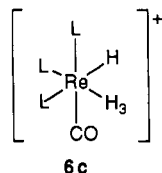


fluxional exchange. At the same temperature, **6a** has an even longer T_1 : 88 ms. The almost flat T_1 vs θ^{-1} curve for **6a** may be the result of the expected V-shaped curve being strongly deformed by the exchange process. As the intrinsic relaxation rate for **6a** falls with increasing θ , contributions due to the exchange steadily increase, leading to little net change in the T_1 (obsd).

The two processes have different activation energies. For the intramolecular exchange, ΔG^\ddagger is 9.8 kcal/mol at 208 K, and for the fluxional process which converts **6b** to **6a**, ΔG^\ddagger is 11.6 kcal/mol at 213 K. This difference seems to be significantly larger than the experimental errors involved. Since the intramolecular exchange between the two types of sites in **6b** has a lower activation energy than does the conversion of **6b** to **6a**, the intramolecular exchange within **6b** cannot proceed via the oxidative addition product **6a**. The exchange requires an associative pathway, e.g., via an H...H...H transition state or intermediate. Such an η^3 -H₃ species would be a pseudooctahedral d⁶ Re(I) complex, **6c**, and so could be particularly stable. η^3 -H₃ complexes have



been proposed,³¹ but none has yet been observed as a

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stable ground-state structure. In this system, the proposed H₃ species could be no more than 10 kcal/mol above the ground state, so a stable H₃ ground state might be accessible in a suitable system.

Conclusion

The structural chemistry of metal hydrides continues to pose challenging problems, but a combination of physical methods is beginning to clarify the picture. Similar types of σ -bond complexes are probably formed with Si-H, C-H, and other species.^{32–34} In the future, we can expect more surprises in hydride chemistry. We will also learn more about how to use σ -bond complexation to activate both H₂ and other covalent bonds.

I thank Maryellen Lavin for her persistence in the early days, Doug Hamilton for putting the method on a more quantitative footing, and Xiao-Liang Luo for his insightful work on the rhenium complexes. The generous exchange of ideas and information of the dihydrogen community has made it a pleasure to work in the area. I particularly thank Greg Kubas, Bob Morris, Martin Poliakoff, Ray Sweany, and Michel Ephritikhine, as well as my colleagues in the Chemistry Department, Mike Heinekey, Kurt Zilm, Jack Faller, and Jim Prestegard. We thank the NSF for funding.

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Vibrational Adiabaticity in Chemical Reactions

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The notion of *electronic adiabaticity* is well-established in many branches of chemistry. It is embodied in the Born–Oppenheimer approximation, which states that electronic and nuclear motions can be treated separately. As a result, although the wave functions and energies of electronic states depend parametrically on the relative positions of the nuclei, the electronic properties are usually independent of the nuclear momenta.

The Born–Oppenheimer separation is usually justified in terms of the large difference between the periods characteristic of electronic and nuclear motions. Even when the approximation breaks down, as in some cases of predissociation, it is usual to begin with the Born–

Oppenheimer states and then to consider nonadiabatic transitions between these states. In fact, the Born–Oppenheimer approximation can be viewed as a special case of Ehrenfest's principle, which states that when two motions are associated with very different time scales they are, to a first approximation, separable. It follows that a motion is likely to adjust adiabatically—that is, without change of quantum state—to a force that is applied relatively slowly.

My aim in this Account is to explore the value of the concept of *vibrational adiabaticity* in collisions between species that interact chemically. It is not, of course, contended that reactions occur with complete vibrational adiabaticity. Indeed, it is necessary to examine what such a concept means in bimolecular chemical reactions. In the simplest case, typified by $A + BC \rightarrow AB + C$, where A, B, and C are all atoms, it is possible to correlate the vibration of BC at $t = 0$ to the vibration of AB at $t = \infty$, through the bond stretching motion orthogonal to the minimum energy path (MEP) at in-

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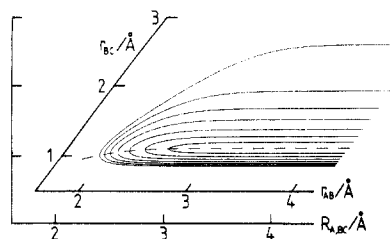


Figure 1. Mass-scaled potential energy surfaces for collinear nonreactive collisions between Ar and N₂. The dashed line represents the minimum energy path across the surface.

intermediate times.¹ That exothermic reactions of this type do not proceed entirely adiabatically, e.g., from BC($v=0$) to AB($v=0$), has been demonstrated for many reactions. Often, a large fraction of the energy released in a reaction is channeled into the vibration of AB, and the distribution of products over their energy states is an indication of the form of the potential energy surface and how the atoms move across it.

Nevertheless, the possibility of *partial* vibrational adiabaticity has important consequences. Thus, it has long been recognized^{1,2} that adiabatic motion as far as the transition state ensures that a thermal distribution of reagents over their internal states is transformed to a thermal distribution over states in the transition state thus justifying transition-state or activated-complex theory for thermal reactions. Similar transition-state treatments can also be used to address the question of how reaction rates depend on the internal energy of the reagents. A growing number of experiments provide rate constants for species in selected vibrational states, and the interpretation of these data is a major point of focus in this Account. A related question concerns the adiabaticity of vibrations involving bonds that remain essentially unchanged during a reaction. Thus, if A and C are taken for the moment to represent molecular radicals, one can ask if internal excitation within A or C is likely to promote reaction and whether energy released in the reaction can excite modes other than the vibration along the newly formed AB bond.

Most recent reviews^{3,4} on the vibrational promotion of bimolecular reactions have emphasized the role of quasiclassical trajectories in demonstrating that the degree of vibrational enhancement depends on the position of the potential energy barrier for reaction. A "late" barrier favors efficient use of BC vibrational energy in a three-atom, A + BC reaction. In this Account, emphasis is placed on the value of vibrationally adiabatic transition state theory in understanding these effects.

Potential Energy Surfaces and Vibrational Adiabaticity. Collisions between diatomic molecules and noble gas atoms at thermal energies provide an outstanding example of vibrational adiabaticity; for example, at 300 K the probability of CO being relaxed from $v = 1$ to $v = 0$ in collisions with Ar is less than 10^{-8} . It is instructive to examine why this is in terms of motion over the potential energy surface that is ap-

propriate for collinear collisions.

Such a surface is shown in Figure 1a, the axes being scaled and skewed so as to diagonalize the kinetic energy⁵ for Ar + N₂ collisions. The probability of energy being transferred from the relative translational motion into the N₂ vibration (V-T) can be considered in terms of classical trajectories initiated along the MEP. A trajectory that exactly retraces its path is one in which no energy transfer takes place.

Two factors may cause a trajectory initially projected along the MEP to depart from it. One is the shape of the surface in the region where the direction of trajectories is reversed and is related to the skewing of the axes in the representation shown in Figure 1. The second factor is especially important in the present context. It is sometimes referred to as the inertial or "bobsled" effect¹ and causes the path of a trajectory as atom A approaches diatomic BC to be straighter than the MEP. Its extent depends on a combination of the curvature of the MEP and the momentum of the trajectory. It is basically this effect that causes V-T energy transfer to become more probable at higher collision energies and as the collisional reduced mass falls.

Another way to examine how the vibrational and translational motions are coupled in A + BC collisions is to evaluate how the frequency of vibration orthogonal to the MEP changes. For the Ar-N₂ interaction, the frequency is increased by only 2.6% at a point on the MEP 6.4 kcal mol⁻¹ above the asymptotic energy. As a result, the vibronic or vibrationally adiabatic states of Ar + N₂(v) are virtually parallel. Indeed, in the celebrated SSH theory of V-T energy transfer,⁶ the (small) probabilities of nonadiabatic, "tunneling" transitions between parallel vibronic states are calculated. Although such calculations do not give quantitative agreement with experiment, they do explain the low transition probabilities that are found when trajectories only penetrate regions of the potential energy surface where the MEP is only slightly curved.

When the dominant intermolecular interactions are repulsive, collinear approach of A to BC tends to compress BC and to raise the vibrational frequency. If A and BC can interact chemically, these features are reversed: r_{BC} increases and the frequency of vibration is lowered as A and BC approach. Trajectory calculations⁷ on moderately attracting systems suggest that it is again the curvature in the MEP that determines the extent of V-T energy transfer. Of course, the attraction makes it easier for trajectories to access the strong curvature region as well as accelerating A and BC toward one another so that the inertial effect is accentuated. Collisions between free radicals can occur on potential energy surfaces that are *strongly* attractive and lead to the formation of collision complexes. Such collisions bring about remarkably efficient vibrational relaxation⁸⁻¹⁰ since the internal motions in the complex are

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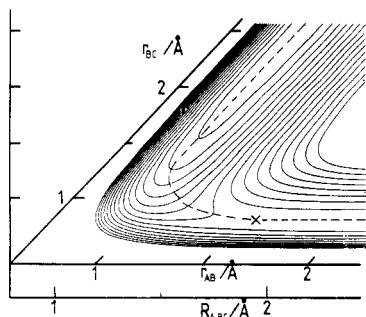


Figure 2. Mass-scaled potential energy surface for the collinear reaction $F + H_2 \rightarrow FH + H$. The dashed line represents the minimum energy path, and the \times represents the position of the saddlepoint.

strongly coupled. The notion of vibrational adiabaticity is useful in estimating the rate constant for formation of the collision complexes.

Exothermic reactions between radicals and saturated molecules proceed over potential energy surfaces with small but significant barriers. Figure 2 displays a surface for the collinear, prototypical reaction: $F + H_2 \rightarrow HF + H$.¹¹ By analogy with the previous discussion, one would anticipate that a classical trajectory, initially projected along the MEP with sufficient energy to surmount the "early" barrier, will remain close to the MEP until well beyond the barrier. After that there will be a large inertial effect as the trajectory gains speed and the MEP curves sharply. As the trajectory evolves into the exit valley, it will undergo wide oscillations corresponding to the considerable excitation of the HF vibration which has been observed experimentally. In general, for simple exothermic $A + BC$ reactions, it appears that vibrational adiabaticity is probably a good assumption during motion up to the transition-state region. For the reverse endothermic processes, nonadiabaticity occurs prior to the transition-state region because of the sharp MEP curvature before the "late" barrier is reached. Further evidence for these conclusions is cited below.

The ideas introduced so far are relatively easy to extend to larger systems, if a mode analysis is performed along the reaction path and the calculated frequencies are correlated with those in the separated reagents and products. Those modes whose frequencies change little can be expected to behave adiabatically. Now it is necessary to see how these qualitative ideas can be incorporated into transition-state theory (TST).

Transition-State Theory and Vibrational Adiabaticity.² One great advantage of TST is that it is possible to include the full dimensionality of a reactive process, while requiring only limited information about the potential energy surface: specifically, the variation of potential energy along, and adjacent to, the MEP. Furthermore, even the simplest versions of the theory incorporate the concept of vibrational adiabaticity or, at least, vibrational adiabaticity on average.^{1,2} This can be illustrated by again considering a collinear $A + BC$ reaction. Then, the rate constant (in centimeters per molecule per second) for reaction via one vibrationally adiabatic state or channel is given by

$$k_v(T) = (kT/h)(1/Q_{tr}) \exp[-V_{ad}^{\max}(v)/kT] \quad (1)$$

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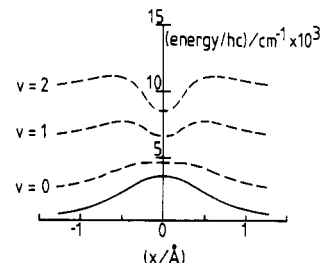


Figure 3. Potential energy curves for the H_3 system. The solid line represents the variation of electronic energy along the minimum energy path on the mass-scaled surface for collinear reaction. The dashed curves show the vibrationally adiabatic paths for $H + H_2(v) \rightarrow H_2(v) + H$.

where Q_{tr} is the partition function per unit length for one-dimensional relative motion of A and BC. $V_{ad}^{\max}(v)$ is the maximum value of $V_{ad}(v,x)$, the energy in the adiabatic state. Its value along the coordinate x describing progress along the MEP is given by

$$V_{ad}(v,x) = V_{el}(x) + [E_{vib}(v,x) - E_{vib}(v,-\infty)] \quad (2)$$

where $V_{el}(x)$ is the electronic potential energy and is independent of v , $E_{vib}(v,x)$ is the energy of the v th state of vibration orthogonal to the MEP at the point x along the MEP, and $E_{vib}(v,-\infty)$ is the vibrational energy of isolated $BC(v)$. To obtain $k(T)$, the thermal rate constant, one takes a weighted sum of the $k_v(T)$,

$$k(T) = \sum f_v k_v(T) \quad (3)$$

with $f_v = \exp[-E_{vib}(v,-\infty)]/Q_{vib}$, so that

$$k_v(T) = (kT/h)(1/Q_{tr}Q_{vib}) \sum \exp\{-[V_{el}^{\max} + E_{vib}^{\max}(v)]/kT\} \quad (4)$$

The last term may be viewed as defining an effective vibrational partition function for the transition state, and the normal TST expression for the thermal rate constant is recovered. However, it should be noted (see below) that, in general, the maxima for different vibrationally adiabatic states occur at different positions x along the MEP and hence have different V_{el}^{\max} .

The position of $V_{ad}^{\max}(v)$ depends on v because, although $V_{el}(x)$ increases toward the potential barrier, $E_{vib}(v,x)$ decreases, and this second contribution to $V_{ad}(v,x)$ assumes increasing importance as v increases. One result is that, even when the potential barrier is symmetrically placed along the MEP, the first adiabatic maxima for channels with $v > 0$ can be displaced into the entrance valley and consequently are reached before the MEP curves significantly. Vibrationally adiabatic curves for collinear $H + H_2(v)$ are displayed in Figure 3. The presence of dual, symmetrically disposed adiabatic maxima is connected with the possibilities of trajectories recrossing the first maximum and hence lowering the true rate constant below its TST value.²

It is straightforward to extend the vibrationally adiabatic TST (VA-TST) treatment of reactions both to three spatial dimensions and to systems of more than three atoms. Equation 2 is replaced by

$$V_{ad}(v_1, v_2, \dots, x) = V_{el}(x) + \sum [E_{vib}(v_i, x) - E_{vib}(v_i, -\infty)] \quad (5)$$

and eq 1 is modified to include partition functions for all the internal motions whose states are not specified in the particular adiabatic channel of interest. Of

Table I
Information about Reactions of the Type
A + BC → AB + C

reagents	ΔH_0° , kJ mol ⁻¹	E_{act} , kJ mol ⁻¹	$\Delta r_{\text{AB}}^{\text{sp}}$, Å ($\Delta r_{\text{AB}}^{\text{sp}}/r_{\text{e,AB}}$)	$\Delta r_{\text{BC}}^{\text{sp}}$, Å ($\Delta r_{\text{BC}}^{\text{sp}}/r_{\text{e,BC}}$)
H + H ₂	0	31.8 ^a	0.19 (0.25)	0.19 (0.25)
O + H ₂	7.5	38.0	0.24 (0.25)	0.18 (0.24)
O + HCl	3.8	28.0	0.18 (0.19)	0.18 (0.14)
O + HBr	-61.5	13.0	0.40 (0.41)	0.06 (0.04)
F + H ₂	-134.3	4.7	0.62 (0.68)	0.023 (0.03)

^a Activation energy for D + H₂.

course, to use these equations it is necessary to evaluate how the energies associated with the states of several modes vary along the MEP. This aspect of TST meshes well with ab initio methods which include "gradient techniques".¹² Moreover, this approach explains why the preexponential factors in the rate constant expressions, as well as the activation energies, depend on the vibrational state of the reagents.

The validity of the vibrationally adiabatic assumption is supported by the results of both quasiclassical and quantum scattering calculations. The interpretation of the latter is slightly clouded by the phenomenon of quantum mechanical tunneling. Nevertheless, the similarity between the VA-TST thresholds for the D + H₂($\nu=1$) and O + H₂($\nu=1$) reactions and the effective thresholds indicated by quantum scattering calculations¹³ is strong evidence for the correctness of the vibrationally adiabatic hypothesis. Similar corroboration is provided by the combined TST-quasiclassical trajectory calculations of Frost and Smith.¹⁴ They initiated trajectories from randomly chosen points in the phase space of transition states chosen according to vibrationally adiabatic criteria. Trajectories were calculated both "backward in time" (i.e., in the direction of separated reagents) and "forward in time" (toward products). For virtually all the A + BC systems studied, both collinearly and in the three dimensions, motion between the transition state and separated reagents was found to exhibit a high degree of vibrational adiabaticity. From the forward trajectories, passing through the region where the MEP was strongly curved, the product-state distributions of the reactions could be predicted.

Vibrational Adiabaticity: The Experimental Evidence

(i) **Direct Atom-Transfer Reactions: A + BC(ν) → AB(ν') + C.** Table I summarizes data for five hydrogen atom transfer reactions that all involve the attack of an atomic radical (A) on a diatomic molecule (BC). Although these reactions all take place by *direct* dynamics across potential energy surfaces on which there are potential barriers to reaction, they can be subdivided into two groups: the first three, which are exactly, or nearly, thermoneutral, and the last two, which are substantially exothermic. The geometry of

ABC at the saddlepoint on the MEP is indicated by giving the values of $\Delta r_{\text{AB}}^{\text{sp}}$ and $\Delta r_{\text{BC}}^{\text{sp}}$:

$$\Delta r_{\text{AB}}^{\text{sp}} = r_{\text{AB}}^{\text{sp}} - r_{\text{e,AB}} \quad \Delta r_{\text{BC}}^{\text{sp}} = r_{\text{BC}}^{\text{sp}} - r_{\text{e,BC}}$$

where r_{ij}^{sp} and $r_{e,ij}$ are the i,j separations at the saddlepoint and in the isolated molecule, respectively. These data support the general rules for potential energy surfaces proposed by Polanyi.³ For the exothermic F + H₂ and O + HBr reactions, the potential energy barriers are "early"; that is, $r_{\text{AB}}^{\text{sp}} \gg r_{\text{e,AB}}$ but $r_{\text{BC}}^{\text{sp}} \approx r_{\text{e,BC}}$, whereas for the thermoneutral reactions the AB and BC bonds are stretched to comparable extents at the saddlepoint. The origin of the data in Table I varies from accurate ab initio calculations on the H₃,¹⁵ FH₂,^{11b} and OH₂¹⁶ surfaces to semiempirical estimates of the surfaces in the cases of OHCl^{17a} and OHBr.^{17b}

Use of VA-TST is likely to be more firmly based the earlier the position of the saddlepoint. Then the MEP up to the barrier will be almost parallel to the $R_{\text{A,BC}}$ axis on the scaled and skewed potential energy surface. The vibrationally adiabatic or vibronic surfaces correlating with different ν states of A + BC(ν) will be nearly parallel in this region, and therefore the rate constants for reaction from different initial vibrational states will be similar. The applicability of VA-TST to thermoneutral reactions with centrally located ($\Delta r_{\text{AB}}^{\text{sp}} \approx \Delta r_{\text{BC}}^{\text{sp}}$) barriers is more debatable, since then the MEP curves appreciably before the saddlepoint is reached. However, although the $\nu = 0$ adiabatic maximum is usually located at the saddlepoint, the maxima for higher states of the bond-stretching vibration may be displaced into the entrance and exit valleys on the potential energy surface. Vibrationally adiabatic motion is then expected up to the first of these maxima ($r_{\text{AB}} > r_{\text{BC}}$), and this expectation is supported by trajectory calculations.¹⁴

For H + H₂($\nu=0$) at energies just above threshold, the overall reaction is necessarily adiabatic as only the $\nu' = 0$ level of the product H₂ is energetically accessible. The best theoretical support for the validity of a VA-TST analysis is that it yields a threshold close to that obtained from scattering calculations. Moreover, experiments show that, in energetic collisions of H atoms with D₂ (1.3 eV)¹⁹ and D atoms with H₂ (0.95 eV),²⁰ approximately 80% of the HD product is formed in $\nu' = 0$. This indicates a strong dynamical bias against vibrational excitation, even in high-energy collisions where the "bobsled effect" should increase the extent of energy transfer between motions along and orthogonal to the MEP. Clearly, if there is a strong adiabaticity throughout the reaction, then motion up to the saddlepoint must also be strongly adiabatic.

The effect of reagent vibrational excitation on the H + H₂ reaction and its isotopic variants is still controversial. Until recently, the experimental rate constants for D + H₂($\nu=1$) exceeded nearly all the theoretical estimates by a factor of about 5, but a recent redetermination²¹ yielded a rate constant that agrees better

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with theory.¹⁸ Despite these uncertainties, it is clear that excitation of H₂ to $v = 1$ does enhance the rate of reaction by a factor of about 250, in fair agreement with the predictions of VA-TST.

The rate of reaction between O(³P) atoms and H₂ at 298 K is enhanced by a factor of about 2.6×10^3 when the H₂ is excited to $v = 1$.²² Remarkably, 95% of the OH is produced in $v' = 1$, indicating a high degree of vibrational adiabaticity. As with the H₃ system, the adiabatic barriers migrate from the saddlepoint for $v = 0$ to progressively earlier positions as v is increased. The barrier falls from 11.0 kcal mol⁻¹ for $v = 0$ to 5.9 kcal mol⁻¹ for $v = 1$, and the observed vibrational enhancement is reproduced quite well both (a) by generalized VA-TST calculations²³ and (b) by TST calculations which include tunneling corrections.¹⁶

The reaction between O(³P) atoms and HCl is nearly thermoneutral, and it is a "heavy-light-heavy" system. The potential energy surface is deeply skewed, and there are substantial changes in the frequency of the bond-stretching vibration along the MEP. Reaction may proceed predominantly by passage over, or tunneling through, the ridge separating the entrance and exit valleys, not via the saddlepoint. This might be expected to lead to adiabatic dynamics with vibrational motion in the entrance valley being transformed into the almost parallel vibrational motion of the product. This expectation is confirmed by measurements on the energy states of HCl formed in the (reverse) reaction of Cl atoms with highly vibrationally excited OH.²⁴ Measurements of the O + HCl rate enhancement brought about by exciting HCl to $v = 1$ are complicated by simultaneous vibrational relaxation but indicate an increase by a factor of 200–1000,²⁵ in agreement with the results of trajectory calculations.^{17a} No VA-TST analysis of this reaction, or that between O(³P) atoms and HBr, has been carried out.

Recent elegant experiments by Zare's group provide detailed state-to-state information about the O(³P) + HCl, HBr reactions. For O(³P) + HCl($v=2$),²⁶ comparable amounts of OH are formed in $v' = 0$ and $v' = 1$ —OH($v'=2$) is energetically inaccessible—whereas for O(³P) + HBr($v=0$), OH is produced almost exclusively in $v' = 1$.²⁷ These reactions are clearly not vibrationally adiabatic, at least not from these relatively low reagent vibrational levels. It may be that, at low excitations, systems reach those parts of the potential energy hypersurface where the MEP curves sharply, and there is strong coupling between bond-stretching and motion along the MEP. At high vibrational energies (as in Polanyi's experiments²⁴), the H atom is transferred without the system ever getting close to the saddlepoint.

Ironically, those systems where the VA-TST hypothesis is least in doubt are also those for which it is hardest to measure rate constants for reagents in dif-

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Table II
Ratios of Rate Constants for Total^a Removal of OH($v=1$), OD($v=1$), and CN($v=1$) to Rate Constants for Reaction of OH($v=0$), OD($v=0$), and CN($v=0$)

reagent	OH	OD	CN
H ₂	<1.5		1.16
D ₂			0.70
HCl	1.4		4.5 ^b
DCl	~1.1	2.3 ^b	
HBr	0.72		0.96
HI			1.15

^aThat is, for reaction *plus* relaxation. ^bThere is some evidence for significant, nonreactive relaxation.

ferent vibrational states. The F + H₂ reaction is prototypical. Although it has proved difficult to find a wholly satisfactory potential energy surface for this reaction,¹¹ there is no doubt that it is characterized by an "early" barrier with the result that motion up to the transition state(s) should be strictly adiabatic, and VA-TST estimates of the rate constants should be accurate as long as the low-frequency bend motion is treated properly. However, the barrier is low, and the adiabatic maxima for F + H₂($v=0$) and F + H₂($v=1$) are only ca. 1.80 and 1.4 kcal mol⁻¹, respectively.^{11b} Consequently, the reaction rate of F + H₂($v=1$) at 298 K should be only about twice that of F + H₂($v=0$), and this enhancement will not be easy to measure accurately, given the difficulty of exciting a sizeable proportion of H₂ to states above $v = 0$.

(ii) **Direct Atom-Transfer Reactions: AB(v_1) + CD(v_2) → ABC + D.** Metathetical reactions of this type have been studied with AB = OH or CN. Electronically, the simplest reaction is that between OH radicals and H₂. Ab initio calculations on the potential energy surface²⁸ predict that at the saddlepoint the HO--H separation is 36% greater than in H₂O, whereas the H--H separation is only stretched by 10% from its initial value. The OH (AB) bond length remains essentially the same throughout the reaction. Experiments show that the reaction rate is accelerated by <50% by excitation of OH to $v_1 = 1$, but by a factor of ca. 120–160 if H₂ is excited to $v_2 = 1$.²⁹ These findings are consistent with a VA-TST analysis, as long as care is taken to correlate the vibrational modes correctly between the reagent and product asymptotes.³⁰ Based on a scaled ab initio surface, the adiabatic maximum is lowered by about 3.1 kcal mol⁻¹ when v_2 is increased from 0 to 1, but only by 0.25 kcal mol⁻¹ when v_1 is raised from 0 to 1.

It seems that the results found for the OH + H₂ reaction, demonstrating mode selectivity, are likely to be quite general for *direct* reactions between diatomic reagents. When the bond between the atoms of the diatomic radical remains roughly the same strength throughout the reaction, its vibration will scarcely be coupled to the reaction coordinate, at least during the motion up to the transition state. Consequently, excitation of this mode scarcely affects the reaction rate. On the other hand, excitation of CD will generally promote reaction, with the extent depending on how

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much the adiabatic maximum is lowered as ν_2 is increased.

The first of these conclusions is supported by studies on the kinetics of $\text{OH}(\nu_1=0,1)$ ³¹ and $\text{CN}(\nu_1=0,1)$,³² for which results are presented in Table II. Although the experiments cannot distinguish between loss of $\text{AB}(\nu_1=1)$ by reaction and by relaxation, in most cases the total rate of loss of vibrationally excited radicals is not significantly greater than the loss of unexcited radicals by reaction, so that one can be sure that the rate of reaction is not significantly increased. Where $k(\nu_1=1)$ is appreciably greater than $k(\nu_1=0)$, there are good reasons for supposing that vibrational relaxation is important. As yet, there is no evidence for the effect of vibrational excitation in the molecular reagents, apart from that for $\text{OH} + \text{H}_2(\nu_2=1)$.

(iii) Four-Center Reactions. Reactions between molecules with fully paired electrons must involve at least four atomic centers, as two bonds break (or are modified) and two are formed. The reactions in which a molecule adds across a double or triple bond are important examples. Moreover, it is reactions like these, involving relatively stable polyatomic reagents, that must exhibit observable effects if vibrationally selective chemistry is going to have much practical significance.

Experiments have been performed on the addition of HCl or HBr to C_2H_2 and of HCl to butadiene.^{33,34} In both cases, one of the reagents was excited to a high vibrational overtone ($\Delta\nu = 5, 6$) in either the HX vibration or a C-H stretch mode of the hydrocarbon using a high-power continuous-wave dye laser. Analysis by gas chromatography yielded no evidence for reaction as a result of enhancement by vibrational excitation. In all cases, it seems that collisional relaxation of the excited molecules was much more rapid than reaction.

These "negative" results can be understood in terms of VA-TST, making use of the ab initio calculations on related systems. Kato and Morokuma³⁵ traced the energy and "form" of the MEP (what they termed "the intrinsic reaction coordinate") for the addition of HF to $\text{CH}_2=\text{CH}_2$ (or conversely, elimination of HF from $\text{CH}_3\text{CH}_2\text{F}$). The calculations demonstrated that as HF approaches $\text{CH}_2=\text{CH}_2$, the electronic potential energy rises by ca. 25 kcal mol⁻¹ before either the $\text{CH}_2=\text{CH}_2$ or the HF molecules begin to distort significantly. Although a mode analysis along the MEP was not performed, it seems certain that the vibrationally adiabatic curves are likely to be closely parallel in this region. Consequently, considerable translational energy will be required to bring the reagents sufficiently close for the HF vibration to be effectively coupled to motion along the reaction coordinate. Furthermore, localized C-H excitations are even less likely to promote any reaction since the calculated C-H bond-stretching frequencies in the transition state and in the isolated $\text{CH}_2=\text{CH}_2$ molecule are very similar, so that adiabatic curves corresponding to excitation in these modes will be nearly parallel. Finally, rapid intramolecular re-

distribution of vibrational energy will also tend to mitigate against vibrationally enhanced reactions between polyatomic species. The implications of VA-TST and what we know about intramolecular and intermolecular energy transfer are disappointing but apparently unavoidable.

(iv) Reactions Involving the Formation of Collision Complexes. Reactions between radicals (and ion-molecule reactions) usually occur on potential energy surfaces with a deep well; $V_{\text{el}}(x)$ falls monotonically as the radicals approach, and unpaired electrons on each radical pair up to form a chemical bond. The transition-state region is usually at large separation, the vibrationally adiabatic curves up to this region should be parallel, and hence the rate constants associated with formation of the complex should be very nearly the same for all vibrational states.

For systems where the complex can only dissociate to the original reagents, the rate of formation of complexes can be observed in two ways. Firstly, one can determine the rates at which a vibrationally excited radical is removed by collisions with a second radical; for example, $\text{OH}(\nu=1)$ by NO or NO_2 ⁹ or $\text{CN}(\nu=1)$ by NO .¹⁰ The rate constants (k_{relax}) should correspond closely to those for formation of complexes, since redistribution of energy in such strongly bound complexes is facile, and the statistical probability of dissociation with the original excitation maintained is very small. The rate constants for formation of complexes should also correspond to the rate constants for radical combination in the limit of high pressure; i.e., k^∞ . Unfortunately, for association of small radicals, the limit is only reached at total pressures in excess of 10 atm, so that values of k^∞ for most systems are only obtained by a rather long extrapolation from results at much lower pressures. In cases where comparisons can be made,⁸⁻¹⁰ k_{relax} and k^∞ agree within a factor of ca. 2.

A number of radical-radical reactions, such as $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$ and $\text{NC} + \text{O}_2 \rightarrow \text{NCO} + \text{O}$, proceed by successive bond-making and bond-breaking steps to yield two products. The initial process leading to formation of a transitory complex is rate-determining, the long-range potential is monotonically attractive, and the rate of reaction is expected to be almost independent of the initial vibrational state. Measurements on the kinetics of $\text{CN}(\nu=0)$ and $\text{CN}(\nu=1)$ with O_2 ¹⁰ endorse this expectation.

One approach to estimating the rate of formation of collision complexes in radical-radical and ion-molecule reactions is the statistical adiabatic channel model.³⁶ This extends VA-TST by taking account of angular momentum effects through the addition of an extra term to eq 5 for the energy associated with adiabatic rotations. Specific rate constants for reaction are then obtained by using the basic expression from microcanonical TST:

$$k(E, J) \leq N^*(E, J) / h\rho(E, J)$$

where $N^*(E, J)$ is the number of channels for which E exceeds the adiabatic channel maximum, and $\rho(E, J)$ is the density of reagent states.

Concluding Remarks. The concept of vibrational adiabaticity and its consequences for chemical reactivity

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are now new, but in order to keep this Account within bounds, I have had to restrict severely the number of references to previous reviews and earlier work. Most of these can be traced via refs 1, 2, and 25. Much of the earlier work on vibrational adiabaticity was concerned with its relationship to transition-state theory, especially as applied to the prediction of thermal rate constants. In the present Account, I have tried to emphasize three aspects of vibrational adiabaticity, illustrating them by reference to a variety of reacting systems. The first point is that colliding systems are likely to remain in the same state, that is, behave adiabatically, as they pass across regions of a potential energy surface where the MEP curves only slightly and where the frequencies of motions orthogonal to that along the MEP change relatively little. Secondly, the region of low MEP curvature frequently includes the path from

the separated reagents to the adiabatic maximum for species in a given vibrational state. In consequence, and finally, VA-TST can be used to predict or explain the effects on reactivity of selectively exciting vibrations of the reagents. In general, any rate enhancement will be most pronounced in simple atom transfers when the bond that is broken in the reaction is excited vibrationally. The degree of enhancement will depend on the details of the potential energy surface between the configuration space of the separated reagents and the saddlepoint on the surface.

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Quantitative Modeling of Proximity Effects on Organic Reactivity

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Understanding the dramatic catalytic power of enzymes is one of the most challenging and exciting chemical problems of our time. In 1948, Pauling¹ proposed that enzymes are complementary to the transition states of the reactions that they catalyze, and that enzymatic catalysis results from stabilization of the transition state by attractive interactions with the enzyme. The close analogy between enzymatic and intramolecular reactions was recognized subsequently and exploited to develop chemical models for enzymatic reactions. Subsequently, a number of theories based on structure-reactivity relationships in intramolecular reactions have been advanced to account for the rates of enzyme-catalyzed reactions. Our successful use of force-field transition-state modeling to rationalize the stereochemistry of organic reactions² led us to investigate a similar approach for the understanding and prediction of the relative rates of intramolecular reactions. This Account describes our development of force-field models to provide quantitative predictions of intramolecular reaction rates and to compare these with intermolecular reactivities.

Bruice's³ pioneering studies of intramolecular nucleophilic catalysis led him to conclude that enzymes

accelerate chemical reactions primarily by bringing the reactants into close proximity. This argument can be cast in free energy terms as shown in Figure 1. In a bimolecular or higher order reaction, the free energy costs that are incurred in the early part of the reaction coordinate consist largely of the enthalpic and entropic costs of bringing the reactants together. Enzyme catalysis results in part from the fact that the gathering of reactants, an entropically unfavorable act, occurs as an integral part of the complexation process, which is enthalpically favorable. Various versions of this principle have been proposed.⁴⁻⁹

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