pointing away from the incoming atom and makes the antisymmetric stretching state the less reactive of the two. This behavior is rooted in the change in symmetry of the system with the approach of the incoming atom (38), but the analysis uses only a single geometry compared with the actual measurement, which averages over geometries and impact parameters. Nonetheless, both the experimental result and the calculation point to the critical role that perturbation of the initially prepared vibrations by the incoming atom play in determining the reactivity of different vibrational states. Even bending excitation alone, with an energy of only  $1,300\text{ cm}^{-1}$ , enhances the reaction of Cl with  $\text{CH}_4$  or with  $\text{CH}_3\text{D}$  by approximately a factor of 2, again reflecting the coupling of vibrational energy during the collision (46).

What about the energy that does not couple into the reaction coordinate? We know that vibrational excitation promotes cleavage of the bond that contains substantial excitation, but there is good evidence that the surviving bonds are largely spectators to the reaction. For example, exciting combination bands in  $\text{CH}_3\text{D}$  (40) or  $\text{CH}_2\text{D}_2$  (41) that place energy in each of two equivalent C—H bonds leads to radical products in which the surviving bond retains its excitation. Exciting combinations that have stretching excitation in both the C—H and C—D bonds of  $\text{CH}_3\text{D}$  produces the same behavior in which the surviving bond, be it C—H or C—D, most often retains its initial vibrational excitation (47).

Vibrational excitation clearly enhances the reaction rate compared with that of molecules without vibrational excitation, but those measurements leave unanswered the question of the efficiency of vibrational energy compared with translational energy. A crossed molecular beam scattering experiment that independently controls the translational and vibrational energy has provided the answer for the reaction of Cl with  $\text{CHD}_3$  (34). In those experiments, a discharge source produces a

beam of Cl atoms and an infrared laser excites the C—H stretching vibration of some of the  $\text{CHD}_3$  molecules in the other beam. Varying the intersection angle of the beams changes the relative collision energy, and detecting the  $\text{CD}_3$  fragments by ion imaging after resonance enhanced multiphoton ionization determines the relative yields and angular distribution of the products. The notable results are that translation is as effective as a C—H stretching vibration in promoting the H atom abstraction and that energy in a bending vibration, obtained by heating the source, is more effective than energy in either C—H stretching excitation or in translation. Fig. 3a shows the relative reaction cross-section,  $\sigma(E_c)$ , as a function of collision energy,  $E_c$ , for ground state and vibrationally excited  $\text{CHD}_3$  molecules. The



**Fig. 3.** Reaction cross sections and angular distributions. (a) Relative reaction cross-sections for reaction of Cl with  $\text{CHD}_3$  molecules either in their ground vibrational state [ $\text{CHD}_3(v=0)$ , open points] or having their C—H stretch [ $\text{CHD}_3(v_1)$ , red points] excited. The horizontal line shows that 35 kJ/mol translational energy increases the reaction cross-section as much as a quantum of C—H stretching excitation. (b) Plots of the data from ion imaging of the vibrational ground state  $\text{CD}_3$  products from the reaction. In this coordinate system, the Cl beams comes from  $0^\circ$ , and the  $\text{CHD}_3$  beam comes from  $180^\circ$ . (Left) Data for scattering of molecules without vibrational excitation. (Right) Data, taken with infrared laser radiation present, are for scattering of vibrationally excited and ground state molecules. The sharp feature at  $0^\circ$  arises from scattering  $\text{CHD}_3(v_1)$  to form  $\text{CD}_3$  and vibrationally excited HCl. (Adapted with permission from ref. 34.)

dotted horizontal line in the figure shows that a  $3,000\text{-cm}^{-1}$  ( $36\text{ kJ/mol}$ ) increment in translational energy is just as useful as the same amount of vibrational energy at a relative translational energy of  $\approx 30\text{ kJ/mol}$ . An article in this Special Feature addresses issues of energy consumption and of the applicability of the Polanyi rules (48), originally obtained for reactions of atoms with diatomic molecules, to polyatomic reactants (49).

These scattering experiments also provide information on the angular distribution of the recoiling fragments by using ion imaging to capture the recoil direction and speed of the products. Fig. 3b shows the angular distribution of the  $\text{CD}_3$  from the reactions of ground or vibrationally excited  $\text{CHD}_3$  with Cl. The data clearly show that vibrational excitation changes the angular distribution

markedly. The  $\text{CD}_3$  from the reaction of ground state  $\text{CHD}_3$  primarily scatters to the side, as indicated by the two prominent features in the distribution for unexcited molecules, but some of the products from the reaction of vibrationally excited  $\text{CHD}_3$  scatter forward relative to the incoming molecule, as shown by the prominent feature at  $0^\circ$ . Thorough analysis shows that the sharp forward maximum is from scattering of  $\text{CD}_3$  accompanied by vibrationally excited  $\text{HCl}(\nu = 1)$ , which comes only from the reaction of the vibrationally excited  $\text{CHD}_3$ . This observation of additional strongly forward scattered vibrationally excited  $\text{HCl}$  agrees qualitatively with the differential cross-section extracted from earlier experiments that analyzed the projection of the laboratory velocity on the time-of-flight detection axis (35, 50).

### Surface Dynamics: Dissociation of Vibrationally Excited Methane on Ni

The single-collision experiments on methane and its isotopologues clearly illustrate the scope and possibilities in bond-selected bimolecular reactions and suggest the possibility of similar behavior for reactions on surfaces. Interaction with a surface involves more degrees of freedom, including phonon modes of the surface, than a collision with an atom, and there is the potential for extensive energy redistribution to degrade the selectivity. However, that behavior is not universally the case, as illustrated by incisive experiments on the dissociative chemisorption of vibrationally excited methane on Ni surfaces (9–18).

The essential questions are again the efficacy of vibrational energy compared with translational energy and the influence that vibrational excitation has on the course of the reaction. Vibrations that promote favorable geometry changes or bond cleavage potentially influence the dissociative chemisorption dramatically. The requirements for exploring the role of vibrations in reactions on surfaces are analogous to those for gas phase studies: the ability to prepare reactants, in this case a well characterized single crystal surface and a beam of vibrationally excited molecules, and a means of detecting the reaction of the vibrationally excited molecule. The complications of preparing and analyzing the surface make these experiments challenging but feasible (51–53).

**Bond-Selected Reactions.** The requirement of analyzing the chemisorbed species is a critical aspect of assessing possible bond selectivity in the dissociative chemisorption of vibrationally excited molecules. Recent experiments have accomplished that goal by using reaction

with subsurface D atoms to identify the species formed in the adsorption of vibrationally excited methane on Ni (111) (18). Those measurements use a high-resolution, continuous laser to excite some of the  $\text{CHD}_3$  molecules in a molecular beam with a quantum of C—H stretching vibration ( $\nu_1$ ). Dissociative chemisorption of these molecules could leave either  $\text{CD}_3$  or  $\text{CHD}_2$  fragments on the surface, depending on the identity of the broken bond. Because methyl radicals react with subsurface atoms, it is possible to identify the fragment on the surface by mass spectrometric detection of the methane released during temperature-programmed desorption from a sample containing subsurface deuterium atoms. The key is detecting desorption of either  $\text{CD}_4$  or  $\text{CHD}_3$  to determine how the  $\text{CHD}_3(\nu_1)$  molecules in the beam dissociate on the surface.

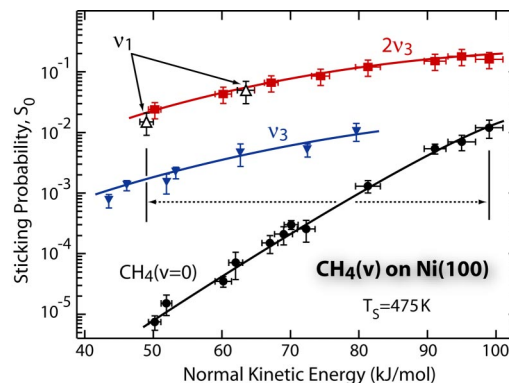
The measurements show that excitation of the C—H stretch in  $\text{CHD}_3$  favors breaking the excited bond by more than a factor of 30 (18), in analogy to the bond-selective reaction of vibrationally excited  $\text{CHD}_3$  and other isotopologues in single collisions with Cl. An important aspect of this result and those on mode-selected reactions described below is that the interaction with the surface does not destroy the selectivity by rapid vibrational energy transfer out of the C—H stretch to other vibrations in the molecule or to the surface.

**Mode-Selected Reactions.** The dissociative chemisorption of methane on Ni also tests ideas about mode-selective reactions, again in analogy to the gas phase investigations, and several studies have made detailed comparisons of different initial vibrations. The two broad ques-

tions are the same as described for bimolecular reactions: Do certain vibrations promote chemisorption preferentially? How effective is vibrational energy compared with translational energy?

Experiments using a Ni(100) surface and  $\text{CH}_4$  molecules with the antisymmetric C—H stretching vibration ( $\nu_3$ ) excited show that dissociation is 1,600 times more likely than for vibrational ground state molecules having the same translational energy (9–11). An informative comparison, analogous to the one described above for gas phase reactions, is with  $\text{CH}_4$  molecules having a quantum of symmetric stretch ( $\nu_1$ ) excitation. Because the symmetry of  $\text{CH}_4$  forbids infrared excitation of the symmetric stretch, the experiments use Raman excitation to prepare the vibrationally excited molecules. They show that symmetric stretch excitation promotes reaction 10 times more effectively than antisymmetric stretch excitation (16), as Fig. 4 illustrates. This increase for  $\text{CH}_4(\nu_1)$  is consistent an adiabatic reaction picture in which the interaction with the surface perturbs the initially excited vibration, converting the symmetric stretch into motion in the bond directed toward the surface and, thus, promoting dissociative adsorption (45).

Excitation of higher levels of vibration or other vibrational modes also alters the reactivity, as demonstrated by experiments that excite the first overtone of the antisymmetric stretching vibration ( $2\nu_3$ ) (12). At a translational energy of 72 kJ/mol, the dissociative adsorption probability of  $\text{CH}_4(2\nu_3)$  on Ni(100) is 2 orders of magnitude larger than that for ground state molecules, and at a translational energy of 12 kJ/mol, it is 4 orders



**Fig. 4.** The sticking probability for  $\text{CH}_4$  in different vibrational states on Ni(100). The data are for molecules in their ground state [ $\text{CH}_4(\nu = 0)$ , black points], molecules with a quantum of antisymmetric C—H stretch excitation [ $\text{CH}_4(\nu_3)$ , blue triangles], molecules with two quanta of antisymmetric stretch excitation [ $\text{CH}_4(2\nu_3)$ , red squares], and molecules with a quantum of symmetric stretch excitation [ $\text{CH}_4(\nu_1)$ , open black triangles]. A quantum of symmetric excitation is  $\approx 10$  times more efficient than a quantum of antisymmetric stretching excitation. The horizontal line shows that a quantum of symmetric stretching excitation (36 kJ/mol) produces as large a change in the sticking probability as 50 kJ/mol translational energy. (Adapted with permission from ref. 16.)

of magnitude larger. The enhancement over molecules excited with a single quantum of antisymmetric C—H stretching excitation ( $\nu_3$ ) is approximately a factor of 10, comparable with that provided by excitation of the symmetric C—H stretch ( $\nu_1$ ). Fig. 4 summarizes all of these results in a plot of the sticking probability as a function of the kinetic energy associated with the component of the velocity normal to the Ni(100) surface. The symmetric stretch ( $\nu_1$ ) and first overtone of the antisymmetric stretch ( $2\nu_3$ ) give methane molecules similar sticking coefficients and translational energy dependences. One quantum of the symmetric stretch ( $\nu_3$ ) is 10 times less effective, but the variation with the translational energy is similar. The reactivity of ground state molecules varies more strongly with translational energy, which produces the translational energy-dependent enhancements described above.

All of these observations and several others point to the nonstatistical nature of the dissociative chemisorption. The horizontal arrow in the figure shows that one must add an additional 50 kJ/mol translational energy to ground state molecules impinging on Ni(100) to produce the same change in reactivity as adding  $\approx 36$  kJ/mol in the symmetric stretching vibration ( $\nu_1$ ) to molecules having 50 kJ/mol translational energy (16). Thus, the reactivity of  $\text{CH}_4(\nu_1)$  with 50 kJ/mol translational energy is approximately the same as that of ground state molecules [ $\text{CH}_4(v = 0)$ ] with 100 kJ/mol translational energy. The data in the figure also suggest that adding  $\approx 35$  kJ/mol translational energy to these ground state molecules produces the same change as adding a single quantum of antisymmetric stretching vibration ( $\nu_3$ ), making the addition of energy to translation or antisymmetric stretching comparably effective for  $\text{CH}_4$  molecules that already have a translational energy of 50 kJ/mol. Because the reactivity of ground state methane varies differently with translational energy than that of vibrationally excited methane, the comparisons of the different forms of excitation depend on the translational energy, as is also the case for the bimolecular reaction of  $\text{CHD}_3$  with Cl described above.

Just as the effects of excitation vary with the identity of the atomic reaction partner in gas phase experiments, the identity of the surface matters for dissociative chemisorption. For example, in the case of Ni(111), ground state molecules require 49 kJ/mol translational energy to produce the same increase in the sticking probability as caused by the 36-kJ/mol antisymmetric stretching vi-

bration ( $\nu_3$ ) (14). This situation contrasts with that for Ni(100), where energy in translation and vibration are comparably effective. Changing the identity of the surface has an even more dramatic effect than changing the crystal face on which the reaction occurs. The enhancement of more than 3 orders of magnitude for  $\text{CH}_4(2\nu_3)$  on Ni(111) decreases to approximately an order of magnitude on Pt(111) (17).

Another manifestation of strong mode selectivity is the effect of exciting other vibrations. The second bending overtone ( $3\nu_4$ ) enhances the reactivity considerably less than either of the stretches despite containing  $\approx 30\%$  more energy (15). The distribution of excitation among the potentially reactive bonds alters the dissociation probability as well. Molecules of  $\text{CH}_2\text{D}_2$  containing 2 quanta of excitation in one C—H bond are five times more reactive than those having a single quantum of excitation in each of two bonds (13). All of these measurements show that a statistical model of the reaction, which predicts that all forms of excitation produce comparable changes in the reactivity, does not describe the dissociative adsorption of  $\text{CH}_4$  on Ni. Collisions with the surface not only fail to equilibrate translational and vibrational energy completely, but they also do not remove the differential reactivity of the vibrational modes.

### A Road Ahead: Chemical Reaction Dynamics in Liquids

These examples of studying the dynamics of vibrationally excited molecules in gases and on surfaces lead to the prospect of studying the analogous processes in liquids. The same questions about the influence of vibrational energy on reactivity, energy consumption, and energy disposal present themselves, but the differences in the environment change the experimental approach and part of the conceptual framework. Studying the fate of an initially energized molecule requires time resolution on the order of the characteristic few hundred femtosecond encounter time, and modern ultrafast laser technology puts experiments in that regime. The most extensive studies of vibrational dynamics in liquids follow the historical pattern of first assessing energy transfer (25), and there are recent examples (54–69) that particularly address the relaxation of C—H stretching excitations. The general picture that emerges from these studies is that in relatively weakly interacting solvents, such as chloroform, the vibrational state structure and couplings of the molecule influence the energy flow within the initially excited molecule most strongly.

Interactions with the solvent play a secondary role, perhaps by slightly altering the state structure of the excited molecules and are more important in determining the rate of energy flow out of the initially excited molecule. Intramolecular energy flow times in these systems range from a few ps to 50 ps, depending on the molecule and initial level of vibrational excitation, and intermolecular energy transfer times range from tens to hundreds of ps. Typically, the time scales for energy flow within the molecule and into the solvent differ by at least a factor of 5.

There are only a few examples of studying bimolecular reactions in solution with time resolution comparable with these energy transfer times. The pioneering work used picosecond-duration pulses to study the reactions of Cl with cyclohexane ( $\text{C}_6\text{H}_{12}$ ) (27) and CN with chloroform ( $\text{CHCl}_3$ ) (28). Those measurements detected the abstraction products, HCl in the first case and either HCN or ClCN in the second case. The experiment on the reaction of CN with  $\text{CDCl}_3$ , which produces some vibrationally excited DCN, was the first measurement of vibrational energy disposal for a bimolecular reaction in solution. In favorable cases, it is possible to extract the rates of the reactions by observing the loss of the reacting radical, and there are examples of measuring rates from Cl atom decay (29) as well as HCl formation (30). One interesting result of a time-resolved study of 16 different molecules (alkanes, alcohols, and chloroalkanes) is that scaling relations designed for gas phase reactions often predict the relative rates in solution, at least for a relatively weakly interacting solvent (29). Thus, these experiments set the stage for studies of the chemical reaction dynamics of vibrationally excited molecules in solution in which one excites a C—H stretch and monitors the change in rate, the identity of the products, and the energy disposal in the products. The same questions about dynamics along with new ones about the role of the solvent arise in reactions in liquids and provide additional tests of models of the details of chemical reactions.

### Concluding Remarks

The bond- and state-selected reaction dynamics of methane and its isotopologues are remarkably similar in the abstraction of hydrogen by an attacking chlorine atom in a single collision and in the dissociative adsorption on a metal surface. Both reactions are bond-selective processes in which initial preparation of a molecular eigenstate containing a large component of C—H



stretching results in preferential cleavage of that bond. For example, it is possible to cleave either the C—H or C—D bond in the reaction of Cl with CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, and CHD<sub>3</sub> and, similarly, to use initial excitation of the C—H stretch to promote dissociation of CHD<sub>3</sub> to CD<sub>3</sub> and H on a Ni surface. Different vibrational modes, such as the symmetric and antisymmetric stretches in CH<sub>3</sub>D or CH<sub>4</sub>, lead to very different reactivities, and molecules with the symmetric stretching vibration excited can be as much as 10 times more reactive than ones with the antisymmetric stretch excited. The key to this behavior is the change in the vibrational motion induced by the interaction with the atomic reaction partner or the surface.

These similarities raise a final question: Is there something special about

methane that produces the observed mode- and bond-selected reaction dynamics? One important aspect is the relatively isolated, high-frequency C—H and C—D stretching vibrations in methane and its isotopologues. There can be specific anharmonic resonances that couple a few states, but in general the molecular eigenstates are not highly mixed. Rather they contain predominantly stretching motion of the bond to the light atom. These favorable characteristics of high-frequency vibrations make them particularly suitable for the mode- and bond-selected chemistry. Although methane is a very favorable case, many of the same considerations apply to other molecules. Similar characteristics for these vibrations in solution, where energy transfer studies find rela-

tively slow relaxation of C—H stretching vibrations, suggest them as likely candidates for vibrationally driven chemistry in liquids. The combination of laser preparation and spectroscopic detection demonstrates the possibility of vibrationally controlled chemistry and illustrates the detailed understanding of chemical reaction dynamics that such approaches provide.

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