JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

pubs.acs.org/JACS

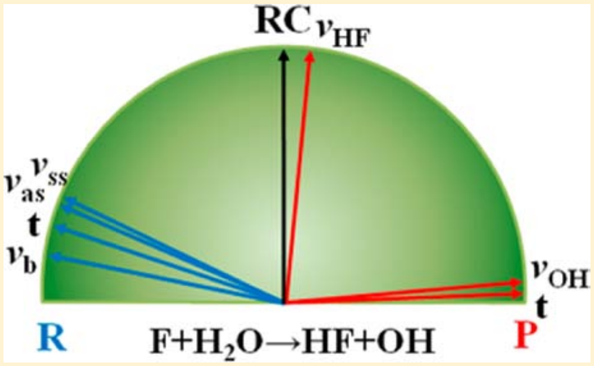
Control of Mode/Bond Selectivity and Product Energy Disposal by the Transition State: X + H_2O (X = H, F, O(^{3}P), and Cl) Reactions

Bin Jiang and Hua Guo*

Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States

Supporting Information

ABSTRACT: The ability to predict mode/bond selectivity and energy disposal is of central importance for controlling chemical reactions. We argue that the transition state plays a critical role in state-to-state reactivity and propose a simple sudden model based on coupling with the reaction coordinate at the transition state. The applicability of this so-called sudden vector projection (SVP) model is examined for several prototypical atom−triatom, namely, X + H_2O (X = H, F, O(^{3}P), and Cl) reactions. It is shown that the SVP model is capable of qualitatively predicting experimental and full-dimensional quantum dynamical results, including those reported in this work, for these polyatomic reactions. These results, and those for other reactions, suggest that the SVP model offers a general paradigm for understanding quantum state resolved reactivity in bimolecular reactions.



INTRODUCTION

Since the introduction by Wigner, Eyring, Evans, and Polanyi, the concept of the activated reaction complex or transition state has played a prominent part in the rate theory of chemical reactions.[1−3] However, its role in controlling state-to-state chemistry is much less well understood. The advances in a crossed molecular beam approach to reaction dynamics and the advent of lasers for pumping and probing molecules have allowed the accumulation of a large body of knowledge concerning state-to-state reactivity for bimolecular reactions,[4−6] which has been distilled into several useful empirical rules. In particular, Polanyi has summarized the experimental and theoretical observations in atom−diatom reactions in what are known today as Polanyi's rules:[7,8] translational energy is more effective in promoting exothermic reactions with an early barrier while vibrational energy is more effective in promoting endothermic reactions with a late barrier. By invoking microscopic reversibility, these rules can also be used to predict energy disposal in reaction products.[7,8] Over the years, these powerful and intuitive rules have served as guiding principles in understanding mode/bond selectivity and energy disposal in chemical processes.[9−12]

Polanyi's insightful use of the barrier location along the reaction path to predict mode selectivity underscores the importance of the transition state in state-to-state dynamics. However, extensions of these venerable rules to polyatomic reactions are not straightforward because all reactant vibrational modes are not expected to have the same effect on reactivity. Indeed, surprising mode selectivities have recently been reported in several polyatomic reactions,[13−18] which demand a more general paradigm to conceptualize these new findings. To answer this challenge, we have recently proposed the sudden vector projection (SVP) model,[19] based on the long-held belief that "initial excitation of a motion that has a large component along the reaction coordinate should accelerate the reaction".[12] The coupling of a particular reactant mode, vibrational or translational, with the reaction coordinate is conveniently computed by projecting the corresponding reactant normal-mode vector onto the vector representing the reaction coordinate at the transition state. Applications of the SVP model to atom−diatom systems have shown that this model yields predictions that are consistent with Polanyi's rules.[19] A distinct advantage of the SVP model is that it is also amenable to polyatomic reactions. Indeed, it has been used successfully to account for the experimentally observed mode and bond selectivities in the dissociative chemisorption of methane on Ni(111).[20,21] Here, we extend the application of the SVP model to several prototypical atom−triatom systems, in particular, the X + H_2O (X = H, F, O(^{3}P), and Cl) reactions (O(^{3}P) will be abbreviated as O thereafter), which have much richer chemistry than atom−diatom reactions but can still be treated with accurate quantum dynamical methods in full dimensionality. The aim is to determine whether this transition-state-based approach is capable of predicting mode/bond selectivity and energy disposal in these reactions.

Received: August 16, 2013
Published: September 17, 2013

dx.doi.org/10.1021/ja408422y | *J. Am. Chem. Soc.* 2013, 135, 15251−15256

■ METHODS

Our full-dimensional quantum scattering calculations were carried out using the Chebyshev real wave packet method,[22] and the details can be found in Supporting Information.

The SVP model[19] is based on the premise that the collision between the reactants happens instantly, which should be valid for most activated bimolecular reactions, particularly at high collision energies. In this sudden regime, intramolecular vibrational energy redistribution (IVR) in the reactant is negligible, even for vibrationally excited ones, until the system reaches the transition state. As a result, the enhancement of reactivity by exciting a particular reactant vibrational mode is largely determined by the projection of the corresponding vibrational vector onto that of the reaction coordinate at the transition state.

To evaluate the projections, the reaction coordinate vector ($\vec{Q}_{RC}$) is first determined at the saddle point via a normal-mode analysis, which corresponds to the mode with an imaginary frequency. Subsequently, the reactants are separated from the saddle point along the scattering coordinate, followed by the determination of the reactant normal-mode vectors ($\vec{Q}_v$) at its optimized geometry. A generalized normal-mode vector can also been determined for the translational motion ($\vec{Q}_t$) by setting up infinitesimal displacements of the two reactants along the scattering coordinate with mass-weighted normalization. As discussed in our initial work,[19] the SVP model can also be used to predict energy disposal in the products by invoking microscopic reversibility. This is done by projecting the product vibrational/translational vectors onto the reaction coordinate at the transition state in the product scattering coordinates.

■ RESULTS

Quantum Dynamics. Due to the hydrogen abstraction nature of these reactions, a full-dimensional quantum treatment of the dynamics is essential to describe quantum effects such as tunneling, zero-point energy, and resonances. The mode selectivity in the late barrier H + H_2O system has been investigated with both classical[23−27] and quantum models.[28−33] Very recently, an extensive investigation of mode selectivity in this reaction was reported by Fu and Zhang[34] on an accurate global PES.[35] Their calculated energy dependence of the integral cross sections (ICSs), which is reproduced in Figure 1, will be used in our analysis. In this figure, (n_1,n_2,n_3) denotes quantum numbers in the symmetric stretching (SS), bending (B), and antisymmetric stretching (AS) modes of rotationless H_2O, and only the first overtones and the ground state are included.

The F + H_2O reaction has an early barrier,[36,37] and its mode selectivity has recently been investigated by us[18] on an ab initio-based PES,[38] using the centrifugal sudden (CS) approximation.[39,40] Here, we have recalculated the excitation function for $H_2O(0,0,0)$ on the spin−orbit (SO)-corrected PES,[41] using the coupled channel (CC) approach, which includes the Coriolis coupling. As shown in Figure S2, the difference in ICS is small, which validates the CS approximation. In Figure 1, the new excitation functions for the F + $H_2O(n_1,n_2,n_3)$ reaction are displayed, which are qualitatively similar to those reported before on the non-SO-corrected PES.[18]

We have also carried out full-dimensional quantum dynamical calculations on the late barrier O + H_2O reaction on a new ab initio-based PES,[42] which represents a significant improvement over previous PESs.[43,44] It is shown in Figure S2 that the CS and CC reaction probabilities are almost identical for $H_2O(0,0,0)$. As a result, excitation functions were computed using the CS approximation, which are also included in Figure 1.

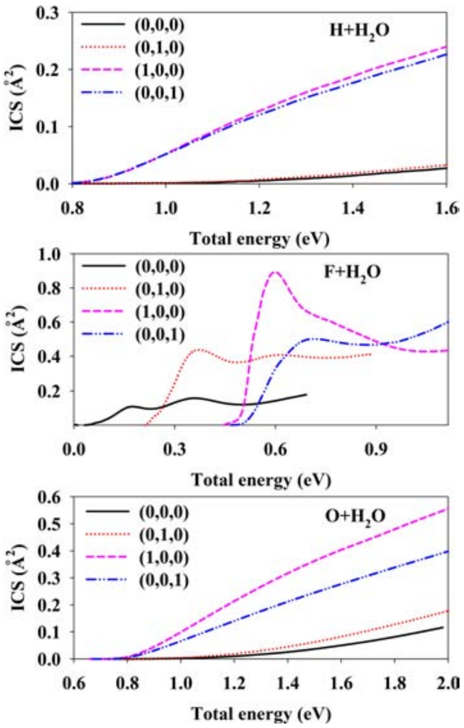


Figure 1. Quantum excitation functions for the X + H_2O (X = H, F, and O) reactions in total energy, which is referenced to the $H_2O(000)$ level. The ground and first overtone excited vibrational states of H_2O are included.

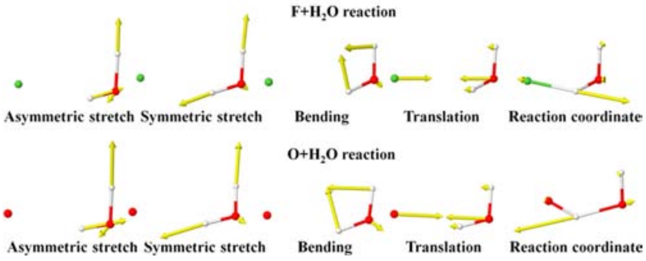
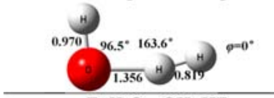
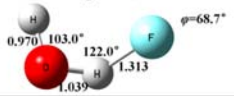
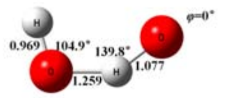
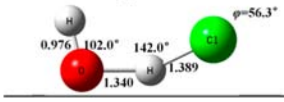


Figure 2. Reactant vibrational and translational mode vectors, and the vector of the reaction coordinate at the transition state displayed in the mass-scaled coordinates for F + H_2O and O + H_2O reactions.

Mode Selectivity. The generalized normal-mode vectors are shown in Figure 2 for the F + H_2O and O + H_2O reactions. As expected, the reaction coordinate vector for the early barrier F + H_2O reaction is dominated by the H−F stretch, while that for the late barrier O + H_2O reaction is dominated by the O−H stretch in H_2O. A large projection for a reactant mode ($\vec{Q}_{RC}\cdot\vec{Q}_t$ or $\vec{Q}_{RC}\cdot\vec{Q}_v$) indicates a strong coupling with the reaction coordinate in the sudden limit and vice versa. The calculated SVP values for the four atom−triatom reactions are listed in Table 1, and the vector alignments are shown in Figure 3.

We first examine the extensively studied late barrier H + H_2O reaction. It is shown in Figure 1 that both stretching modes of H_2O greatly promote the reaction while the bending mode enhances the reactivity only slightly. As shown in Table 1, the SVP model predicts that both stretching modes are strongly coupled with the reaction coordinate with equal overlaps of 0.66, while the bending mode has a weaker coupling with an overlap of 0.15. The only inconsistency is that the bending

Table 1. Projections of the Reactant Vibrational and Translational Vectors onto the Reaction Coordinate at the Transition State for the X + H_2O (X = H, F, O, and Cl) Reactions and Their Reverses

Reaction Saddle Point Geometry[a]	Reactant		Product
$H+H_2O \rightarrow OH+H_2$ 	ν_{as}	0.66	H_2: 0.36 OH: 5×10^{-4}
	ν_{ss}	0.66	
	ν_b	0.15	
	trans.	0.33	0.90
$F+H_2O \rightarrow OH+HF$ 	ν_{as}	0.34	HF: 0.99 OH: 0.083
	ν_{ss}	0.36	
	ν_b	0.16	
	trans.	0.27	0.023
$O+H_2O \rightarrow OH+OH$ 	ν_{as}	0.69	OH: 0.76[b] OH: 0.01[b]
	ν_{ss}	0.72	
	ν_b	0.037	
	trans.	0.053	0.27
$Cl+H_2O \rightarrow OH+HCl$ 	ν_{as}	0.69	HCl: 0.70 OH: 0.02
	ν_{ss}	0.71	
	ν_b	0.055	
	trans.	0.096	0.36

[a]Bond length in Ang., and bond angle in degrees. [b]The two OH species are distinguishable in our model.

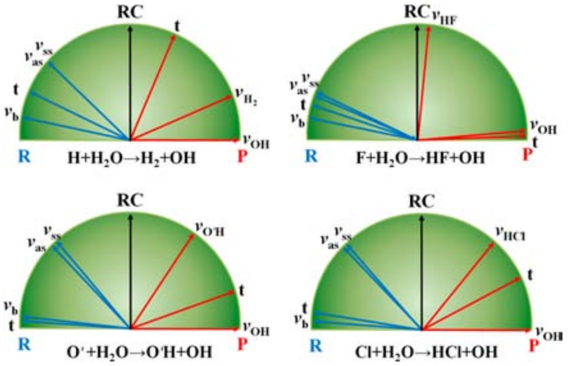


Figure 3. Alignment of reactant (R, blue) and product (P, red) vibrational and translational vectors relative to the reaction coordinate vector at the transition state (RC, black) for the X + H_2O (X = H, F, O, and Cl) reactions.

mode is predicted by SVP to be less potent than the translational mode ($\vec{Q}_{RC}\cdot\vec{Q}_t = 0.33$) in promoting the reaction, while the quantum results indicate comparable efficacies. We note that there have been some experimental mode-selective studies on this reaction,[45,46] but the vibration of H_2O is highly excited (up to 4 stretching quanta). We will defer the interpretation of the experimental findings to the next section.

Next, we focus on the F + H_2O reaction, which has a low early barrier. As shown in Figure 1, our quantum scattering calculations on an ab initio PES of the ground electronic state[38,41] suggested that excitations in all three vibrational modes of H_2O enhance the reaction more than translational energy.[18] A naive extension of Polanyi's rules would have predicted that translation is more effective than vibration in promoting such a reaction. This inconsistence can be largely resolved by SVP, which predicts that all vibrational modes of H_2O couple with the reaction coordinate in the order of symmetric stretch, asymmetric stretch, and bend. This is largely consistent with the quantum results, although the SVP model seems to slightly underestimate the enhancement of the bending excitation. The larger enhancement of bending excitation is likely due to the strong stereodynamic forces from the unusually deep prereaction van der Waals well,[47,48] which is not taken into account in the SVP model.

The new quantum excitation functions for the late barrier O + H_2O reaction in Figure 1 indicate again that the two stretching modes of the H_2O reactant are much more effective in promoting this reaction than the bending or translational mode. This is consistent with Polanyi's rules as well as the SVP model. We note that the symmetric stretch is predicted by SVP to better aligned with the reaction coordinate, which is borne out by the quantum results. The slightly larger enhancement by bending excitation than that by translational excitation is not quantitatively predicted by SVP, although it does predict that neither mode is well-aligned with the reaction coordinate.

Finally, the SVP values for the Cl + H_2O reaction listed in Table 1 serve as predictions because neither experiment nor full-dimensional quantum scattering calculations have been reported on this reaction. The situation here is very similar to the O + H_2O case, as both reactions are endothermic and have a late barrier.

We note in passing that similar mode selectivity has been found in the dissociative adsorption of H_2O on a metal surface.[49,50]

Energy Disposal. There have been several experimental studies on the energy disposal in the X + $H_2O/D_2O/HOD$ reactions (X = H, F, O, and Cl).[45,46,51−61] The SVP predictions are given in Tables 1 and 2 and are illustrated in Figure 3. For the H + H_2O/D_2O reaction, the SVP predictions are consistent with both the experimental[45,46,52−54,57] and theoretical results,[26,27,62] which showed some internal excitation in H_2 while OH behaves as a spectator.

SVP predictions are also consistent with experimental[58−60] and theoretical results[38,41] for the F + H_2O reaction, in which the HF is found vibrationally hot while OH stays as a spectator. Similar predictions are borne out in experimental[61] and QCT studies[42,43,63] of the O + H_2O reaction, where the nascent OH product has significant internal excitation while the spectator OH is internally cold. Finally, the vibrational excited HCl product is consistent with the experimental reports on the Cl reaction with vibrationally excited H_2O and HOD.[51,55]

Bond Selectivity. There have been many experimental studies on the bond selectivity in the X + HOD (X = H, O, and Cl) reaction.[45,46,51,54,55,61,64−66] These experiments, along with theoretical studies,[24,26,29] showed the propensity of bond breaking when the corresponding vibration is excited. In Table 2, SVP predictions of bond selectivity for these atom−triatom reactions are summarized. As expected, the excitation of the OH (OD) local mode vibration is predicted to greatly enhance the reaction leading to the cleavage of the O−H (O−D) bond. Analogous bond selectivity was noted in HOD dissociative chemisorption on a metal surface.[67]

■ DISCUSSION AND SUMMARY

The comparison with available experimental and high-level theoretical results has demonstrated that the SVP model is capable of predicting general trends in both the mode/bond selectivity and energy disposal for these atom−triatom reactions. The success strongly suggests that both quantum state resolved reactivity and energy disposal are controlled to a large extent by the transition state. This is an important but not

Table 2. Projections of the Reactant Vibrational and Translational Vectors onto the Reaction Coordinate at the Transition State for the X + HOD (X = H, F, O, and Cl) Reactions and Their Reverses

		OH cleavage		OD cleavage	
reaction	mode	reactant	product	reactant	product
$H + HOD \rightarrow OD + H_2$ $H + HOD \rightarrow OH + HD$	ν_{OH}	0.93	H_2: 0.36	0.05	HD: 0.30
	ν_{OD}	0.04	OD: 6×10^{-3}	0.96	OH: 0.01
	ν_b	0.14		0.16	
	trans	0.32	0.89	0.24	0.93
$F + HOD \rightarrow OD + HF$ $F + HOD \rightarrow OH + DF$	ν_{OH}	0.49	HF: 0.99	7×10^{-3}	DF: 0.99
	ν_{OD}	0.04	OD: 0.03	0.49	OH: 5×10^{-4}
	ν_b	0.17		0.12	
	trans	0.27	0.02	0.36	0.05
$O + HOD \rightarrow OH + OD$	ν_{OH}	0.99	OH: 0.76	0.04	OH: 9×10^{-3}
	ν_{OD}	0.08	OD: 0.01	0.99	OD: 0.75
	ν_b	0.03		0.02	
	trans	0.05	0.27	0.08	0.36
$Cl + HOD \rightarrow OD + HCl$ $Cl + HOD \rightarrow OH + DCl$	ν_{OH}	0.99	HCl: 0.71	0.06	DCl: 0.69
	ν_{OD}	0.08	OD: 7×10^{-3}	0.99	OH: 5×10^{-3}
	ν_b	0.06		0.05	
	trans	0.09	0.35	0.09	0.46

unexpected conclusion. It is long known that quantum dynamics near the transition state plays a central role in state-to-state reaction dynamics. For example, Duff and Truhlar pointed out that the reaction path curvature at the transition state has a large impact on reactivity.[68] Levine and co-workers have shown that reactivity is controlled by the cone of acceptance, determined by the anisotropy of the saddle point.[69] A similar observation for product energy disposal was made by Blais, Truhlar, and Garrett.[70] It is also widely known that product state distributions in photodissociation, which can be considered as a half-collision, can often be approximated by Franck−Condon overlaps between the initial wave packet and product state wave functions.[71] Similarly, impulsive models such as DIPR (direct interaction with product repulsion)[72] have been used to predict product energy disposal.[73,74] In addition, Truhlar and co-workers have emphasized the role of quantum bottleneck states in reactivity.[75] More recently, Skodje and co-workers have shown that state-to-state reaction probabilities can be approximated by Franck−Condon overlaps between reactant/product and transition-state wave functions.[76] A similar idea to extract state-to-state attributes was proposed earlier by Schatz and Ross using Franck−Condon overlaps between single arrangement channel scattering wave functions.[77] Very recently, Manthe and co-workers have demonstrated that S-matrix elements can be obtained via a transition-state wave packet method.[78] Our key contribution is the realization that the alignment between a reactant/product normal-mode vector and the vector representing the reaction coordinate at the transition state is tied to reactivity/energy disposal.

It is interesting to contrast SVP with the vibrationally adiabatic model (VAM)[3] based on the reaction path Hamiltonian.[79] In contrast to SVP, VAM assumes that the collision dynamics is adiabatic and reaction probability is proportional to the vibrationally adiabatic barrier. Extensive VAM analyses have been performed on the X + CH_4 type reactions.[80−84] For the X + H_2O type reactions, VAM shows that the H_2O symmetric and antisymmetric stretching modes localize as X approaches.[18,42,85] As a result, the former adiabatically "softens" near the saddle point with a significantly reduced frequency, which leads to a lower vibrationally adiabatic barrier than that for the ground vibrational state of H_2O. The bending mode also softens to produce a lower adiabatic barrier. It was thus argued that the barrier lowering leads to enhanced reactivity when these modes are excited. On the other hand, the reactivity enhancement by exciting the antisymmetric stretching mode has to be explained by vibrationally nonadiabatic transitions to the symmetric stretching mode, akin to IVR.[86] However, it is difficult to extract quantitative information about the enhancement of the antisymmetric stretch excitation without doing dynamics. As argued previously,[19] the SVP and VAM represent two limiting cases for bimolecular reactions, but the X + H_2O reactions studied here appear to be closer to the sudden limit, thanks to the sparse density of vibrational states and thus slow IVR in H_2O.

It is however important to emphasize that the SVP model is no panacea. While it does provide a more quantitative picture about the coupling between reactant vibrational/translational modes and the reaction coordinate at the transition state, there is some arbitrariness in the way the projections are computed, which might be responsible for the less accurate prediction of the enhancement of the reactant translational mode. In addition, this model cannot assess the efficacy of multiquanta excitation in the reactant. Furthermore, it is expected to neither capture the influence of weak anisotropic forces in prereaction complexes that might dominate reaction dynamics at low collision energies[14,47,87] nor describe reactions that have more than one transition state or strong final state interaction. However, the SVP model could be used as the starting point to assess the influence of factors mentioned above by comparing with experimental results, in which any departure from this sudden limit would suggest the importance of these factors.

In summary, a simple and general model based on the sudden approximation is proposed to extend Polanyi's rules to reactions involving polyatomic systems. This so-called SVP model attributes reactivity to the coupling between a reactant normal mode and the reaction coordinate at the transition state, which can be readily computed once the potential energy surface near the transition state is known. Tests in atom−diatom,[19] atom−triatom (this work), and reactions involving penta-atomic reactants[20,21] have demonstrated its prowess.

These successes underscore the long-held belief that reactivity and energy disposal of bimolecular reactions are largely controlled by the transition state, particularly the reaction coordinate traversing the barrier. This model can be readily implemented in transition-state theory packages such as POLYRATE[88] and might be useful for predicting mode/bond selectivity and energy disposal in reactions in the gaseous phase, surface, and perhaps in solutions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of theoretical methods and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hguo@unm.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Science Foundation (Grant No. CHE-0910828). We thank Joel Bowman, Fleming Crim, Bill Hase, Kopin Liu, Uwe Manthe, David Nesbitt, John Polanyi, Don Truhlar, and Dick Zare for some stimulating discussions, and Jun Li for his help on the potential energy surfaces.

■ REFERENCES

(1) Levine, R. D. *Quantum Mechanics of Molecular Rate Processes*; Clarendon: Oxford, 1969.
(2) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, NJ, 1989.
(3) Truhlar, D. G.; Issacson, A. D.; Garrett, B. C. In *Theory of Chemical Reaction Dynamics*; Bear, M., Ed.; CRC: Boca Raton, FL, 1985; p 65.
(4) Herschbach, D. In *Nobel Lectures in Chemistry 1981−1990*; Malmstrom, B. G., Ed.; World Scientic Publishing: Singapore, 1993; p 265.
(5) Lee, Y. T. *Science* **1987**, *236*, 793.
(6) Zare, R. N. *Science* **1998**, *279*, 1875.
(7) Polanyi, J. C. *Acc. Chem. Res.* **1972**, *5*, 161.
(8) Polanyi, J. C. *Science* **1987**, *236*, 680.
(9) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, 2005.
(10) Crim, F. F. *Acc. Chem. Res.* **1999**, *32*, 877.
(11) Liu, K. *Annu. Rev. Phys. Chem.* **2001**, *52*, 139.
(12) Crim, F. F. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12654.
(13) Zhang, W.; Kawamata, H.; Liu, K. *Science* **2009**, *325*, 303.
(14) Czakó, G.; Bowman, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 17534.
(15) Yan, S.; Wu, Y. T.; Zhang, B.; Yue, X.-F.; Liu, K. *Science* **2007**, *316*, 1723.
(16) Czakó, G.; Bowman, J. M. *Science* **2011**, *334*, 343.
(17) Zhang, Z.; Zhou, Y.; Zhang, D. H.; Czakó, G.; Bowman, J. M. *J. Phys. Chem. Lett.* **2012**, *3*, 3416.
(18) Li, J.; Jiang, B.; Guo, H. *J. Am. Chem. Soc.* **2013**, *135*, 982.
(19) Jiang, B.; Guo, H. *J. Chem. Phys.* **2013**, *138*, 234104.
(20) Jiang, B.; Liu, R.; Li, J.; Xie, D.; Yang, M.; Guo, H. *Chem. Sci.* **2013**, *4*, 3249.
(21) Jiang, B.; Guo, H. *J. Phys. Chem. C* **2013**, *117*, 16127−16135.
(22) Guo, H. *Int. Rev. Phys. Chem.* **2012**, *31*, 1.
(23) Schatz, G. C.; Colton, M. C.; Grant, J. L. *J. Phys. Chem.* **1984**, *88*, 2971.
(24) Kudla, K.; Schatz, G. C. *Chem. Phys. Lett.* **1992**, *193*, 507.
(25) Wu, G.-S.; Schatz, G. C.; Lendvay, G.; Fang, D. C.; Harding, L. B. *J. Chem. Phys.* **2000**, *113*, 3150.
(26) Troya, D.; Gonzalez, M.; Schatz, G. C. *J. Chem. Phys.* **2001**, *114*, 8397.
(27) Castillo, J. F.; Santamaria, J. *J. Phys. Chem. A* **2000**, *104*, 10414.
(28) Zhang, D. H.; Light, J. C. *J. Chem. Phys.* **1996**, *104*, 4544.
(29) Zhang, D. H.; Light, J. C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 691.
(30) Zhang, D. H.; Collins, M. A.; Lee, S.-Y. *Science* **2000**, *290*, 961.
(31) Zhang, D. H.; Yang, M.; Lee, S.-Y. *Phys. Rev. Lett.* **2002**, *89*, 103201.
(32) Mayneris, J.; Gonzalez, M.; Gray, S. K. *Comput. Phys. Commun.* **2008**, *179*, 741.
(33) Jiang, B.; Xie, D.; Guo, H. *J. Chem. Phys.* **2011**, *135*, 084112.
(34) Fu, B.; Zhang, D. H. *J. Chem. Phys.* **2013**, *138*, 184308.
(35) Yang, M.; Zhang, D. H.; Collins, M. A.; Lee, S.-Y. *J. Chem. Phys.* **2001**, *115*, 174.
(36) Deskevich, M. P.; Nesbitt, D. J.; Werner, H.-J. *J. Chem. Phys.* **2004**, *120*, 7281.
(37) Li, G.; Zhou, L.; Li, Q.-S.; Xie, Y.; Schaefer, H. F., III. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10891.
(38) Li, J.; Dawes, R.; Guo, H. *J. Chem. Phys.* **2012**, *137*, 094304.
(39) McGuire, P.; Kouri, D. J. *J. Chem. Phys.* **1974**, *60*, 2488.
(40) Pack, R. T. *J. Chem. Phys.* **1974**, *60*, 633.
(41) Li, J.; Jiang, B.; Guo, H. *J. Chem. Phys.* **2013**, *138*, 074309.
(42) Li, J.; Guo, H. *J. Chem. Phys.* **2013**, *138*, 194304.
(43) Braunstein, M.; Panfili, R.; Shroll, P.; Bernstein, L. *J. Chem. Phys.* **2005**, *122*, 184307.
(44) Conforti, P. F.; Braunstein, M.; Braams, B. J.; Bowman, J. M. *J. Chem. Phys.* **2010**, *133*, 164312.
(45) Sinha, A.; Hsiao, M. C.; Crim, F. F. *J. Chem. Phys.* **1991**, *94*, 4928.
(46) Hsiao, M. C.; Sinha, A.; Crim, F. F. *J. Phys. Chem.* **1991**, *95*, 8263.
(47) Li, J.; Jiang, B.; Guo, H. *Chem. Sci.* **2013**, *4*, 629.
(48) Li, J.; Li, Y.; Guo, H. *J. Chem. Phys.* **2013**, *138*, 141102.
(49) Jiang, B.; Ren, X.; Xie, D.; Guo, H. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 10224.
(50) Jiang, B.; Li, J.; Xie, D.; Guo, H. *J. Chem. Phys.* **2013**, *138*, 044704.
(51) Sinha, A.; Thoemke, J. D.; Crim, F. F. *J. Chem. Phys.* **1992**, *96*, 372.
(52) Adelman, D. E.; Filseth, S. V.; Zare, R. N. *J. Chem. Phys.* **1993**, *98*, 4636.
(53) Jacobs, A.; Volpp, H. R.; Wolfrum, J. *J. Chem. Phys.* **1994**, *100*, 1936.
(54) Bronikowski, M. J.; Simpson, W. R.; Zare, R. N. *J. Phys. Chem.* **1993**, *97*, 2194.
(55) Thoemke, J. D.; Pfeiffer, J. M.; Metz, R. B.; Crim, F. F. *J. Phys. Chem.* **1995**, *99*, 13748.
(56) Brouard, M.; Burak, I.; Joeseph, D. M.; Markillie, G. A.; Minayev, D.; O'Keeffe, P.; Vallance, C. *J. Chem. Phys.* **2001**, *114*, 6690.
(57) Brouard, M.; Burak, I.; Marinakis, S.; Minayev, D.; O'Keeffe, P.; Vallance, C.; Aoiz, F. J.; Banares, L.; Castillo, J. F.; Zhang, D. H.; Xie, D.; Yang, M.; Lee, S.-Y.; Collins, M. A. *Phys. Rev. Lett.* **2003**, *90*, 093201.
(58) Ziemkiewicz, M.; Wojcik, M.; Nesbitt, D. J. *J. Chem. Phys.* **2005**, *123*, 224307.
(59) Zolot, A. M.; Nesbitt, D. J. *J. Chem. Phys.* **2008**, *129*, 184305.
(60) Ziemkiewicz, M.; Nesbitt, D. J. *J. Chem. Phys.* **2009**, *131*, 054309.
(61) Pfeiffer, J. M.; Woods, E.; Metz, R. B.; Crim, F. F. *J. Chem. Phys.* **2000**, *113*, 7982.
(62) Zhang, D. H.; Xie, D.; Yang, M. *Phys. Rev. Lett.* **2002**, *89*, 283203.
(63) Braunstein, M.; Conforti, P. F. *J. Chem. Phys.* **2013**, *138*, 074303.
(64) Bronikowski, M. J.; Simpson, W. R.; Zare, R. N. *J. Phys. Chem.* **1993**, *97*, 2204.

(65) Barnes, P. W.; Sharkey, P.; Sims, I. R.; Smith, I. W. M. *Faraday Discuss. Chem. Soc.* **1999**, *113*, 167.
(66) Metz, R. B.; Thoemke, J. D.; Pfeiffer, J. M.; Crim, F. F. *J. Chem. Phys.* **1993**, *99*, 1744.
(67) Jiang, B.; Xie, D.; Guo, H. *Chem. Sci.* **2013**, *4*, 503.
(68) Duff, J. W.; Truhlar, D. G. *J. Chem. Phys.* **1975**, *62*, 2477.
(69) Schechter, I.; Levine, R. D. *J. Phys. Chem.* **1989**, *93*, 7913.
(70) Blais, N. C.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1985**, *82*, 2300.
(71) Schinke, R. *Photodissociation Dynamics*; Cambridge University Press: Cambridge, 1993.
(72) Kuntz, P. J.; Mok, M. H.; Polanyi, J. C. *J. Chem. Phys.* **1969**, *50*, 4623.
(73) Truhlar, D. G.; Dixon, D. A. In *Atom-Molecular Collision Theory: A Guide for the Experimentalist*; Bernstein, R. B., Ed.; Plenum: New York, 1979.
(74) Bowman, J. M. *Adv. Chem. Phys.* **1985**, *61*, 115.
(75) Chatfield, D. C.; Friedman, R. S.; Schwenke, D. W.; Truhlar, D. G. *J. Phys. Chem.* **1992**, *96*, 2414.
(76) Gustafsson, M.; Skodje, R. T. *J. Chem. Phys.* **2006**, *124*, 144311.
(77) Schatz, G. C.; Ross, J. *J. Chem. Phys.* **1977**, *66*, 1021.
(78) Welsch, R.; Huarte-Larrañaga, F.; Manthe, U. *J. Chem. Phys.* **2012**, *136*, 064117.
(79) Miller, W. H.; Handy, N. C.; Adams, J. E. *J. Chem. Phys.* **1980**, *72*, 99.
(80) Duncan, W. T.; Truong, T. N. *J. Chem. Phys.* **1995**, *103*, 9642.
(81) Corchado, J. C.; Truhlar, D. G.; Espinosa-García, J. *J. Chem. Phys.* **2000**, *112*, 9375.
(82) Halonen, L.; Bernasek, S. L.; Nesbitt, D. J. *J. Chem. Phys.* **2001**, *115*, 5611.
(83) Yoon, S.; Holiday, R. J.; Sibert, E. L., III; Crim, F. F. *J. Chem. Phys.* **2003**, *119*, 9568.
(84) Yan, S.; Wu, Y.-T.; Liu, K. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12667.
(85) Li, J.; Dawes, R.; Guo, H. *J. Chem. Phys.* **2013**, *139*, 074302.
(86) Fair, J. R.; Schaefer, D.; Kosloff, R.; Nesbitt, D. J. *J. Chem. Phys.* **2002**, *116*, 1406.
(87) Skouteris, D.; Manolopoulos, D. E.; Bian, W.; Werner, H.-J.; Lai, L.-H.; Liu, K. *Science* **1999**, *286*, 1713.
(88) Corchado, J. C.; Chuang, Y.-Y.; Fast, P. L.; Hu, W.-P.; Liu, Y.-P.; Lynch, G. C.; Nguyen, K. A.; Jackels, C. F.; Fernandez Ramos, A.; Ellingson, B. A.; Lynch, B. J.; Zheng, J.; Melissas, V. S.; Villà, J.; Rossi, I.; Coitiño, E. L.; Pu, J.; Albu, T. V.; Steckler, R.; Garrett, B. C.; Isaacson, A. D.; Truhlar, D. G.; *POLYRATE*; University of Minnesota, Minneapolis, 2007.