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Vibrational Control in the Reaction of Methane with Atomic Chlorine

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Driving a chemical reaction to a specific, desired product continues to be a central theme of chemistry. If we picture a chemical reaction as the transformation from reagents to specific products along a minimum energy path called the reaction coordinate, an intuitive way of driving the reaction to a desired product is to excite one of the reagents so that its internal motion is along the reaction coordinate.[1] Depending on the nature of the transition state, the vibrational mode of a reagent along the reaction coordinate can be as simple as a bond stretch of one of the reagents or it can be as complex as the collective motion of the overall reagent. By studying the effect of vibrational excitation on the chemical reaction, we not only test the concept of vibrational control but also learn how the reaction takes place.

To date, only a few experimental realizations of vibrational control of simple chemical reactions have been achieved. The first example of controlling a reaction in which different vibrational motions of the reagents are excited is H + HOD.[2,3] These studies showed that vibrational excitation of the OH bond in HOD leads almost exclusively to the H_2 + OD product channel, whereas the excitation of OD stretching produces the HD + OH products. Similar results were reported on Cl + HOD.[4] These results indicate that the unexcited part of the molecule acts merely as a *spectator*; it plays no role in influencing the outcome of the reaction. The effectiveness of vibrationally controlled chemistry as applied to the reactions involving larger, more complex molecules remains an unsettled issue thus far, partly because of the scarcity of examples. Some limited selectivity has also been demonstrated in various ion−molecule and gas−surface reactions.[1b]

In this communication, we report on the vibrational control of the Cl + CH_4 reaction and its partially deuterated relatives. We prepare methane either with one quantum in each of two different C−H stretches, called the $|11\rangle$ state, or with two quanta in one C−H stretch, called the $|20\rangle$ state (see Figure 1A). We find that C−H bond activation leads exclusively to H-atom abstraction for partially deuterated methanes. Also, different C−H stretching modes of methane lead to different vibrational states of the methyl radical product. Thus, this work represents an important extension of reagent vibrational steering in chemical reactions.

In this study, we used direct infrared excitation of methane to prepare either the $|11\rangle$ or the $|20\rangle$ state. The CH_4 was excited to the $|11\rangle$ state,[5] and CHD_3 was excited to the $|20\rangle$ state.[6] Neither the excitation of CH_4 to the $|20\rangle$ state nor the excitation of CHD_3 to the $|11\rangle$ state was feasible because these transitions are too weak. For CH_2D_2, we can prepare both the $|11\rangle$ and the $|20\rangle$ states.[7]

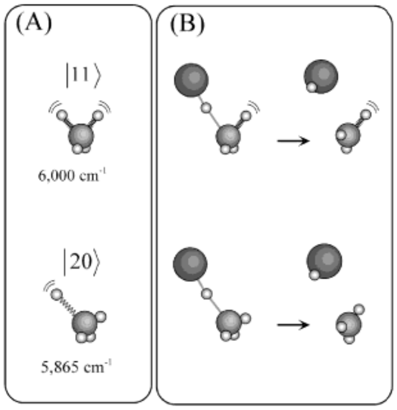

Figure 1. (A) Vibrational modes of methane used in this study, and the approximate frequencies of IR transitions. In the $|11\rangle$ state shown at the top each of the two C−H oscillators in the methane have one stretching quantum (CH_4, 6000 cm^{-1}; CH_2D_2, 5999 cm^{-1}). In the $|20\rangle$ state shown at the bottom only one C−H oscillator in the methane has two stretching quanta (CH_2D_2, 5879 cm^{-1}; CHD_3, 5865 cm^{-1}). (B) Schematic of the reaction mechanism. Methane prepared in the $|11\rangle$ state mainly produces the C−H stretch-excited methyl radical, whereas methane prepared in the $|20\rangle$ state leads to the ground-state methyl radical.

These two states are close in energy (~6000 cm^{-1} for $|11\rangle$ and ~5900 cm^{-1} for $|20\rangle$), but they correspond to quite different vibrational motions (see Figure 1A). It must be cautioned that the actual vibrational motion of the methane is not entirely the localized motion of a C−H oscillator because the vibrational eigenstate we prepare has some normal-mode character.[5a] Nevertheless, we found it sufficient to use the local mode labeling of vibrational motion in methane for the interpretation of the results.

Experimental details can be found in previous publications;[8] only a brief description is given here. A 1:4:5 mixture of molecular chlorine (Matheson, research grade, 99.999%), methane (Matheson, research purity, 99.999%), and helium (Liquid Carbonic, 99.995%) gases was expanded supersonically into the extraction region of a time-of-flight (TOF) mass spectrometer. Methane, CHD_3, and CH_2D_2 (Cambridge Isotopes Laboratory, >98% isotopic purity) were excited to the first overtone stretching modes by pulsed, tunable IR radiation (~1.6 μm, Q-branch band head). The IR bandwidth is 1 cm^{-1}, which is narrow compared to the separation between the $|11\rangle$ and the $|20\rangle$ states. The Cl_2 was photolyzed by a 355-nm laser beam, generating fast ground-state ($^2P_{3/2}$) chlorine atoms with a center-of-mass collision energy of 1200 cm^{-1}. After a 100 ns delay for the accumulation of products, the resulting methyl radicals were probed by 2 + 1 resonantly enhanced multiphoton ionization (REMPI) via $3p_z$−X transitions near 333 nm.[9] Mass-selected methyl radicals from the reaction with vibrationally excited methane were obtained by taking the difference of the signal with and without IR excitation on an every-other-shot basis while scanning the frequency of the probe laser.

Figure 2 shows the REMPI spectra of methyl radical products from the reactions we have studied:

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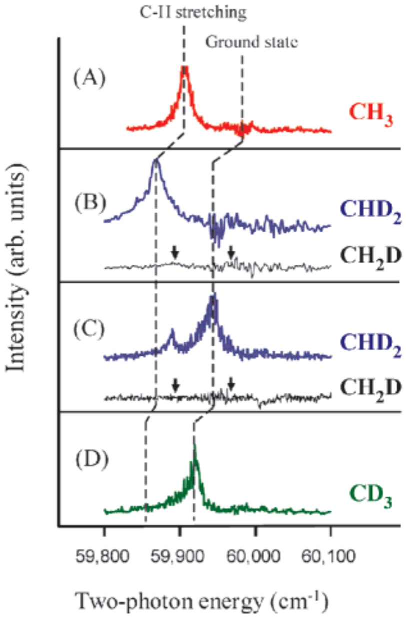

Figure 2. REMPI spectra of the methyl radicals from the following reactions: (A) Cl + $CH_4|11\rangle \rightarrow$ HCl + CH_3 (red), (B) Cl + $CH_2D_2|11\rangle \rightarrow$ HCl + CHD_2 (blue) or DCl + CH_2D (black), (C) Cl + $CH_2D_2|20\rangle \rightarrow$ HCl + CHD_2 (blue) or DCl + CH_2D (black), and (D) Cl + $CHD_3|20\rangle \rightarrow$ HCl + CD_3 (green). For (B) and (C), methyl radical spectra corresponding to H-atom (blue) and D-atom abstraction channels (black) were obtained simultaneously. The dotted lines represent the correlations of band positions for ground and C−H stretched states for different isotopomers of methyl radicals. The shifts of the bands for different methyl isotopomers result from the differences in vibrational frequencies of electronic ground and excited states of methyl radicals. Expected positions of the bands (ground and C−H stretching) for D-atom abstraction product, CH_2D, are shown as arrows.

$$\mathrm{Cl} + \mathrm{CH_4}|11\rangle \rightarrow \mathrm{HCl} + \mathrm{CH_3} \qquad \text{(A)}$$

$$\mathrm{Cl} + \mathrm{CH_2D_2}|11\rangle \rightarrow \mathrm{HCl} + \mathrm{CHD_2} \text{ or } \mathrm{DCl} + \mathrm{CH_2D} \qquad \text{(B)}$$

$$\mathrm{Cl} + \mathrm{CH_2D_2}|20\rangle \rightarrow \mathrm{HCl} + \mathrm{CHD_2} \text{ or } \mathrm{DCl} + \mathrm{CH_2D} \qquad \text{(C)}$$

$$\mathrm{Cl} + \mathrm{CHD_3}|20\rangle \rightarrow \mathrm{HCl} + \mathrm{CD_3} \text{ or } \mathrm{DCl} + \mathrm{CHD_2} \qquad \text{(D)}$$

In reactions B, C, and D, both H-atom and D-atom abstraction are energetically allowed, but as seen in Figure 2, only methyl radicals that correspond to H-atom abstraction are produced. Clearly, these reactions show strong bond selectivity—only vibrationally activated C−H bonds in the methane react with atomic chlorine.

Figure 2 also shows that a dramatic change occurs in the methyl vibrational state distribution upon exciting either the $|11\rangle$ or the $|20\rangle$ state of methane. We find that methane prepared in the $|11\rangle$ state ($CH_4|11\rangle$ and $CH_2D_2|11\rangle$) mostly generates the methyl radical with C−H stretching excitation with little or no ground-state product. On the other hand, methane prepared in the $|20\rangle$ state ($CH_2D_2|20\rangle$ and $CHD_3|20\rangle$) produces mainly the ground-state methyl radical, with no sign of C−H or C−D stretching excitation. In particular, CH_2D_2 excited to the $|11\rangle$ state produces completely different vibrational distributions of the methyl products than CH_2D_2 excited to the $|20\rangle$ state, despite an energy difference of only $\sim$100 cm^{-1} (2% of the total available energy, 7200 cm^{-1}). Therefore, we believe that this change originates from the different initial vibrational motions of methane rather than the difference in total available energy. The close similarity between the methyl REMPI spectra from the $CH_4|11\rangle$ and $CH_2D_2|11\rangle$ reactions, and between the $CH_2D_2|20\rangle$ and $CHD_3|20\rangle$ reactions also indicates that partial deuteration of the methane does not alter the reaction dynamics as far as the H-atom abstraction channel is concerned.

We can easily interpret the pattern of internal excitation of methyl products once we assume that the reaction involves the attack of a chlorine atom on a localized vibrating C−H oscillator, and that the reaction proceeds without perturbation of the initial vibrational motion of the methane molecule (see Figure 1B). For methane prepared in the $|11\rangle$ state, the chlorine atom attacks only one of the two vibrationally excited C−H bonds, abstracts an H atom, and leaves the methyl radical exclusively in the C−H stretching mode. On the other hand, for methane excited to the $|20\rangle$ state, only one C−H bond is activated with two stretching quanta. All of the vibrational energy is available for the abstraction reaction, and consequently the resulting methyl radical is formed in its ground state.

In conclusion, we have observed both bond selectivity and mode specificity in the reaction of vibrationally excited methane with atomic chlorine. Excitation of the C−H stretching mode in partially deuterated methane promotes only the H-atom abstraction reaction. Excitation of different modes, $|11\rangle$ or $|20\rangle$, leads to different vibrational states of the methyl radical product: methane excited to the $|11\rangle$ state primarily produces the C−H stretch-excited methyl radical, whereas methane excited to the $|20\rangle$ state leads to ground-state methyl products. In all these examples involving C−H excitation of methane and its deuterated isotopomers, the H-atom abstraction reaction proceeds as if the rest of the molecule plays only the role of an innocent bystander. The local-mode character of the C−H oscillator accounts for the simplicity of this result. We believe that the bond selectivity and mode specificity demonstrated in Figure 2 is general whenever the following conditions are met: (1) the vibrational motion is localized; (2) the reaction is direct; and (3) the vibrational motion prepared in the reagent has a large projection on the reaction coordinate.

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