

Intramolecular energy flow and nonadiabaticity in vibrationally mediated chemistry: Wave packet studies of Cl+H₂O

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Time-dependent and time-independent quantum scattering methods are used to investigate state-to-state inelastic and reactive collision dynamics for a three-dimensional (3D) atom+triatom model of Cl+H₂O→HCl+OH. The results elucidate the role of (i) intramolecular vibrational energy transfer and (ii) vibrational nonadiabaticity on the time scale of a reactive encounter in systems with nearly degenerate stretching “local modes.” Adiabatic two-dimensional (2D) vibrational eigenfunctions [$\psi_n(r_1, r_2, R)$] and eigenvalues [$E_n(R)$] are first obtained in OH bond coordinates (r_1, r_2) as a function of Cl–H₂O center-of-mass separation (R), which then provides the requisite adiabatic potential energy curves and nonadiabatic coupling matrix elements for full 3D quantum wave packet propagation. Inspection of these 2D vibrational eigenfunctions indicates that near degeneracy between H₂O symmetric $|01^+\rangle$ and antisymmetric $|01^-\rangle$ states is systematically lifted as R decreases, causing vibrational energy to flow into *local-mode* OH excitations pointing either *toward* (“proximal”) or *away from* (“distal”) the approaching Cl atom, respectively. This suggests a simple yet powerful physical model for mode-specific reactive scattering dynamics, the predictions of which are confirmed by full 3D quantum wave packet calculations over a range of collision velocities. © 2002 American Institute of Physics. [DOI: 10.1063/1.1429651]

I. INTRODUCTION

Influencing chemical reaction pathways by selective vibrational excitation has long been a topic of fundamental interest to the chemical physics community. However, this field has recently become a particularly intense target of research interest, stimulated by the elegant experimental results by Crim, Zare, and co-workers on vibrationally mediated reactions of H with H₂O, HOD, and D₂O.^{1–4} Since these initial pioneering efforts, vibrational control of reactivity has been demonstrated^{1–17} with several reactive atoms (Cl, O) and molecular reaction partners (H₂O, HOD, HCN, CH₄, HCCH). The justification for exploring such vibrationally mediated chemical phenomena is clear; these systems offer the tantalizing prospect for molecule-specific control of reaction pathways via spectroscopic excitation of a particular vibrational mode.

One means of exploring the selectivity offered by vibrational excitation has been to examine branching ratios among various product channels. For example, in the reaction of H with vibrationally excited HOD, Bronikowski *et al.*¹ showed a 25-fold excess of OD versus OH formation with $\nu_{\text{OH}}=1$ excitation, while the corresponding propensity for generating OD versus OH fragments from $\nu_{\text{OD}}=1$ excited HOD molecules was less than 1:8. Similar mode-specific effects have been demonstrated for other reactive atoms and levels of vibrational excitation, both experimentally^{2–7} and theoretically.^{14–20} The Crim group has compared H atom reaction propensities for a series of vibrationally isoenergetic H₂O states containing differing amounts of local-mode OH

stretch versus H–O–H bend excitation. These studies reveal a substantially increased reactivity for quanta placed in stretch versus bend coordinates^{2,3} as well as a greater reaction propensity for all stretch quanta concentrated in a single local mode bond.

One alternate assay of vibrationally mediated chemical phenomena has been to monitor how excitation in the non-reactive “spectator” bond translates into product-state excitation. For example, the Crim group has monitored OH(ν) product resulting from reaction of H and Cl atoms with H₂O in two overtone states, $|04^-\rangle$ and $|13^-\rangle$. (Throughout this paper, we use the notation $|nm^{(+/-)}\rangle$, which denotes symmetric–antisymmetric combination of n and m quanta of local mode stretch excitation.^{3,4}) These studies reveal a marked production of OH($\nu=0$) from H₂O $|04^-\rangle$ reagent and OH($\nu=1$) from H₂O $|13^-\rangle$, respectively, which would be consistent with a propensity to maintain vibrational nodal patterns in the bond that remains asymptotically intact.

These groundbreaking demonstrations of mode-specific reactivity have led to strong support of the simple spectator bond paradigm, whereby vibrational excitation in the non-reactive bond does not participate in the reaction, and thus initial excitation in that bond is likely to be retained in the final product distribution. This view of vibrationally mediated reaction dynamics is also extremely attractive from a theoretical perspective, specifically providing motivation for reduced-dimensionality reactive scattering calculations that fix the length of the nonreactive bond²¹ and greatly reduce computational demands for four-atom reactive scattering. Of course, the reliability of such approximation methods hinges fundamentally on an absence of fast intramolecular vibrational energy flow in the entrance channel, i.e., the asymp-

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totically prepared vibrational state must remain unaffected by approach of the reactant species. However, this common assumption of vibrational adiabaticity is most likely to fail for systems with nearly degenerate vibrational manifolds, due to strong intramolecular mixing of vibrational states already present in the isolated reagent. Such near degeneracy effects would in fact be most evident in vibrationally mediated reaction dynamics of highly symmetric molecules (e.g., H_2O , CH_4), which form the major focus of this paper.

Indeed, there is a growing body of experimental and theoretical evidence demonstrating that the nonreactive bond may not always play the role of a spectator in mode-specific reactions. Such effects have been clearly demonstrated in experiments by Sinha *et al.*³ on $\text{Cl} + \text{HCN}$, which produce similar excitation of the product CN stretch from both $\text{Cl} + \text{HCN}(004)$ and $\text{Cl} + \text{HCN}(302)$, where the first and third quantum numbers reflect normal modes of predominately CN and CH stretch character, respectively. One proposed explanation for this phenomenon was that the $\text{Cl} + \text{HCN}$ reaction proceeds via a complex, resulting in intramolecular vibrational redistribution (IVR) prior to the reaction event. To test this hypothesis, Takayanagi and Schatz carried out quantum scattering calculations on the related $\text{H} + \text{HCN}$ reactions allowing the CN bond to vibrate while constraining HHC to be collinear, a geometry that removes the possibility of complex formation.²² These calculations confirm that excitation to $\text{HCN}(100)$, i.e., one quantum of mostly CN stretch character, significantly enhances the reaction cross section to form $\text{H}_2 + \text{CN}$ and lowers the threshold energy relative to $\text{H} + \text{HCN}(000)$. In fact, the threshold is predicted to be lowered by nearly 100% of the added vibrational energy, which would be more consistent with direct vibrationally mediated coupling into the reaction coordinate.

Similar effects are also evident in studies of water and isotopomers. For example, Sinha *et al.*⁴ note a decreased propensity for vibrationally excited $\text{OH}(v=1)$ production from slower heavy atom ($\text{Cl} + \text{H}_2\text{O}|13^-$) versus faster light atom ($\text{H} + \text{H}_2\text{O}|13^-$) attack. This observation is inconsistent with a simple spectator bond model and suggests a sensitivity to reagent collision velocities. In a similar vein, early quasiclassical trajectory studies of Schatz and co-workers reveal that excitation of the spectator OD bond in HOD (or of highly excited bending states of H_2O) enhances H atom reactivity with respect to the ground vibrational state.^{14,15} By way of confirmation, full six-dimensional (6D) quantum calculations of $\text{H} + \text{HOD}$ by Zhang and Light indicate that excitation of the OD bond causes partial enhancement of reaction probability for OH bond cleavage.²⁰

These observations signal at least a partial breakdown of the spectator bond paradigm. One intriguing scenario for such dynamics is that approach of the reagent species *redistributes* vibrational energy in the entrance channel of the chemical reaction. As this paper attempts to illustrate, such intramolecular vibrational redistribution effects can be especially important for molecules with the *degenerate* “local” vibrational modes, such as CH or OH stretch manifolds in symmetric systems (e.g., CH_4 and H_2O). Here the dynamical issues are both simple and yet quite profound. Asymptotically far away, the local modes are phased by strong intramo-

lecular coupling into symmetric versus asymmetric stretch “normal mode” manifolds characteristic of the molecular point group symmetry. In the entrance channel to the chemical reaction, however, strongly anisotropic interactions due to incipient bond breaking can *uncouple* these vibrations, generating highly *localized* vibrational modes with specific directionality with respect to the reagent species. Depending on whether this vibrational energy ends up localized in the *reactive* versus *spectator* bond, such symmetry breaking effects with respect to reagent approach can, therefore, significantly influence subsequent elastic, inelastic, and reactive scattering processes. Thus, two fundamental questions emerge that constitute the central focus of this paper: (1) How do nearly degenerate vibrations adiabatically evolve in the entrance channel of a reactive encounter? (2) Is such an evolution sufficiently fast or slow on the time scale of the bond breaking event to impact vibrationally adiabatic versus nonadiabatic trajectories?

In order to address this issue of intramolecular energy flow in chemical reactions, we explore exact 3D quantum wave packet reactive scattering dynamics for a simple atom + triatom system with nearly degenerate vibrational modes. As a specific example of experimental interest, these calculations are modeled after the well-studied $\text{Cl} + \text{H}_2\text{O}$ system, approximating the collision with three internal degrees of freedom (r_1, r_2, R). The first task is to determine in a time-independent fashion how the adiabatic vibrational eigenfunctions of the $\text{Cl}-\text{H}_2\text{O}$ system are affected by approach of the reagent Cl atom (R), focusing primarily on entrance-channel energies corresponding to the first excited OH stretch polyad in water, specifically $|01^+\rangle$ and $|01^-\rangle$. This elucidates how the asymptotically degenerate OH vibrational manifold becomes adiabatically “decoupled” and “recoupled” in the entrance channel, converting symmetric and asymmetric stretch excitation into localized proximal and distal vibrations pointing toward (r_1) and away from (r_2) the reactive Cl atom, respectively. Whether such reactions proceed on a single vibrationally adiabatic curve, however, depends on many factors, including nonadiabatic coupling strengths, relative velocity, and asymptotic quantum state of the reagents.²³ These 2D wave functions provide a requisite basis for expanding the incident wave packet, which in conjunction with nonadiabatic coupling matrix elements between these adiabatic curves, permits one to directly follow the elastic, inelastic and reactive scattering dynamics of $\text{Cl} + \text{H}_2\text{O}$ in real time.

The organization of this paper is as follows. Computational details of wave propagation methods used in this work are briefly summarized in Sec. II. In Sec. III, these methods are used to solve for the vibrationally adiabatic eigenfunctions of H_2O as a function of $\text{Cl}-\text{H}_2\text{O}$ center-of-mass separation (R), along with distance-dependent coupling matrix elements between these vibrational states. This permits full time-dependent wave packet reactive scattering results for $\text{Cl} + \text{H}_2\text{O}$ to be calculated, which indeed exhibit strong mode specificity in the elastic, inelastic, and reactive collision dynamics. These results are discussed in terms of simple symmetry breaking models for intramolecular energy flow between degenerate local mode manifolds, with summarizing and concluding comments presented in Sec. IV.

TABLE I. LEPS parameters for the Cl+H₂O potential surface.

Parameter	Bond		
	O–H	H–Cl	O–Cl
β (Å ⁻¹)	2.295	1.868	2.290
D_e (cm ⁻¹)	37 230	37 250	23 600
r_e (Å)	0.970	1.275	1.570
k	0.170	0.158	-0.250
$r^\ddagger$ (Å)	1.154	1.453	

II. COMPUTATIONAL METHODS

A complete quantum scattering calculation for a multi-atom encounter is a formidable task due to the exponential scaling with dimensionality. For 3 or even 4 degrees of freedom, a direct approach is possible by constructing a direct product discrete variable representation (DVR) or fast Fourier transform (FFT) base for representing the wave function. A time-dependent or time-independent propagation scheme can then lead from the initial state to the final product branching probabilities. Without ways to reduce the complexity, however, these schemes cannot scale up to higher degrees of freedom. In this work we explore an adiabatic reduction scheme that not only divides the problem into smaller tasks, but also offers new insights into the fundamental reaction mechanism.

The wave packet propagation methods require an approximate potential surface for the four-atom interaction, as well as a means of efficiently calculating the eigenfunctions. The Cl atom approach toward one side of the H₂O leads to an asymmetry in the two OH groups, which we label as proximal (r_1) and distal (r_2), respectively, with R as the distance between Cl and the H₂O center-of-mass (com). The proximal Cl–H₂O interaction is modeled by the triatomic O+HCl London–Eyring–Polanyi–Sato (LEPS) potential surface given by Persky and Broida,²⁴ with the distal HO–H stretch described by the Morse parameters in Table I. This leaves out the HOH bending mode, but this coordinate is not expected to be relevant to predicting vibrationally mediated reaction versus inelastic branching ratios. A 2D slice through this 3D surface $V(r_1, r_2; R)$ at $R=4.2$ Å is shown in Fig. 1 (with superimposed eigenfunctions described below), which clearly indicates two stable wells associated with localized reactant (i.e., Cl+H₂O) and product (i.e., HCl+OH) states. Since the bond strength in OH is weaker than H–OH, this O+HCl reference potential underestimates the true surface endothermicity by ≈ 16 kcal/mol.²⁵ The approximate nature of this model potential surface, as well as the zero impact parameter (collinear) approach geometry for Cl+H₂O, limits any quantitative comparison with experimental results. However, this choice does permit convenient access to a topologically realistic four-atom surface from very well characterized three-atom surfaces. As a further advantage, the increased exothermicity of this potential surface makes the reaction energetically favorable with OH stretch excitation at the $|01^+\rangle$ and $|01^-\rangle$ level, significantly reducing the grid size necessary for converged wave packet calculations.

In the vibrationally adiabatic reduction, the total wave

Cl + H₂O EIGENFUNCTIONS: R=4.2 Å

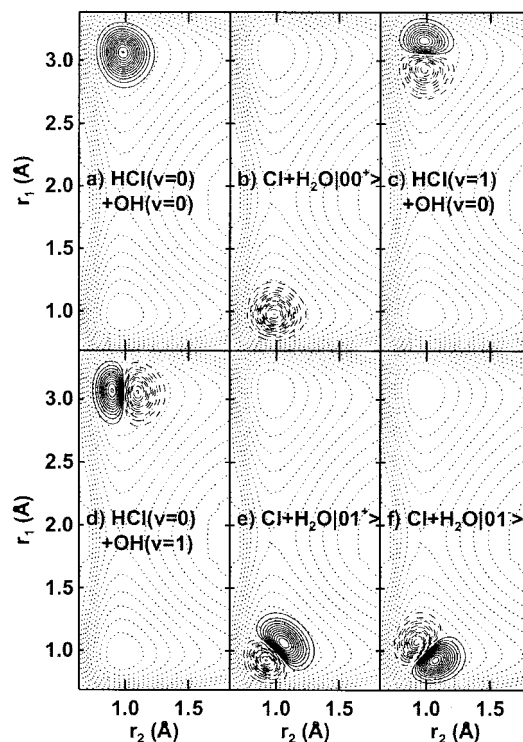


FIG. 1. 2D eigenfunctions for Cl+H₂O at $R=4.2$ Å, superimposed on a potential surface from a LEPS potential (Ref. 24) for O+HCl and HO–H Morse parameters for the distal OH stretch (see text for details). The minima near $r_1 \approx 1$ and 3 Å represent the reactant Cl+H₂O and product OH+HCl wells. The eigenfunctions (a)–(f) are listed in order of increasing energy.

function is separated into vibrational and internuclear motion, i.e.

$$\Psi^{\text{total}} = \sum_n \psi_n(R) \chi_n(r_1, r_2; R), \quad (1)$$

where ψ_n and χ_n represent wave functions in internuclear (R) and vibrational (r_1, r_2) degrees of freedom. The adiabatic functions χ_n are solutions of the time-independent Schrödinger equation for the OH bonds at fixed R

$$\mathbf{H}(r_1, r_2; R) \chi_n(r_1, r_2; R) = E_n(R) \chi_n(r_1, r_2; R). \quad (2)$$

Any changes in χ_n with R reflect the influence of Cl on H₂O vibrational states, while the associated eigenvalues $E_n(R)$ provide a set of 1D adiabatic potential curves for propagating relative Cl–H₂O motion throughout a scattering event. To generate these adiabatic eigenstates and potential curves, a propagation scheme is employed which requires the adiabatic Hamiltonian to operate on the wave function χ . For this task an evenly spaced Fourier grid²⁶ of 128×16 points, with coordinates ranging from $r_1 = 0.63$ – 7.94 Å and $r_2 = 0.63$ – 1.90 Å. The $\approx$ sixfold larger grid in the proximal (r_1) versus distal (r_2) coordinate is necessary to adequately represent the wave function in both reactant (Cl+H₂O) and product (HCl+OH) wells.

Our strategy to determine the family of adiabatic solutions $\chi_n(r_1, r_2; R)$ is based on the property that they are smooth functions; we therefore exploit the eigenfunctions at a particular R as the starting point to calculate the set at a

neighboring point $R + \Delta R$. The method is based on propagating the time-dependent Schrödinger equation in imaginary time, $\tau = it$ ^{27,28}

$$\chi_{\text{trial}}(\tau) = e^{-\mathbf{H}\tau/\hbar} \chi_{\text{trial}}(0). \quad (3)$$

For sufficiently large τ , the trial wave function will approach the ground state of the Hamiltonian $\mathbf{H}$. This process is then repeated to converge any selected excited state eigenfunction, provided that contributions in the trial wave function from *all* eigenstates at *lower* energy have been rigorously eliminated by projection operators. Specifically, the K th eigenstate becomes the ground state of a new Hamiltonian, $\mathbf{H}' = \mathbf{H} \Sigma_{j=0}^{K-1} (1 - |\chi_j\rangle\langle\chi_j|)$, where χ_j are all the previous eigenstates up to K . Thus, once the ground-state eigenfunction is determined, successively higher eigenfunctions can be obtained by iteration. Due to numerical instabilities, all lower eigenfunction contributions must be projected out after each time step to avoid collapse to a lower state. Numerical implementation of Eq. (4) is carried out by a Chebychev polynomial expansion of the exponent following Refs. 27 and 28 where computational effort is proportional to the number of terms in the Chebychev expansion N . Once $N > (\Delta E \tau / 2\hbar)^{1/2}$, the series converges exponentially fast. This means that the numerical effort scales as the square root of the imaginary time τ and energy range ΔE . Convergence onto a specific target eigenstate can be estimated from the energy dispersion relationship²⁹

$$D(\tau) = \sqrt{\langle\chi(\tau)|\mathbf{H}^2|\chi(\tau)\rangle - \langle\chi(\tau)|\mathbf{H}|\chi(\tau)\rangle^2}, \quad (4)$$

which decreases uniformly for increasing “purity” of eigenfunction and vanishes in the limit of an exact eigenstate. The purity $D(\tau)$ of an eigenstate converges with τ at a rate that is inversely proportional to the difference in energy with the adjacent eigenvalues, which could lead to problems for nearly degenerate levels. The adiabatic following method circumvents this difficulty by exploiting as an initial guess the previously determined eigenstate for a nearby value of R . Since this state is almost orthogonal to the adjacent levels, this results in very fast convergence. For this reason, the method is comparable in efficiency to filter diagonalization³⁰ in calculating eigenvalues, with the additional advantage of directly calculating eigenfunctions. Moreover it guarantees that the phase of the wave functions is continuous, therefore eliminating instabilities in calculating the nonadiabatic coupling matrix elements. Due to the exponential properties of Chebychev propagation methods, calculations at each R rapidly converge to the machine precision limit, generating both (i) adiabatic eigenfunctions for H₂O vibration at each R , and (ii) a set of adiabatic potential curves, $E_n(R)$, governing the Cl–H₂O (or HCl–OH) intramolecular motion.

Adiabatic eigenfunctions at typical internuclear distances far out in the entrance channel ($R = 4.23$ Å) are shown in Fig. 1 in order of increasing energy. Panels (b), (e), and (f) clearly reflect Cl+H₂O *reactant* state eigenfunctions, corresponding to the nodeless ground-state ($|00^+\rangle$) followed by the $|01^+\rangle$ and $|01^-\rangle$ OH stretching eigenstates, respectively. Note that the nodal plane orientation for the two excited Cl

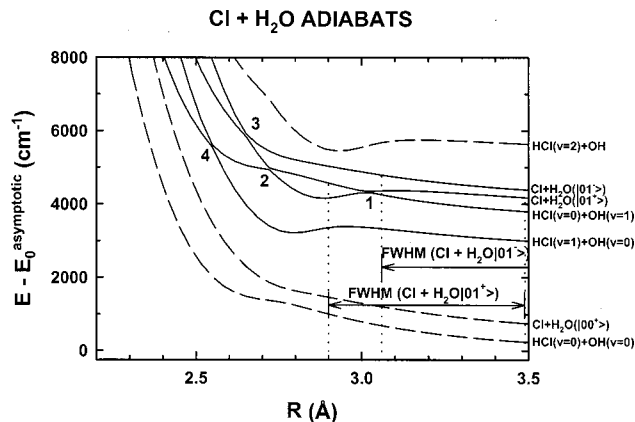


FIG. 2. 1D adiabatic potential energy curves obtained by calculating reactant Cl+H₂O and product OH+HCl eigenenergies as a function of R . Strongly avoided crossings between two curves are designated by numbers with characteristic Massey velocities given in Table II. Classical turning points corresponding to full width at half maximum (FWHM) energies for wave packet propagation at the lowest collision energy ($E_{\text{com}} = 504$ cm⁻¹) are indicated with dashed lines for Cl+H₂O $|01^+\rangle$ and $|01^-\rangle$ asymptotic reactant states.

+H₂O states corresponds to either a symmetric ($\Delta r_1 \approx \Delta r_2$) or antisymmetric ($\Delta r_1 \approx -\Delta r_2$) stretch vibration, i.e., a normal mode excitation *delocalized* over both OH bonds. The three lowest energy *product* state channels are shown in panels (a), (c), and (d), which by similar examination of the nodal structure can be readily identified as corresponding to HCl($v=0$)+OH($v=0$), HCl($v=1$)+OH($v=0$), and HCl($v=0$)+OH($v=1$), respectively. The adiabatic potential curves (Cl+H₂O “adiabats”), $E_n(R)$, are plotted in Fig. 2 as a function of R , each correlating with well defined reagent and product asymptotic states. For later reference, the dashed vertical lines near 2.90 and 3.06 Å correspond to innermost classical turning points on the Cl+H₂O $|01^+\rangle$ and $|01^-\rangle$ adiabats for the lowest mean collision energy studied. It is worth noting that this family of adiabats exhibits a detailed network of both strongly and weakly “avoided” crossings; these prove important in interpreting pathways for nonadiabatic branching between elastic, inelastic and reactive collisional processes.

The curve-crossing probabilities linking these adiabatic curves, $E_n(R)$, for finite reagent approach velocities are governed by the *nonadiabatic* terms in the full 3D Hamiltonian that reflect coupling between vibrational (r_1, r_2) and intermolecular (R) motion. The exact *coupled* Schrödinger equation can be written as³¹

$$\left[\frac{-\hbar^2}{2\mu_{\text{Cl-OH}}} \frac{\partial^2}{\partial R^2} + E_n(R) - E \right] \psi_n(R) = \sum_m \left[\tau_{nm}(R) \frac{\partial}{\partial R} + \rho_{nm}(R) \right] \psi_m(R), \quad (5)$$

where the $E_n(R)$ are the adiabatic vibrational potential energy curves previously calculated, E is the total energy of the system, and τ_{nm} and ρ_{nm} represent matrices of explicit derivative coupling terms

TABLE II. Cl+H₂O curve-crossing velocities (v_{nm}) from Eq. (6) (see Fig. 2 for designation of strongly avoided crossings).

Crossing	Velocity (cm/s)
1	<50
2	800
3	3200
4	1000

$$\tau_{nm}(R) = \frac{\hbar^2}{\mu_{\text{Cl-HOH}}} \left\langle \chi_n \left| \frac{\partial}{\partial R} \right| \chi_m \right\rangle, \quad (6a)$$

$$\rho_{nm}(R) = \frac{\hbar^2}{2\mu_{\text{Cl-HOH}}} \left\langle \chi_n \left| \frac{\partial^2}{\partial R^2} \right| \chi_m \right\rangle. \quad (6b)$$

Exact wave packet propagation requires calculating the complete set of nonadiabatic coupling matrix elements between all pairs of uncoupled states; by Eqs. (6a) and (6b), this information is already available in the R dependence of $\chi_n(R)$. For numerical stability, however, we follow the method of Tuvi and Band³² to symmetrize these coupling terms and preserve the hermiticity of the Hamiltonian.

These coupling matrix elements also provide a simple means for estimating a characteristic crossing velocity between adiabatic curves, which is relevant for semiclassical interpretation of the wave packet dynamics. As described by Child,³¹ nonadiabatic transitions are typically dominated by τ_{nm} , and thus the most relevant coupling term is $|\tau_{nm}\partial/\partial R|$. Recast in terms of the momentum operator, $|\partial/\partial R|$ can be semiclassically expressed as $|\mu_{\text{Cl-HOH}}\mathbf{v}_{\text{rel}}(\mathbf{R})/\hbar|$, where $v_{\text{rel}}(\mathbf{R})$ is the intermolecular Cl–H₂O velocity at a given R . The coupling term $|\tau_{nm}\partial/\partial R| \approx |\tau_{nm}\mu_{\text{Cl-HOH}}\mathbf{v}_{\text{rel}}(\mathbf{R})/\hbar|$ becomes most significant when it equals $|E_n(R) - E_m(R)|$, i.e., the energy spacing between adiabats near a localized crossing. Equating these two terms yields

$$v_{nm}(R) = \frac{|E_m(R) - E_n(R)|}{\left\langle \chi_n \left| \frac{\partial}{\partial R} \right| \chi_m \right\rangle \hbar}, \quad (7)$$

for transitions between n th and m th adiabatic curves. These curve crossing estimates can be quantified by comparison with the Landau–Zener (LZ) model³¹ for *constant* coupling (β_{nm}) between linear *diabatic* curves, $V_n(R)$ and $V_m(R)$. For a slope difference $\Delta F = |\partial(V_n(R) - V_m(R))/\partial R|$, the crossing probability is given by $P_{\text{Landau-Zener}}(v) = \exp(-v_{\text{LZ}}/v)$, where $v_{\text{LZ}} = 2\pi(\beta_{nm}^2)/\Delta F$. However, for linearly intersecting curves, $v_{nm}(R) = (|\Delta F|^2 R^2 + 4(\beta_{nm})^2)^{3/2}/(\beta_{nm}|\Delta F|)$ which yields $\{v_{nm}(R)\}_{\min} = 8(\beta_{nm})^2/|\Delta F| = 8/(2\pi)v_{\text{LZ}}$ at the crossing point. Thus semiclassical motion at $v_{nm}(R)$ corresponds to a Landau–Zener crossing probability of $\exp(-2\pi/8) \approx 0.456$. There are several sharply avoided crossings between isolated Cl+H₂O adiabats clearly evident in Fig. 2. The characteristic velocities associated with these curve crossings (see Table II) are all small ($v_{nm} \approx 10^4$ cm/s or less), but can be important in the classically forbidden region. The more significant nonadiabatic interactions in Fig. 2 are due to multiple state couplings over a broad range of R , which therefore, are difficult to identify as isolated avoided crossings. Nevertheless, these

much stronger nonadiabatic interactions are responsible for the most dramatic R dependent changes in the adiabatic wave functions.

With the complete set of adiabats $[E_n(R)]$ and coupling matrix elements $[\tau_{nm}(R)$ and $\rho_{nm}(R)]$, time-dependent scattering calculations can be initiated on a given adiabatic curve at large Cl–H₂O separation, using Chebychev wave packet propagation in real time.^{26–29} The choice of a $\Delta t = 12.5$ fs time step requires a Chebychev polynomial expansion out to 300–400 terms, which preserves of the total wave packet norm to better than 10^{-8} per time step and 10^{-6} over the 2500 fs duration of the wave packet trajectory. As the Cl–H₂O wave packet flows in from the “entrance channel” region, nonadiabatic coupling terms are responsible for transferring amplitude between different adiabatic potentials, which eventually leads to outgoing flux into several different asymptotic “exit channels.” Indeed, in the context of a vibrationally adiabatic picture, such surface hopping represents the mechanism for inelastic and reactive scattering between the various adiabatic manifolds. Propagation into each exit channel is measured via flux counters³³

$$F = \sum_i J(t_i) \Delta t = \frac{\Delta t}{\mu_{\text{Cl-HOH}}} \sum_i \text{Re} \left[\psi^*(R, t_i) \frac{\hbar}{i} \frac{\partial}{\partial R} \psi(R, t_i) \right], \quad (8)$$

where Δt is the 12.5 fs time step. Immediately past this flux-calculation region, the wave packet is irreversibly attenuated by damping operators, which prevents reflection/transmission of the wave packet at the end of the grid. Following Mandelshtam and Taylor,^{34,35} this damping operator is taken to be $e^{-\gamma(R)}$, where

$$\gamma(R) = c(R - R_0)/(R_{\text{max}} - R_0), \quad R \geq R_0 \quad (9a)$$

$$= 0, \quad R < R_0 \quad (9b)$$

with R_{max} equal to the largest initial Cl–H₂O separation (7.94 Å), and adjustable parameters c and R_0 that cause $e^{-\gamma(R)}$ to decrease monotonically from 1 for $R < R_0$ to $\exp(-c)$ at $R = R_{\text{max}}$. Damping behavior is then optimized for all nonadiabatic couplings turned off by (i) fixing $R_{\text{max}} - R_0 = 1.32$ Å, i.e., significantly larger than the de Broglie wavelength ($\lambda \approx 0.32$ Å) for the lowest momentum wave packet, and (ii) varying c to minimize wave packet reflection and transmission. Numerical convergence has been carefully investigated by varying the position of the absorbing boundaries; accumulated fluxes for each adiabatic channel remain constant to better than 1% for all conditions explored and correctly sum over all channels to the total incident wave packet probability.

III. RESULTS

A. Vibrational eigenfunctions, adiabats, and coupling elements

As outlined above, the reactant (Cl+H₂O) and product (HCl+OH) vibrational eigenfunctions are adiabatically calculated as a function of R , with the corresponding eigenenergies yielding the manifold of adiabatic potential curves shown in Fig. 2. The eigenstates asymptotically represent the

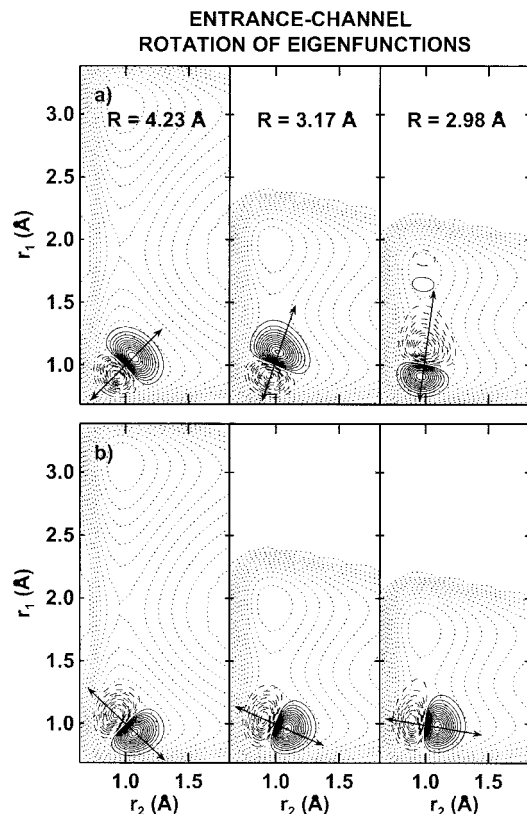


FIG. 3. Entrance channel evolution of symmetric (a) and antisymmetric (b) stretch $\text{Cl} + \text{H}_2\text{O}$ eigenfunctions as R decreases from 4.23 to 2.98 Å. The symmetric stretch nodal pattern rotates toward the *proximal* OH bond (r_1) with Cl approach, so that vibrational excitation points toward the reactive atom. In contrast, the antisymmetric stretch rotates to localize primarily along the *distal* OH bond (r_2). The growth of probability density in the product well for the upper panel signifies that the symmetric stretch wave function is also strongly mixing with $\text{HCl}(v=1) + \text{OH}(v=0)$ product.

ground vibrational states in $\text{Cl} + \text{H}_2\text{O}$ and $\text{OH} + \text{HCl}$, the first excited OH stretching states in $\text{Cl} + \text{H}_2\text{O}$, excited product channels $\text{OH}(v=1) + \text{HCl}$ and $\text{OH} + \text{HCl}(v=1)$, as well as a higher excited-state $\text{HCl}(v=2) + \text{OH}(v=0)$ to sample at least one energetically closed channel. In order of asymptotic energies, the fifth and sixth lowest states correspond to the symmetric ($|01^+\rangle$) and antisymmetric ($|01^-\rangle$) stretch excitation of H_2O , respectively, which serve as input channels for all dynamics calculations described in this work.

The adiabatic energies vary steeply as R approaches 3 Å due to nonadiabatic couplings between the various states, which makes it especially interesting to examine the vibrational eigenstates in this region. Figure 3 focuses on the symmetric ($|01^+\rangle$) and antisymmetric ($|01^-\rangle$) stretch eigenstates at three $\text{Cl}-\text{H}_2\text{O}$ distances: Near-asymptotically ($R = 4.23$ Å), close to the interaction region ($R = 3.17$ Å), and just inside this region ($R = 2.98$ Å). At large R , the nodal patterns for these states are clearly parallel or perpendicular to the $r_1 \approx r_2$ axis, as expected for symmetric and antisymmetric stretch excitation. As the Cl atom approaches, however, the nodal pattern of the symmetric stretch eigenfunction “rotates” clockwise towards the *proximal* OH bond (r_1), adiabatically *localizing* so that the vibrationally excited OH points *toward* the reactive Cl atom. By way of contrast, the

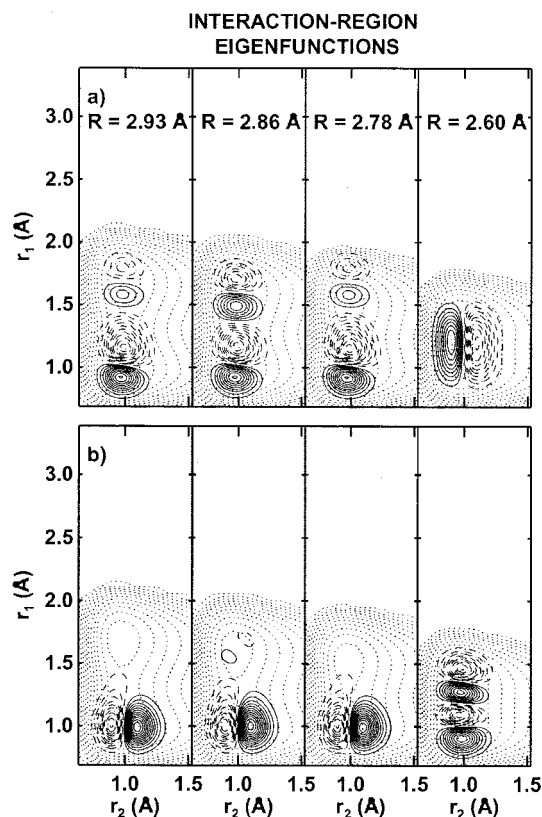


FIG. 4. Evolution of symmetric (a) and antisymmetric (b) stretch $\text{Cl} + \text{H}_2\text{O}$ eigenfunctions in the chemically strong interaction region ($R \approx 2.93\text{--}2.60$ Å). (a) The symmetric stretch shows nearly complete mixing with product channels, specifically $\text{HCl}(v=1) + \text{OH}(v=0)$, despite a significant energy separation between these two states. (b) In contrast, the asymmetric stretch shows little mixing with any product channels, with a nodal pattern remaining predominantly directed along the non reactive distal OH bond.

antisymmetric stretch nodal pattern rotates counterclockwise to localize the nodal pattern along the *distal* OH bond (r_2), i.e., pointing away from the reactive Cl atom. In other words, the Cl atom approach breaks the symmetry of the potential to convert *normal-mode* into *local-mode* stretches, with *symmetric* ($|01^+\rangle$) and *asymmetric* ($|01^-\rangle$) stretch excitation funneling energy into the OH bonds *most* and *least* likely to react, respectively. Based on this simple physical picture, symmetric stretch excitation would be anticipated to yield a greater mode-specific enhancement of chemical reactivity over antisymmetric stretch excitation.

We can explore this prediction in more detail by examination of these symmetric–asymmetric stretch eigenfunctions at progressively smaller R values (see Fig. 4). As shown in Fig. 4(a), the symmetric stretch wave functions remain adiabatically localized in the proximal OH bond, but also develop strong amplitude to be in the $\text{HCl} + \text{OH}$ product well, highlighting the strong propensity toward chemical bond rearrangement. Indeed, examination of eigenfunctions in this region for the next lower energy adiabat (which asymptotically correlates with $\text{HCl} + \text{OH}$ products) confirms this strong mixing by revealing the lost quantum amplitude as $\text{Cl} + \text{proximally excited H}_2\text{O}$. In fact, the additional nodal structure in these wave functions corresponds to formation of

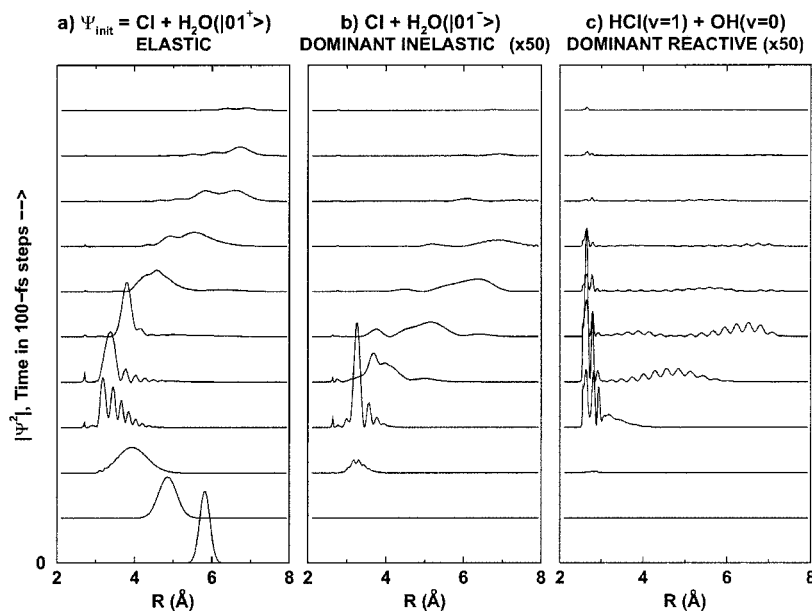


FIG. 5. Sample wave packet propagation ($E_{\text{com}} = 504 \text{ cm}^{-1}$) for initial symmetric stretch excitation, monitoring scattering into (a) elastic [$\text{Cl} + \text{H}_2\text{O}(|01^+\rangle)$], (b) dominant inelastic [$\text{Cl} + \text{H}_2\text{O}(|01^-\rangle)$], and (c) dominant reactive [$\text{HCl}(v=1) + \text{OH}(v=0)$] channels. Each trace (bottom to top) represents incremental 100 fs time steps, with eventual loss of probability from damping at large R . Though most of the wave packet remains elastically in the initial $\text{Cl} + \text{H}_2\text{O}(|01^+\rangle)$ state, there is substantial transfer into both inelastic (b) and reactive (c) scattering channels.

vibrationally excited $\text{HCl}(v=1) + \text{OH}(v=0)$ product, though this prediction depends on the energetics of the specific potential surface. Simply stated, these two $\text{Cl} + \text{H}_2\text{O}(|01^+\rangle)$ reactant and $\text{HCl}(v=1) + \text{OH}(v=0)$ product states are strongly coupled in an adiabatic representation, which would imply a propensity for mode-specific chemical reaction dynamics. By way of contrast, the $|01^-\rangle$ asymmetric stretch excitation remains localized in the $\text{Cl} + \text{H}_2\text{O}$ reagent well, even up to the point where the reagent and product wells nearly coalesce [see Fig. 4(b)]. This is consistent with weaker promotion of the reaction coordinate with distal OH excitation, and again would suggest a *diminished* reactivity for asymmetric versus symmetric stretch excitation.

B. $\text{Cl} + \text{H}_2\text{O}$ wave packet propagation

This simple physical picture for mode specific asymmetric versus symmetric stretch reactivity makes predictions that can be tested explicitly by inclusion of vibrationally nonadiabatic effects. As the next step, therefore, we investigate the full nonadiabatic dynamics by propagating wave packets on each of the adiabatic curves. Gaussian wave packets are chosen with center momenta of 10.0, 15.0, and 20.0 a.u., corresponding to collision speeds of 1.01×10^5 , 1.52×10^5 , and $2.02 \times 10^5 \text{ cm/s}$ and relative kinetic energies of 504, 1130, and 2020 cm^{-1} , respectively. By way of comparison, at 300 K the mean relative speed of Cl and H_2O is 7.3

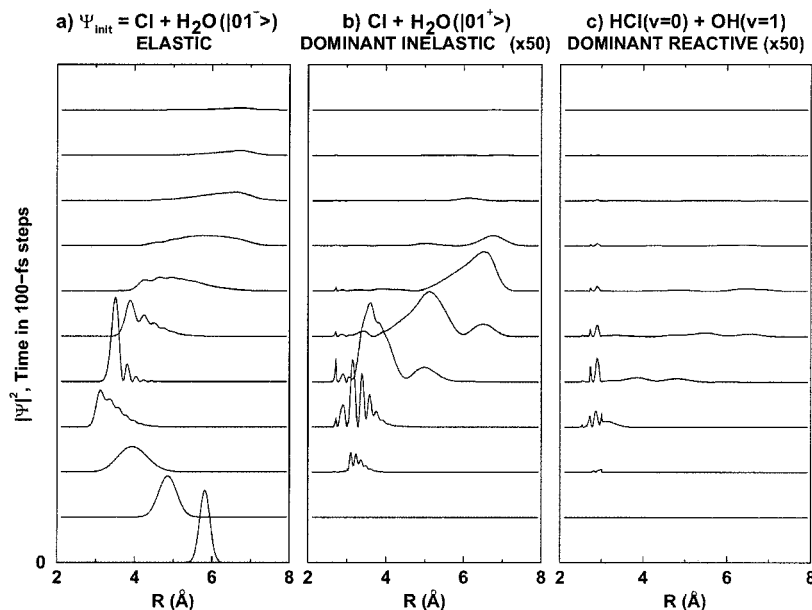


FIG. 6. Sample wave packet propagation ($E_{\text{com}} = 504 \text{ cm}^{-1}$) for initial asymmetric stretch excitation, monitoring scattering into (a) elastic [$\text{Cl} + \text{H}_2\text{O}(|01^-\rangle)$], (b) dominant inelastic [$\text{Cl} + \text{H}_2\text{O}(|01^+\rangle)$], and (c) dominant reactive [$\text{HCl}(v=0) + \text{OH}(v=1)$] channels. Similar to Fig. 6, most of the wave packet probability remains elastically in the initial $\text{Cl} + \text{H}_2\text{O}(|01^-\rangle)$ state. However, the reactive channel represents only a very small fraction of the nonelastically scattered flux, approximately an order of magnitude smaller than observed for reagents with asymptotic symmetric stretch excitation.

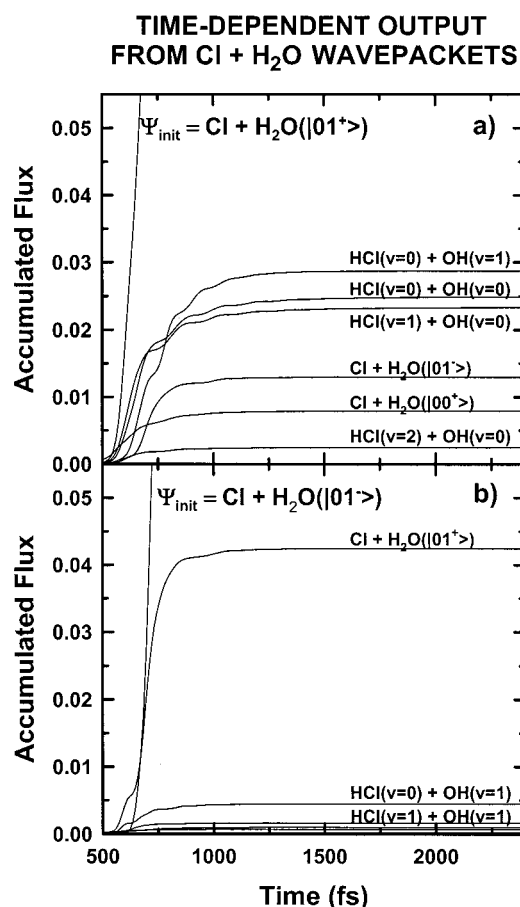


FIG. 7. Accumulated fluxes vs time for scattering of (a) Cl+H₂O(|01⁺) and (b) Cl+H₂O(|01⁻) at $E_{\text{com}} = 504 \text{ cm}^{-1}$. The scattering interactions are predominantly elastic, with >90% probability of exiting on the same adiabat. Of the chemically interesting channels, however, reaction predominates over inelastic scattering for H₂O(|01⁺). By way of contrast, reactive scattering from H₂O(|01⁻) accounts for <10% of the inelastic scattering channel.

$\times 10^4 \text{ cm/s}$, with a mean collision energy of $4kT/\pi = 265 \text{ cm}^{-1}$. In the interest of simplicity, we focus initially on the lowest-velocity collisions of Cl+H₂O at $1.0 \times 10^5 \text{ cm/s}$ ($E \approx 504 \text{ cm}^{-1}$).

Figure 5(a) plots the probability density as a function of time for sample wave packet initiated on the Cl+H₂O(|01⁺) adiabatic curve, beginning at $t=0$ at the bottom and progressively incrementing in 100 fs steps toward the top of the page. Most of the probability remains in the initial |01⁺ state during its pass through the interaction region, disappearing only when attenuated by damping operators at the edge of the grid. As expected, the dominant outcome ($\approx 90\%$) for these collisions between Cl and H₂O(|01⁺) is purely elastic, which is typical for inefficient V-T collision dynamics at thermal energies. Inelastic scattering to Cl+H₂O(|01⁻) asymmetric stretch state plays only a minor role, as demonstrated in Fig. 5(b), which has been increased 50-fold relative to the elastically scattered wave packet for visual clarity. Specifically, symmetric stretch excited reagents at 504 cm^{-1} inelastically scatter to form asymmetric stretch states in only roughly $\approx 1.3\%$ of the collision events,

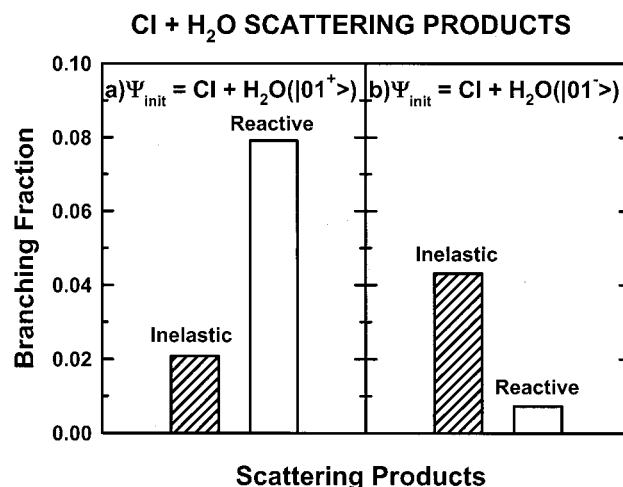


FIG. 8. Branching fractions for $E_{\text{com}} = 504 \text{ cm}^{-1}$ wave packets summed over all inelastic and all reactive channels for (a) Cl+H₂O(|01⁺) and (b) Cl+H₂O(|01⁻) at $\langle E_{\text{com}} \rangle = 504 \text{ cm}^{-1}$. The calculations clearly predict symmetric stretch excitation to be more than an order of magnitude more reactive than antisymmetric stretch excitation, consistent with a simple physical picture of semiclassical localization of OH excitation toward the approaching Cl atom.

with another $\approx 0.7\%$ relaxing all the way to ground state |00⁺)H₂O.

Most relevantly, however, the remaining flux represents reactive scattering between Cl and H₂O(|01⁺). By way of example, Fig. 5(c) demonstrates the time-dependent evolution of the wave packet into the HCl($v=0$)+OH($v=1$) state (also expanded by 50-fold), which indicates a significant ($\approx 2.9\%$) reaction probability per collision. Indeed, comparable probability is also predicted for the other two energetically accessible reactive channels, i.e., 2.5% into HCl($v=0$)+OH($v=0$) and 2.4% into HCl($v=1$)+OH($v=0$). Thus, for *symmetric* stretch excitation, the model predicts a 7.8% total reactive scattering probability, which is $\approx$ four fold larger than the propensity for inelastic scattering. By way of comparison, similar wave packet trajectories at 504 cm^{-1} with asymmetric stretch excited H₂O(|01⁻) are shown in Fig. 6. As expected, the elastic channel predominates, this time with $\approx 95\%$ of the total flux coming out as the initial Cl+H₂O(|01⁻). However, for asymmetric OH excitation, the majority of nonelastic events now occur by *inelastic* scattering ($\approx 4.3\%$) into the Cl+H₂O(|01⁺) channel, with a $\approx$ six fold smaller ($\approx 0.7\%$) branching ratio for *reactive* events. These results are clearly consistent with the simple physical picture of greater reactivity for *distal* versus *proximal* OH stretch localization in the entrance channel.

A more quantitative analysis of branching probability into each exit channel can be obtained by monitoring the accumulated output flux as a function of time. Figure 7 displays accumulated fluxes into each channel versus time for the $E_{\text{com}} = 504 \text{ cm}^{-1}$ calculations of (a) Cl+H₂O(|01⁺) and (b) Cl+H₂O(|01⁻), respectively. Both figure panels emphasize the direct nature of the collisional encounters and the absence of any long-lived resonance states. Figure 8 summarizes the results of these wave packet calculations, separated into reactive and inelastic events. Summed over all channels,

there is a strong propensity for *reactive* ($\approx 7.8\%$) versus *inelastic* ($\approx 2.0\%$) scattering with $\text{Cl} + \text{H}_2\text{O}(|01^+\rangle)$. In contrast, the inelastic channel ($\approx 4.3\%$) for asymmetric stretch excited $\text{Cl} + \text{H}_2\text{O}(|01^-\rangle)$ dominates over the reactive channel ($\approx 0.7\%$). Most importantly is the clear prediction for mode-specific reaction dynamics. Specifically, these wave packet calculations indicate more than one order of magnitude difference in total reactivity between symmetric and asymmetric stretch excited reagents at low energies.

IV. DISCUSSION

A valuable step in the analysis of such a model system is to interpret which trends are likely to be experimentally robust, i.e., independent of the specific details of the potential surface and reduced dimensional collision geometry. The clockwise versus counterclockwise rotation of the $|01^+\rangle$ and $|01^-\rangle$ eigenfunction nodal planes in the presence of a reactive Cl atom arises fundamentally from weakening of the proximal bond and is insensitive to the exact potential energy surface used in these calculations. From an adiabatic perspective, such a localization of symmetric stretch excitation into the proximal OH bond follows immediately from the lower asymptotic energy for $(|01^+\rangle)$ and the noncrossing rule for states of the same point group symmetry. Thus, one would predict qualitatively similar behavior for *any* model of atom+triatom reactive scattering with nearly degenerate $|01^+\rangle$ and $|01^-\rangle$ stretching vibrational states in increasing order. Alternatively stated, the local-mode, reactive bond stretch will always be *lowered* in energy by the approaching reactant relative to the unreactive spectator bond. For only slightly bent molecular hydrides such as H_2O , this leads to a lower energy symmetric versus antisymmetric stretch, which thus predicts a correlation between fundamental symmetric stretch excitation and a propensity for enhanced H atom abstraction in near collinear systems.

Indeed, Schatz³⁶ postulated that this correlation should exist generally in systems with symmetric and antisymmetric stretch modes. This principle was demonstrated with quasiclassical trajectory calculations for $\text{O} + \text{CS}_2$, which preferentially yield more $\text{OS} + \text{CS}$ product from *symmetric* stretch versus *antisymmetric* stretch excited reagent CS_2 .³⁶ Two points are notable here. First of all, similar mode specific trends are observed from quasiclassical calculations in full dimensionality, implying that the qualitative predictions presented in this work for $\text{Cl} + \text{H}_2\text{O}$ would survive averaging over impact parameter and reagent rotation in the entrance channel. Second, this effect appears in both $\text{O} + \text{CS}_2$, in which $\text{O}-\text{S}-\text{C}$ is a light-heavy-light atom combination, and in $\text{Cl} + \text{H}_2\text{O}$, with a $\text{Cl}-\text{H}-\text{O}$ as a heavy-light-heavy combination, in calculations at comparable collision energies. This is important, because the light-heavy-light mass combination in $\text{O} + \text{CS}_2$ leads to much more widely spaced symmetric ($\approx 658\text{ cm}^{-1}$) and antisymmetric ($\approx 1535\text{ cm}^{-1}$) stretch vibrational energies in CS_2 , which would tend to suppress such mode mixing effects. The presence of such mode specific reaction propensities should be even easier to achieve in heavy-light-heavy mass combinations, as evidenced in this paper for the more closely spaced symmetric (3657 cm^{-1}) and antisymmetric (3756 cm^{-1}) stretch vibrations in H_2O .

The precise structure of the interior adiabatic curve crossings in Fig. 2 depends on the exact form of the $\text{Cl} + \text{H}_2\text{O}$ potential surface. However, at low energies, the relevant adiabatic curves and nonadiabatic couplings sampled by vibrationally excited reagents will be similar, irrespective of the precise form of the $\text{Cl} + \text{H}_2\text{O}$ potential. Specifically, for any potential where the reaction is exothermic with respect to OH stretch excited reagents, there will always be $\text{OH} + \text{HCl}$ product state(s) at lower energies, which will mix preferentially with the energetically closer symmetric stretch reagent channel. This implies the model predictions for mode-specific reaction dynamics to be qualitatively robust with respect to precise arrangement of product state channels, at least for low-collision energies that do not sample the interior curve crossing regions. By way of supporting evidence, the full wave packet calculations for symmetric stretch excited $|01^+\rangle$ reagent do not funnel product into a *single* channel, but (as shown in Fig. 7) instead distribute nearly equivalent population in each of the three available product channels [$\text{HCl}(v=1) + \text{OH}(v=0)$, $\text{HCl}(v=0) + \text{OH}(v=1)$, and $\text{HCl}(v=0) + \text{OH}(v=0)$]. Furthermore, we have also seen similar mode-specific trends with symmetric and asymmetric stretch excited D_2O , for which reagent and product state adiabats are significantly shifted from those of H_2O by both isotopic mass and zero-point effects.³⁷

At higher collision energies, however, deeper classical turning points are sampled which can in turn influence predictions of the proposed model. Figure 9 plots the output fluxes from (a) $\text{Cl} + \text{H}_2\text{O}(|01^+\rangle)$ and (b) $\text{Cl} + \text{H}_2\text{O}(|01^-\rangle)$, respectively, as a function of increasing momentum and illustrates two major points. First of all, the total fraction of inelastic and reactive scattering events *increases* with increasing momentum for both vibrationally excited reagents. This reflects the more extensive network of avoided crossings accessed by wave packets at higher momenta, as evidenced by the location of the classical turning points further into the interaction region. Second, there is a more rapid *increase* in the reactive branching fraction for asymmetric stretch $|01^-\rangle$ excitation, which eventually becomes comparable to the branching fraction for symmetric stretch $|01^+\rangle$ excited reagents. Based on Fig. 2, this can be rationalized by the additional crossing between $|01^-\rangle$ and $|01^+\rangle$ adiabatic curves near $R \approx 2.66\text{ \AA}$ (labeled #3) accessed at higher collision energies. Such a crossing transfers amplitude between these two states and, therefore, tends to equalize the more dramatic mode-specific effects evident at lower energies. These higher energy predictions could depend on the precise location of the curve crossings between $|01^+\rangle$ and $|01^-\rangle$ states and, therefore, may depend on exact details of the potential surface, unlike the more robust predictions of mode specificity at lower energies. However, this energy dependent behavior is also completely consistent with our simple physical model. Specifically, for faster collisions, there is not sufficient time in the entrance channel for vibrational energy to localize into proximal and distal excitations, and thus the reactivity of symmetric and asymmetric stretch excitation becomes more equivalent.

Based on the ubiquitous presence of nearly degenerate H-stretching manifolds in chemistry, such mode-specific pre-

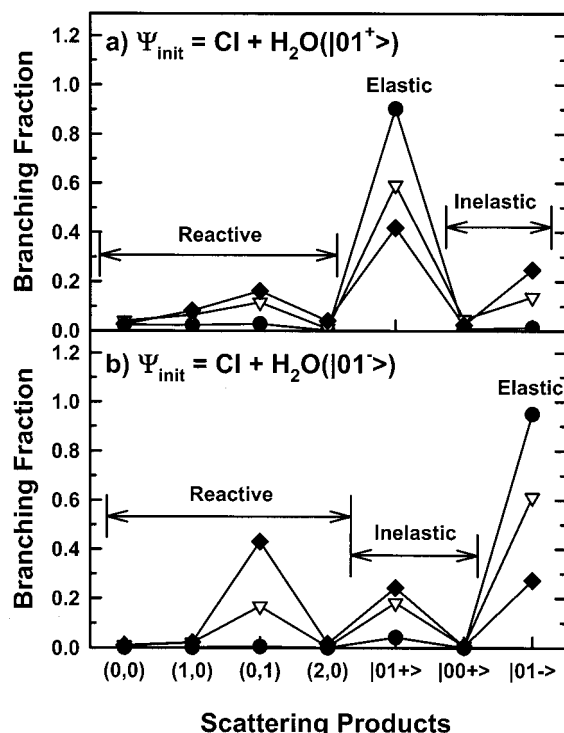
ENERGY-DEPENDENT
BRANCHING RATIOS

FIG. 9. Energy dependence of output fluxes in each channel from (a) Cl + H₂O(|01⁺) and (b) Cl + H₂O(|01⁻), with $E_{\text{com}} = 504$ (●), 1130 (▽), and 2020 cm⁻¹ (◆). The reactive HCl + OH product channels are labeled by (v_{HCl} , v_{OH}) vibrational quanta, while the elastic and inelastic states are labeled by the vibrational state of H₂O. Total inelastic and reactive cross sections increase with increasing E_{com} for both symmetric and antisymmetric stretch excitation. However, the propensity for reactive scattering from symmetric stretch vs asymmetric stretch excited reagents equalizes with increasing E_{com} , due to avoided crossings between Cl + H₂O(|01⁺) and Cl + H₂O(|01⁻) adiabats accessed at higher collision energies.

dictions could have potential relevance in many molecular systems. By way of example, we have recently performed 5D calculations for CH stretch excited CH₄ approaching Ni (111) metal surfaces, in order to explore mode-specific dynamics of vibrationally mediated surface adsorption.³⁸ The results are fully consistent with the trends observed in this work for Cl + H₂O reactive/inelastic scattering. Specifically, the lowest (nondegenerate, v_1 symmetric CH stretch) vibration correlates strongly with the localization of CH stretch energy in the proximal CH bond pointing toward the metal surface, whereas the next higher energy (triply degenerate, asymmetric v_3 CH stretch) vibration splits into an A and E state, each of which corresponds to localized CH stretch excitation in the distal methyl CH₃ group itself. Though full wave packet calculations have not yet been performed for intermolecular approach of CH₄ to the Ni(111) surface, these results once again highlight the general propensity for vibrational localization of nearly degenerate stretches into proximal versus distal ends of the molecule. This concurrence of results in both H₂O and CH₄ strengthens our intuition that such vibrationally mode-specific dynamics are likely to play an important role in a variety of reaction systems and repre-

sent interesting candidates for further experimental and theoretical investigation.

V. SUMMARY

The role of intramolecular vibrational redistribution (IVR) in vibrationally mediated chemistry has been explored using a simple model system representing the reaction of Cl with water isotopes. For the vibrational eigenfunctions, the near-resonance of the H₂O symmetric and antisymmetric stretch allows these states to couple strongly as the Cl atom approaches. These couplings transform the symmetric and antisymmetric stretches of H₂O into local-mode excitations, with the symmetric stretch pointing *towards* the Cl, and the antisymmetric stretch pointing *away from* the Cl atom. Time-dependent wave packets propagated from each of these two states thus yield greater total product formation (i.e., HCl + OH) from the symmetric stretch than the antisymmetric stretch at low collision velocities. The adiabatic correlation between (i) nearly degenerate vibrations and (ii) distal versus proximal excitation in the entrance channel is quite general and should hold qualitatively for a wide range of atom + triatom systems. This suggests that the vibrationally mode-specific effects observed in this model system will survive treatment in higher dimensionality, and represent a dynamical paradigm worthy of further exploration with more realistic intermolecular potentials.

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