Reaction Mechanisms

Effects of Bending Excitation on the Reaction of Chlorine Atoms with Methane**

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Many chemical reactions are accelerated by heating the reagents. This effect is caused by more energy being partitioned into the reagents' electronic, translational, vibrational, and rotational degrees of freedom that ultimately becomes available for overcoming the reaction barrier. Which degrees of freedom are most effective at driving chemical reactions? For endoergic reactions involving an atom and a diatom, Polanyi[1] showed that vibrational excitation of the reagent diatom is the most effective means of overcoming the reaction barrier because the stretching motion along the diatomic internuclear axis efficiently couples to the reaction coordinate, that is, the set of motions that transforms the reagents into the products. For reactions involving polyatomic reagents, the simple concepts associated with atom + diatom reactions become complicated by the $3N-6$ extra degrees of freedom available for internal motions of a nonlinear N-atom polyatomic molecule. Intuitively, stretching vibrations of polyatomic molecules are expected to have the largest effects on abstraction reactions because energy is placed directly into the breaking bond and they most resemble the stretching vibration of diatomic molecules. This notion is confirmed for the $Cl + CH_4$ reaction, where one quantum of antisymmetric stretch excitation enhances the reaction by a factor of approximately 30.[2]

The effects of reagent bending vibrations on chemical reactions, on the other hand, are less intuitive because they require the concerted motion of three or more atoms in the reagent. Is the energy in these modes available for overcoming the reaction barrier? Unlike the stretching vibrations, the bending vibrations are low-frequency and consequently have less energy. They do not obviously map onto the reaction coordinate. Moreover, it is known from previous studies of the $Cl + CH_4$ reaction[3] that internal energy placed in more than one C–H stretch of methane remains localized in the methyl product, that is, all the internal energy is not available to appear in internal motion of HCl or in translational motion of the escaping product pair. The effects of bending vibrations have been largely unexplored experimentally despite the fact that these low-frequency vibrations are more easily populated at thermal temperatures. To date, the influence of bending vibrations on chemical reactions remains ambiguous, and many theoretical studies of direct polyatomic reactions treat the system in reduced dimensionality, simply assuming that these low-frequency modes play little or no role.[4]

Herein we present direct measurements of the effects of bend-excitation on an atom + polyatom reaction system under single collision conditions. We have chosen the $Cl + CH_4$ reaction [Eq. (1)] both as a prototype and for its practical importance to combustion and atmospheric chemistry. This reaction is thought to be responsible for the removal of chlorine in the stratosphere, and kinetic studies have shown a nonlinear variation of the logarithm of the rate constant versus the reciprocal of the temperature (Arrhenius plot).[5]

$$Cl + CH_4\,(\nu_4 = 1) \rightarrow HCl + CH_3 \qquad (1)$$

Contrary to intuitive expectations, we find that excitation of the low-frequency $CH_4(\nu_4{=}1)$ and $CH_3D(\nu_3{=}1)$ bending vibrations enhances the cross section for reaction with Cl atoms by a factor of two or more. This enhancement, which is constant over the collision-energy range 0.12 eV to 0.26 eV, implies that shearing motions, in addition to stretching

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[**] This material is based upon work supported by the National Science Foundation under Grant No. CHE-0242103. H.A.B, J.P.C., and M.R.M. thank the National Science Foundation for graduate fellowships. H.A.B. also acknowledges Stanford University for the award of a Stanford Graduate Fellowship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200462837

motions, can facilitate C–H bond cleavage in this direct reaction. Moreover, the nonlocalized motion in the methane reagent is transferred almost exclusively to translational motion of the escaping products, which is in sharp contrast to theoretical calculations[6–9] that predict formation of methyl radicals predominantly excited into the umbrella bending mode. We also observe both H-atom and D-atom abstraction products from the Cl + $CH_3D(\nu_3{=}1)$ reaction, indicating that the reaction is not bond selective although the C–H and C–D motions are different in bend-excited CH_3D.

The Cl + CH_4 reaction is slightly endoergic, $\Delta H = 7.2\,\mathrm{kJ\,mol^{-1}}$ (0.07 eV),[10] and has an estimated activation barrier of $32.8\,\mathrm{kJ\,mol^{-1}}$ (0.34 eV).[11] The best estimate of the vibrationally adiabatic ground-state barrier, which is a better predictor of threshold energies neglecting tunneling, is $16.4\,\mathrm{kJ\,mol^{-1}}$ (0.17 eV).[8,11] Theoretical calculations[6–9] have predicted that the umbrella bending mode should enhance the reaction rate by lowering the barrier. Experimental verification has been lacking in part because selective preparation of low-frequency modes has proven difficult. The few experimental measurements[12–16] that probe the effects of bend excitation on the Cl + CH_4 reaction have been performed using indirect methods, leading to disparate results. Early studies[12] showed no enhancement from the bending mode, whereas more recent measurements[14,15] estimate the enhancement factor to be approximately 200 or approximately 3, respectively, based on studies of residual bend-excited methane present in their molecular beam. We have examined the Cl + $CH_4(\nu_2{+}\nu_4)$ reaction and showed the $\nu_2+\nu_4$ mode to be at least 15% as reactive as the ν_3 (antisymmetric stretch) mode.[16] None of these more recent measurements, however, unambiguously distinguishes the effects of the ν_2 and ν_4 bending modes, although Zhou et al.[15] suggest that the ν_4 mode is the more reactive. Herein, we use a novel IR source to excite directly the $\nu_4 = 1$ mode, which permits us to demonstrate explicitly that bend excitation of methane enhances the Cl + CH_4 reaction.

Figure 1 shows an action spectrum obtained by monitoring the CH_3 reaction signal on the Q branch bandhead of the 2 + 1 resonance-enhanced multiphoton ionization (REMPI) 0_0^0 band while scanning the IR light over the CH_4 4_0^1 bending band. The action spectrum successfully reproduces the absorption spectrum, albeit at a significantly lower temperature (ca. 80 K). This result demonstrates that the umbrella bending vibration (ν_4) enhances the Cl + CH_4 reaction. To determine the enhancement factor, we position the IR laser on the 4_0^1 Q branch bandhead, scan the probe laser over the CH_3 0_0^0 Q branch, and measure the ratio of the IR-on signal (S_{ON}) to the IR-off signal (S_{OFF}). We note that S_{ON} has contributions from both the IR-enhanced reaction and the ground-state reaction, that is, $S_{ON} = \sigma_{GS}(1-f) + \sigma_{IR}f$, where σ_{GS} and σ_{IR} are the cross sections of the ground and vibrationally excited reactions, respectively, and f is the fraction of methane molecules pumped to the vibrationally excited state. In contrast, S_{OFF} arises purely from reaction with ground-state methane, $S_{OFF} = \sigma_{GS}$. Solving for the enhancement factor $F = \sigma_{IR}/\sigma_{GS}$ gives $F = (S_{ON}/S_{OFF} + f - 1)/f$. Assuming $f = 0.5$ (complete saturation of the transition), we find that although the action spectrum in Figure 1b suggests that individual rotational lines are power broadened, the power dependence of the 4_0^1 Q branch is nearly linear, indicating that all the Q-branch lines are not saturated. Thus, a factor of two is strictly a lower bound for the enhancement. Using a more realistic estimate of the fraction pumped, $0.1 < f < 0.3$, the enhancement of bend excitation is $F(0.16\,\mathrm{eV}) = 3 \pm 1$, which is in excellent agreement with the value Zhou et al. determined by more indirect means at a collision energy of 0.20 eV.[15]

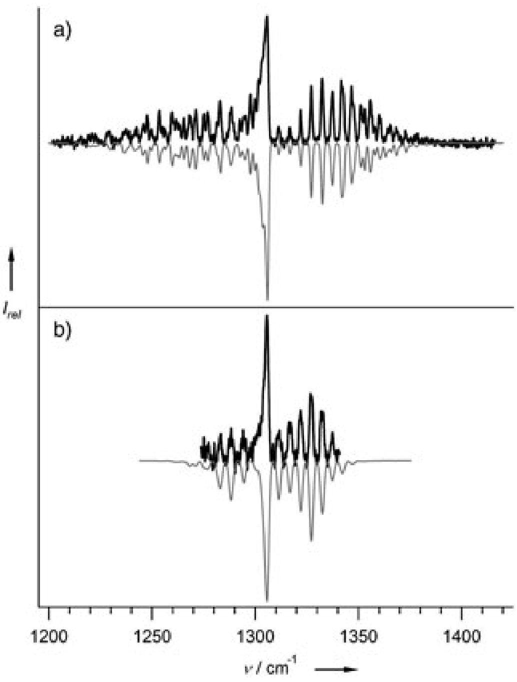

Figure 1. IR spectra of the CH_4 4_0^1 infrared band. a) The upper trace (black, thick line) is the room temperature photoacoustic absorption spectrum, and the lower trace (gray, thin line) is the simulated absorption spectrum at 300 K from the HITRAN database[21] convoluted with a Gaussian line width (1.2 cm^{-1}). b) The upper trace (black, thick line) is the action spectrum (0.16 eV) obtained by monitoring the $CH_3(\nu{=}0)$ reaction products while scanning the vibrational excitation laser wavelength. The lower trace (gray, thin line) is the simulated absorption spectrum at 80 K convoluted with a Gaussian line width of 2.0 cm^{-1}; the larger line width is most likely due to power broadening.

We have measured the enhancement factor over a range of center-of-mass (CM) collision energies (0.12–0.25 eV) and found it to be constant within our experimental uncertainty (Figure 2). This result is particularly surprising for the lowest collision energies because we expect a larger enhancement near the threshold, which is estimated to lie in the middle of the experimental energy range.[8,11] Theoretical calculations[6–9] have predicted the umbrella bending vibration to lower the barrier and thus significantly enhance the reaction rate. In particular, Corchado et al.[8] have calculated that excitation of the ν_4 vibration lowers the barrier by approximately 0.02 eV, which should have a significant effect near the energy threshold. Their calculations, however, do not provide a quantitative estimate of the enhancement nor do they predict the lack of energy dependence. In light of these results, we believe that the energy of the bending vibration is

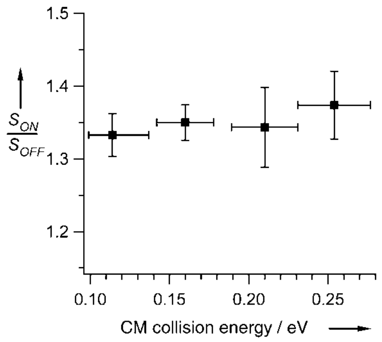

Figure 2. Ratio of S_{ON} to S_{OFF} as a function of center-of-mass (CM) collision energy. This ratio is the direct experimental measurement and makes no assumptions about the fraction of molecules pumped to $CH_4(\nu_4)$. The vertical uncertainty is the 95% confidence interval of replicate measurements, and the horizontal uncertainty represents the full width at half maximum height (FWHM) of the collision energy distributions[22] assuming a translational temperature of 10 K.

not available to overcome the reaction barrier without a minimal amount of translational energy.

Theoretical calculations[7] also predict forward-scattered CH_3 products, which is in agreement with our results (Figure S1 in the Supporting Information). Both the CH_3 vibrational distributions and angular distributions from the bend-excited reaction are essentially identical to those of the ground-state reaction, indicating that the energy of the bending vibration is transferred into translation and the new HCl bond. Although this result might be unexpected considering the nonlocalized motion of the bending vibration, Corchado et al.[8] have shown theoretically that the internal motion of the methane reagent can be rearranged upon approach of the Cl atom and thus couple energy into the new HCl bond. The same calculations,[6–8] however, have also predicted the $CH_4(\nu_4)$ umbrella bend to promote umbrella-bend-excited $CH_3(\nu_2)$ products, in contrast to our observations (Figure 3) that most of the products are formed in the vibrationless ground state with only a small fraction of the products formed with umbrella bend excitation ($\nu_2 = 1$).

Although the umbrella bending motion does not obviously participate in the bond breaking or forming process, the coupling of the umbrella bend mode to the reaction coordinate might be expected because the methyl radical must change from pyramidal to planar geometry as the reaction proceeds. On the other hand, the enhancement may arise simply because more energy is available for the reaction. To investigate these possibilities, we examine the effects of umbrella bend excitation on the Cl + $CH_3D(\nu_3{=}1)$ reaction, where the predominant motion arises from the three C–H oscillators with little movement of the C–D oscillator. If the reaction is enhanced by facilitating the methyl radical geometry change, then the D-atom abstraction channel (CH_3) should dominate because the CH_3 fragment motion more closely maps onto the product state geometry. If the reaction is enhanced by placing extra energy into the system, then the H-atom abstraction channel (CH_2D) should dominate because the energy is localized into the C–H bonds. Figure 4 shows that both product channels are enhanced by bend-excitation, with only a slight preference for the H-atom abstraction channel. Thus, we conclude that neither mechanism alone accounts for what is observed. Furthermore, these

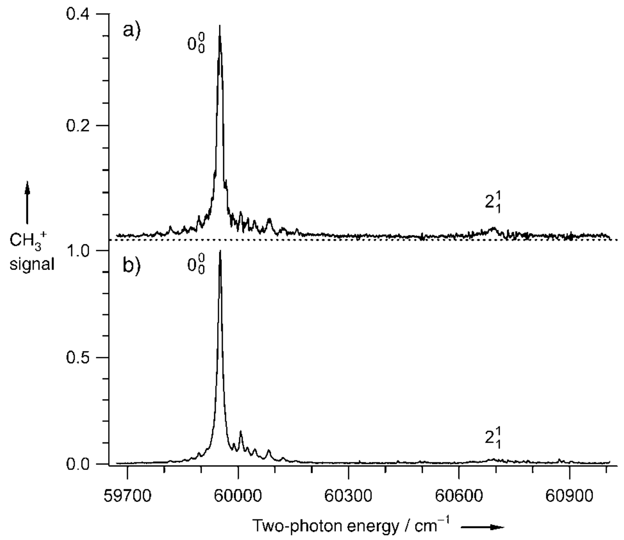

Figure 3. (2+1) REMPI spectra of the methyl radical products from the Cl + CH_4 reaction at a collision energy of 0.16 eV. a) the spectrum from the bend-excited reaction (obtained by subtracting S_{OFF} from S_{ON}) and b) the spectrum from the ground-state reaction (S_{OFF}). The signals have been normalized such that the maximum ground-state reaction signal is 1.

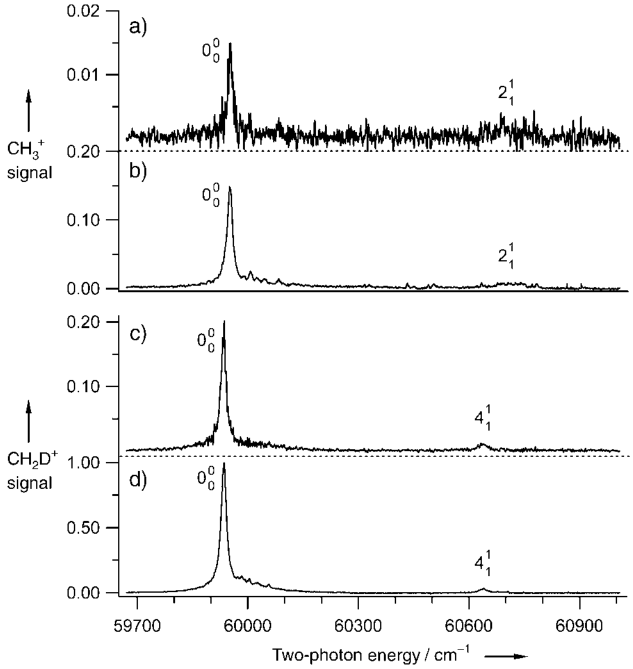

Figure 4. (2+1) REMPI spectra of the methyl radical products from the Cl + CH_3D reaction at a collision energy of 0.16 eV. a) and b) show the D-abstraction channel, c) and d) show the H-abstraction channel. Panels (a) and (c) show the spectra from the bend-excited reaction and panels (b) and (d) show the spectra from the ground-state reactions. The signal intensities have been normalized such that the maximum ground-state signal of the CH_2D product is 1.

results also suggest that the approach of the Cl atom rearranges the initial vibrational motion of the methane reagent. The lack of bond selectivity is in striking contrast to the bond selectivity observed in the stretch-excited reactions, where excitation of a C–H stretching motion in methane leads almost exclusively to H-atom abstraction by the Cl atom.[2,17] As expected, the bending motions are not nearly as efficient at providing chemical control because the vibrations are not as localized. These results help to explain why the optimum pulse shapes for laser control of chemical reactions are often so complex in form.[18]

We have demonstrated that excitation of the ν_4 vibration significantly enhances the cross section of the $Cl + CH_4$ reaction. As a result, we might expect the $CH_4 \nu_2$ vibration to have similar effects. Theoretical calculations[8] and indirect experimental measurements[15] have suggested, however, that the ν_2 vibration is less effective at promoting reaction. Clearly, more work is needed to understand the effects of low-frequency bending motions on polyatomic chemical reactions.

Experimental Section

We supersonically expand a 1:4:7 mixture of molecular chlorine, methane (CH_4 or CH_3D), and helium into the extraction region of a Wiley-McLaren time-of-flight (TOF) spectrometer.[19] The vibrational state of methane is prepared by an IR laser that is generated using BBO and GaSe nonlinear crystals. The reaction is initiated by photolysis of Cl_2 with linearly polarized light (303 nm–386 nm), which produces monoenergetic Cl atoms primarily in their ground electronic state ($^2P_{3/2}$).[20] After a delay of 80 ns, the products are state selectively ionized by 2 + 1 resonance-enhanced multiphoton ionization (REMPI), separated by mass, and detected by microchannel plates. The reactive signal from vibrationally excited methane is separated from the ground-state reactive signal by turning the IR light off and on and subtracting the resultant signals on a shot-by-shot basis.

The IR radiation required to prepare the vibrational state of methane is generated in a two-step process involving difference-frequency generation (DFG, see Supporting Information). Near-IR light at $\lambda = 1.24$ μm is first generated by DFG by combining the 1.064 μm fundamental of a Nd^{3+}:YAG laser with the output of a dye laser (Exciton R590/R610 mix) in a BBO crystal. The near-IR radiation is then combined with another 1.064 μm beam in a GaSe crystal to produce approximately 150 μJ of tunable light between 7–10 μm. The photolysis wavelengths are generated by mixing a dye laser output (Exciton R610) with 1.064 μm light in a BBO crystal, by doubling the output of a dye laser (Exciton R610, DCM, or LDS698), or by using the third harmonic of a Nd^{3+}:YAG laser. The probe laser light is generated by doubling the output of a dye laser (Exciton DCM/LDS698 mix). The IR light is focused into the chamber using an $f = 15$ cm BaF_2 lens, and the photolysis and probe lasers are focused using separate $f = 25$ cm fused silica lenses.

Received: December 6, 2004

Keywords: gas-phase reactions · kinetics · molecular dynamics · reaction mechanisms · vibrational spectroscopy

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