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How Active Is the Bend Excitation of Methane in the Reaction with O(^{3}P)?

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The role of bending excitation of methane in the reaction with O(^{3}P) is investigated in a crossed-beam experiment. Previous theories predicted that either stretch or bend excitation of the reactant promotes chemical reactivity and that initial bending excitation of CH_4 preferentially yields umbrella-excited CH_3 products. Experimentally, both predictions for bend-excited reagent were not borne out in this investigation. We found instead that compared to the ground-state reagent, bend-excited methane yields more vibrational excitation of the hydroxyl coproduct. The first reported product angular distributions show predominant backward scatterings for both ground-state and bend-excited methanes, which corroborate well with a direct rebound reaction mechanism.

I. Introduction

The reactions of ground-state atomic oxygen, O(^{3}P), with hydrocarbons are important initial steps of oxidation in combustion processes.[1] Among those reactions, the abstraction reaction of $O(^3P) + CH_4 \rightarrow OH + CH_3$ is the simplest one for all saturated hydrocarbons, serving as the prototype for detailed investigations; as such, this reaction has attracted considerable interests, both experimental[2−4] and theoretical,[5−18] over the past decades. The reaction is slightly endothermic by 1.59 kcal/mol with a substantial barrier to reaction. The thermal rate constants have been measured with a wide variety of methods. The most recent recommended expression for the rate constant over the temperature range 300−2500 K is $k = 1.15 \times 10^{-15}\ T^{1.56}\ \exp(-4720/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.[4] There is also a considerable body of experimental work[19−23] devoted to the dynamics studies, mostly on the product state distribution of the OH($X^2\pi$) product. A small amount of OH rotational excitation was found,[19−22] which has been interpreted as resulting from a direct abstraction mechanism with a preferentially collinear O−H−C approach of the O(^{3}P) atom to the C−H bond under attack. A monotonically declined excitation of the umbrella mode of CH_3 products, from $\nu = 0$ to $\nu = 4$, was also reported,[23] suggesting that the CH_3 moiety is gradually relaxed to a planar structure during the reaction. To our best knowledge, no product angular distribution has been reported.

On the theoretical side, ab initio calculations at different levels have been performed to obtain the energetics, geometries, and frequencies of the stationary points.[9,11,12,16] Those calculations showed that this reaction has indeed a collinear $O-H-CH_3$ transition state due to the conical intersection of the two lowest electronic states. A classical barrier height lays around 13−14 kcal/mol (or 9−10 kcal/mol when the zero-point energy is included). Several dynamics investigations, using quasi-classical trajectories (QCT)[10,16] or reduced-dimensionality quantum models,[5−8,13,14] have been reported, and the calculated kinetic behaviors and product state distributions are generally in good agreement with experimental findings.[22] In addition, the mode-specific reactivity has been under scrutiny using reduced-dimensionality quantum scattering approaches.[5−8,13,14] It was found that vibrational excitation of either the stretch or the bend of the CH_4 reagent enhances reactivity substantially. This prediction is similar to the findings for a better-studied, both experimentally and theoretically, reaction of $Cl + CH_4$.[24] Qualitatively, its origin, analogous to the $Cl + CH_4$ case,[25,26] could be ascribed to the evolution and couplings of generalized normal-mode vibrational frequencies along the reaction path. In the context of the reaction path Hamiltonian model, the reaction path is strongly coupled to both reactive stretch and umbrella motions of CH_4,[11] suggesting that these modes could promote the forward reaction rate. It has also been predicted[7] that the symmetric stretch of methane is more efficient in promoting the $O + CH_4$ reaction than the asymmetric stretch.

The predicted vibrational enhancements in reactivity await experimental confirmations. While the notion of vibrationally adiabatic dynamics might be anticipated for a stretch-excited reagent and can provide an intuitively appealing way to rationalize its higher reactivity, the physical understanding of the predicted enhancement in reactivity for a bend-excited methane is less obvious.[25−27] Theoretically, bending excitation of CH_4 was predicted to lead to a hotter distribution of CH_3 in umbrella mode,[5,6,8,13] which was interpreted as an adiabatic mapping of the bending motion of the CH_4 reagent directly onto the analogous motion of the CH_3 product. In the other words, umbrella-mode excitation of CH_4 was partially preserved in the analogous nuclear motion of the CH_3 product, suggesting a spectator behavior of the CH_3 moiety in the reaction.[10] This view seems in keeping with a noninverted umbrella excitation of CH_3 products found experimentally[23] for the ground-state reagents. On the other hand, the concept of adiabaticity has its root on the relative time scales of nuclear motions. While the

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high-frequency stretch that is necessarily a faster motion may be regarded approximately adiabatic en route to the barrier, how well the same concept can be applied to a low-frequency mode, such as methane distortion vibrations, remains unclear. The aim of the present study is to clarify the relative reactivity of bend-excited methane. For experimental reasons, we chose the fully deuterated reaction O + CD_4 and an isotopomer CHD_3 for investigations. For clarity, the "mode-specific" behavior in this work refers to the differential enhancement or reduction of reactivity for a mode- (or a subset of modes) selected reagent in respect to the translational factor from the vibrational ground-state reaction with an equivalent amount of total energy.

II. Experimental Section

The experimental apparatus and methods are essentially the same as the previously reported studies on the Cl*($^2P_{1/2}$) reactivity and the effect of bend excitation in the Cl + CH_4/CD_4 reactions.[28] Only the relevant features are presented here. The O(^{3}P)-atom beam was generated by photolyzing SO_2 at 193 nm near the throat of a pulsed valve. To achieve the desired beam speed, 4−5% SO_2 was seeded in H_2 at a total pressure of 12 atm. To remove the small chemical interferences from the OH reaction, as evidenced from the image acquired (i.e., the images were contaminated by some faint features that are identical to those shown in ref 29), the ArF laser was loosely focused and a Teflon block was attached to the pulsed valve to deactivate the trace amounts of the OH radical in the beam. Previous investigations,[30,31] using a similar setup, demonstrated that most O atoms (∼98%) were supersonically cooled to the lowest fine-structure state O($^3P_2$). Because of a relatively high barrier to reaction, the target beams, CD_4 and CHD_3, were also seeded (∼20%) in H_2 for acceleration. Two source temperatures, 18 °C and 160 °C from the thermocouple measurements, were used to vary the initial populations of bend-excited methanes. The beam speeds were determined from the time-of-flight measurement using two fast ionization gauges. To isolate the effect of initial vibration excitation, the intersection angles of the two molecular beams were adjusted according to their speeds, so that the experiments under different source temperatures yield essentially the same collision (or translation) energy. The reaction products CD_3 (or CHD_2) were probed by (2 + 1) resonance-enhanced multiphoton ionization (REMPI),[32,33] in combination with a time-sliced ion velocity imaging technique.[34] The laser frequencies of the probe were fixed at the peaks of the 0_0^0, 2_1^1, and 2_2^0 Q-heads[32] of the $X^2A_2 \rightarrow 3p_z{}^2A_2$ transition, respectively, for interrogating different umbrella-mode excitations of methyl radical products. As a result, only the low N-states of methyl radicals were sampled.[34] Acquired REMPI spectra (not shown), nonetheless, indicate that they represent the majority of the total reactivity.

III. Results and Discussion

Figure 1 exemplifies a few typical raw images of CD_3 products from the O(^{3}P) + CD_4 reaction. Superimposed on the images are product scattering angles in the center-of-mass frame. The zero-degree represents the scattering of CD_3 products in the same direction as the incident CD_4 beam. As is seen, for every image the reaction product is predominantly backward-scattered, which supports the previous notion of a direct rebound mechanism for this abstraction reaction.[22]

A closer inspection of the image reveals the effect of heating the target beam source. The image for the vibrational ground-state CD_3 at 18 °C exhibits two backward-scattered rings, which energetically correspond to the concomitantly formed OD (ν' = 0) and (ν' = 1), respectively. Their clear separation indicates unequivocally low rotational excitation of the OD product, in excellent agreement with previous experiments.[19−22] At 160 °C, a new feature appears, lying between these two rings. As will be demonstrated shortly, this new feature can be assigned to the formation of the CD_3 (ν = 0) + OD (ν' = 1) product pair from a reaction of bend-excited CD_4 with O(^{3}P). On the other hand, the effect of heating the CD_4 beam is hardly discernible when CD_3 (ν_2 = 1) is formed (e.g., the image for the 2_1^1 band). As to the first overtone excitation of the umbrella mode of CD_3 (the 2_2^0 band), a faint and slightly faster feature adjacent to the intense ring can be noticed. Again, it is energetically in keeping with the CD_3 (ν_2 = 2) + OD (ν' = 0) formation from the reaction of bend-excited CD_4 with O(^{3}P).

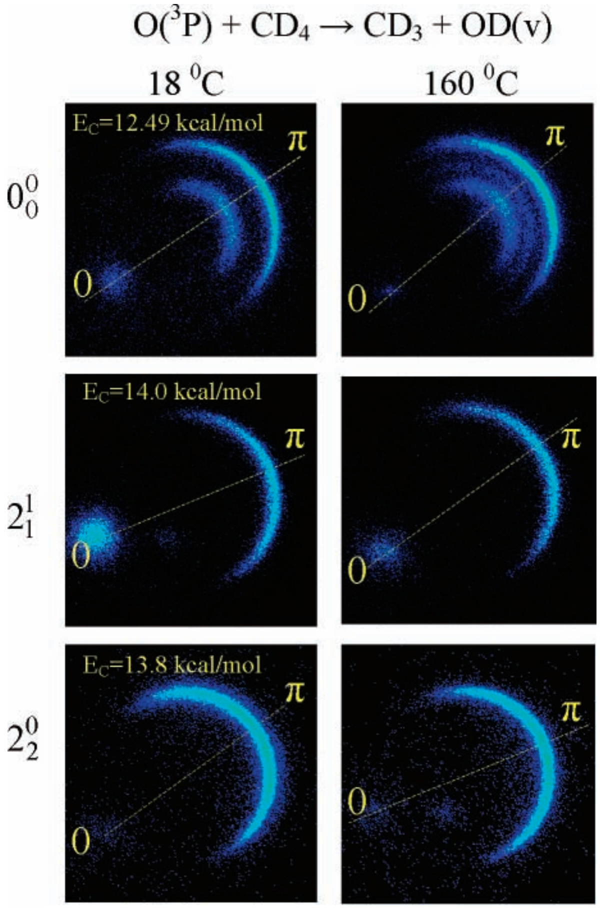


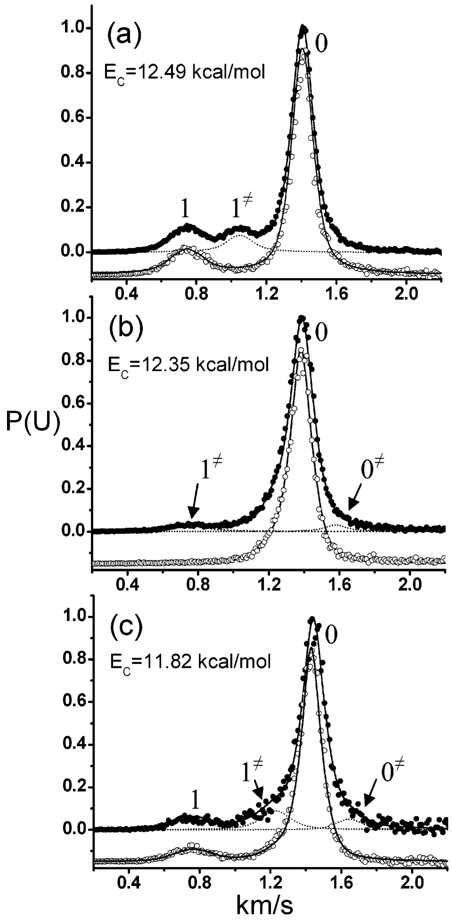
Figure 1. A few representative time-sliced raw images. The images on the left are from the source temperature at 18 °C ("cold"), and those on the right are from a heated source ("hot"). The probed methyl product states are labeled on the left by the REMPI bands. Some backgrounds in the forward direction arise from collisions of the CD_4 beam with unknown species in the radical beam, are easily identified, and do not affect the data analysis.

For more quantitative information, the raw images were corrected for the density-to-flux transformations[34,35] to obtain the corresponding doubly differential cross-sections $d^2\sigma/d\mu\, d(\cos\theta)$. Integrating all angles then yields the product speed distribution $P(\mu) = d\sigma/d\mu$. A few $P(\mu)$ distributions of this study are presented in Figure 2 for illustration. In each panel, two distributions are displayed: the open and the solid circles corresponding to that for 18 °C and 160 °C, respectively. The solid lines are the best fits to the distributions, and assignments of the observed peak features for 18 °C are entirely consistent with the well-established energetics of the reaction. Subtracting the solid line for 18 °C from the corresponding "hot" distribution

TABLE 1: Vibrational Enhancement Factors in the O(^{3}P) + Methane Reactions[a]

probed state	E_c (kcal/mol)	$\sigma_1/(\sigma_0+\sigma_1)$	$\Delta S_0^\ddagger/(S_0+S_1)$	$\Delta S_1^\ddagger/(S_0+S_1)$	$\sigma^\ddagger/\sigma^\circ$	hot-band population
$O + CD_4 \rightarrow CD_3(\nu) + OD(\nu')$; $\Delta H^\circ_{rx} = 2.34$ kcal/mol						
$CD_3\,(\nu = 0)$	12.49	0.152	~0	0.09	0.68	$\Delta n(\nu_4 = 1)/n_0 = 0.088$
$CD_3\,(\nu_2 = 1)$	14.0	~0	~0	~0	~0	$\Delta n(\nu_2 = 1)/n_0 = 0.044$
$CD_3\,(\nu_2 = 2)$	13.8	~0	0.029	~0	0.22	
$O + CHD_3 \rightarrow CD_3(\nu) + OH(\nu')$; $\Delta H^\circ_{rx} = 1.73$ kcal/mol						
$CD_3\,(\nu = 0)$	12.35	~0	0.035	0.051	0.92	$\Delta n\,(\nu_6 = 1)/n_0 = 0.052$
$CD_3\,(\nu_2 = 2)$	13.41	~0	0.029	~0	0.31	$\Delta n(\nu_3 = 1)/n_0 = 0.029$ $\Delta n(\nu_5 = 1)/n_0 = 0.012$
$O + CHD_3 \rightarrow CHD_2(\nu) + OD(\nu')$; $\Delta H^\circ_{rx} = 1.93$ kcal/mol						
$CHD_2\,(\nu = 0)$	11.82	0.09	0.093	0.061	1.6	

[a] Notes: The subscripts, 0 and 1, indicate the vibrational quantum state ν' of the OD(OH) coproducts. σ/σ° listed here are estimated ratios of total reactivity of bend-excited reagents to that of ground-state reagent, based on the assumption that all bend-excited methanes (hot bands) contribute with equal reactivity.



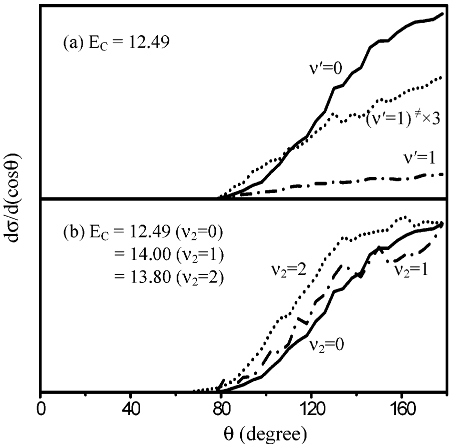
(a) : $O(^3P) + CD_4 \rightarrow CD_3\,(0^0_0) + OD$
(b) : $O(^3P) + CHD_3 \rightarrow CD_3\,(0^0_0) + OH$
(c) : $O(^3P) + CHD_3 \rightarrow CHD_2\,(0^0_0) + OD$

Figure 2. Methyl product speed distributions in the center-of-mass frame. The reactions and collisional energies are labeled, and the peak features are assigned as vibrational states of the OD (OH) coproduct based on energetic grounds. The superscript "‡" indicates the corresponding OD (OH) state formed from the bend-excited reagent.

at 160 °C and then fitting the difference distribution yield the dotted line. On energetic grounds, those extra peaks in the "hot" distribution are unambiguously ascribed to the formation of the OD (or OH) coproduct states, as labeled, from the vibrationally bend-excited reagents, and the integrated area of each peak yields the respective contribution, $S = n\sigma$. At 18 °C, one has $S_c = n_c^\circ\sigma^\circ + n_c^\ddagger\sigma^\ddagger$, and at 160 °C, $S_h = n_h^\circ\sigma^\circ + n_h^\ddagger\sigma^\ddagger$, where the superscripts "°" and "‡" denote the vibrationally ground and excited reagents, respectively.[28] The subtraction procedure described above essentially normalizes the two distributions by contributions from the ground-state reaction. The difference between the two distributions can therefore be entirely attributed to the reactivity from the vibrationally excited reagents, i.e., $\Delta S^\ddagger = \Delta n^\ddagger\sigma^\ddagger/\sigma^\circ$.

The results of data analysis are summarized in Table 1. In addition to the normalized vibrational branching of the OD (or OH) coproduct resulted from the ground-state and excited-state reagents, the population differences of a few low-lying vibration states of reagents at the two temperatures are listed. The Boltzmann distribution at the source temperature was assumed, which has been shown from the previous Cl + methane study[28] to be valid under the experimental conditions. Because of the proximity of some of the low-lying states, e.g., the fundamental frequencies of ν_4 and ν_2 of CD_4 are 998 and 1092 cm^{-1}, respectively, we were not be able to distinguish their contributions with our energy resolution. Nonetheless, by comparing the values of $\Delta S_i^\ddagger$ with the listed Δn's, it becomes clear that $\sigma^\ddagger/\sigma^\circ$ in general will not be much different from unity. For example, the relative cross-sections, i.e., $\sigma^\ddagger/\sigma^\circ$ for the reactions of vibrationally excited/ground-state methane, listed in Table 1 are based on an equal reactivity of those hot-band reagents. The ratio of $\sigma^\ddagger/\sigma^\circ$ will increase somewhat, within a factor of 2, if only the most populated hot-band reagent, ν_4, is considered. Not listed in Table 1 is the similar experiment for O + CH_4, for which the images at the two source temperatures are essentially indistinguishable, i.e., no hot-band effects can be detected.

Several semiquantitative conclusions can be drawn from Table 1. First, for ground-state reagent, the ground vibrational state of OD (or OH) is always the major product regardless of the vibrational levels of the coproduct CD_3 (or CHD_2). This is consistent with the previous dynamics studies,[22] for which no vibrationally excited OH can be detected. Thus, the reaction is predominantly vibrationally adiabatic. Second, on the basis of the estimated $\sigma^\ddagger/\sigma^\circ$, the total reactivity of bend-excited methane is not much different, within a factor of 2 or so, from the ground-state reaction. Hence, the bend-excited methane does not promote the reactivity, contrary to the theoretical prediction.[5−8,13] Moreover, judging from the signal strengths at the two source temperatures, bend-excited methane appears to produce somewhat less umbrella-excited methyl radical than that from the ground-state methane. This is also in sharp contrast to the current theoretical prediction[5,6,8,13] that the bend-excited methane leads preferentially to the umbrella-mode excitation of methyl products. Third, in terms of the vibrational branching of the OD (or



(a) $O(^3P) + CD_4 (\nu=0)/CD_4^{\neq} (\nu=1) \rightarrow CD_3 (\nu=0) + OD (\nu')$
(b) $O(^3P) + CD_4 (\nu=0) \rightarrow CD_3 (\nu_2) + OD (\nu'=0)$

Figure 3. Correlated angular distributions of product pairs from the O + CD_4/*$CD_4^{\ddagger}$* reactions.

OH) coproducts from reaction with a bend-excited methane, for CD_3 ($\nu = 0$), one has $\sigma_1^{\ddagger} > \sigma_0^{\ddagger}$, i.e., an inverted correlated branching from a bend-excited reagent; and for CD_3 ($\nu_2 = 2$), $\sigma_0^{\ddagger} > \sigma_1^{\ddagger}$. And compared to the ground-state reagent, reactions with bend-excited methanes generally tend to enhance the ($\nu' = 1$)/($\nu' = 0$) ratio of the OD or OH products. Apparently, the energy of the initial bending vibration is preferentially transferred into the vibration of the hydroxyl product. In this regard, a very recent QCT study on $O(^3P) + CH_4$ concluded that initial vibrational excitation of methane promotes internal excitation of the OH product.[36] Although in that calculation the initial vibrational excitation is not mode-specific, the predicted enhancement for the OH ($\nu' = 1$) product is in line with the present finding.

For completeness, Figure 3 exemplifies the correlated angular distributions for a few product pairs from the $O(^3P) + CD_4$ (or $OD_4^{\ddagger}$) → CD_3 (ν_2) + OD ($\nu' = 0$, 1) reaction. This also represents the first experimental report on product angular distribution for the reaction of $O(^3P)$ + methane. Presented in Figure 3a are the correlated angular distributions for the $O(^3P) + CD_4 (0) \rightarrow CD_3 (\nu = 0) + OD (\nu' = 0)$ and $CD_3 (\nu = 0) + OD (\nu' = 1)$ product pairs at $E_c = 12.49$ kcal/mol. The dominant production of OD ($\nu' = 0$) is apparent, and its distribution seems confined more in the backward direction. Also depicted in Figure 3a is the distribution for the $CD_3 (\nu = 0) + OD (\nu' = 1)$ product pair from the bend-excited $CD_4^{\ddagger}$ reagent, which exhibits a similar shape as the same product pair from the ground-state reaction. Shown in Figure 3b are the distributions for the umbrella-excited CD_3 ($\nu_2 = 0, 1, 2$) + OD ($\nu' = 0$) pairs from the ground-state reagent. Because of the changes in optical setup from the previous work, no attempt was made in this work to recalibrate the probe sensitivities of the REMPI bands for normalizing the relative cross-sections for $\nu_2 = 0$, 1, and 2. For closer comparisons, these three angular distributions are normalized to give the same backward intensity. A systematic shift, albeit small, away from backward peaking with higher umbrella excitation is noticeable.

Generally speaking, all pair-correlated differential cross-sections are predominantly backward-peaking with similar shapes. This observation supports the general belief that the abstraction reaction O + CH_4 proceeds mainly through a direct rebound mechanism.[22] It is instructive to contrast this finding to that reported recently for the Cl + CH_4 reaction.[27,37] In the latter case, the correlated angular distributions for the CH_3 ($\nu = 0$) + HCl ($\nu' = 0$) and CH_3 ($\nu = 0$) + HCl ($\nu' = 1$) pairs display distinctly different characteristics.[27] It was proposed that the former pair is dominated by a direct rebound mechanism as in the present reactions, while the latter pair is likely governed by a dynamical resonance pathway.[27]

How do the present findings on the effect of reagent bend excitation on reactivity compare to the Cl + methane reaction?[28,38] Both reactions are slightly endothermic and proceed as a direct abstraction pathway. For Cl + CH_4/CD_4, the excitation of the bending/torsional modes exhibits modest enhancement at $E_c \approx 4.8$ kcal/mol,[28,38] whereas almost no enhancement is found here for O + CD_4/CHD_3 at 12 kcal/mol. The difference in collision energies of the two studies is perhaps not as significant as indicated, in view of the large disparity in respective reaction thresholds, ~3.5 kcal/mol[37] versus ~10 kcal/mol. In comparison to the translational enhancement factor, i.e., the increase in reactivity with the same amount of energy in initial translation as in vibration, a threefold increase found for Cl + methane appears about the same as translation and is, thus, not mode-specific.[28] Also, the disposal of the initial bending energy is mostly into the product kinetic energy release, just as the effect by increasing initial translation energy.

For the O + methane reaction, the little vibration enhancement reported here turns out to be substantially smaller than the translational enhancement factor. Thus, bend-excited methane exhibits mode-specific behavior in suppressing reactivity. Apparently, the extra energy from the bending motion of reagents in the present reaction does not channel in the right way to help surmount the reaction bottleneck. This finding appears to be an interesting counterexample to the Polanyi's rule,[39] which is based on atom + diatom reactions, that vibration is usually more effective in promoting a late-barrier reaction, which is the case for the present endothermic reaction.[40] Moreover, when a bend-excited CD_4 or CHD_3 does react with $O(^3P)$, the initial bending energy is then transferred into OD vibration, a distinctly different behavior from the Cl + methane reaction.[28] Clearly, the issue of mode-specific behaviors of bend-excited reagents, which are usually of lower frequencies and involve nonlocalized, concerted motions of three or more atoms, is subtler than the stretching vibration.[41]

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