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This perspective reviews experiments in which spectroscopy rather than scattering is used to probe reactive potential energy surfaces. The application of negative ion photodetachment to the transition state spectroscopy of benchmark reactions is described, followed by a brief description of recent transition state spectroscopy experiment starting from clustered precursor anions that probe the effects of solvation on transition state spectroscopy and dynamics. Experiments on the spectroscopy of open-shell “pre-reactive” complexes are also discussed.

Introduction

The concept of potential energy surfaces is central to the field of reaction dynamics. Potential energy surfaces describe the interactions between reacting species and, in the absence of non-adiabatic effects, the development of an accurate potential energy surface is equivalent to mapping out the microscopic, interatomic forces that govern a particular chemical reaction. The process by which a potential energy surface is developed generally involves a close interaction between scattering experiments and theory, in which experimental quantities such as rate constants, angular distributions, translational and internal energy distributions, and angular momentum polarization are compared to scattering calculations on model potential energy surfaces that are determined through some combination of *ab initio* electronic structure calculations and empirical corrections. In this case, one is dealing with asymptotic properties of the reaction, through measurement and calculation of the reaction attributes long after the products have separated and ceased to interact with one another.

An alternative and conceptually appealing approach is to develop spectroscopic probes of the transition state region, the region of the potential energy surface in which chemical bonds are broken and formed.^{1–3} Kinetics and scattering experiments are of course sensitive to the attributes of the transition state region, but direct, spectroscopic probes of the transition state can, at the very least, complement scattering experiments, and often yield much richer detail through the determination of the geometry, vibrational frequencies and lifetime of the transition state complex. This perspective summarizes past efforts to characterize the spectroscopy of the transition state and includes some of the more recent and likely future directions in this area.

Essentially all successful transition state spectroscopy (TSS) experiments performed to date are “half-collision” experiments in which the transition state is accessed through photoexcitation of a stable transition state precursor, such as a closed shell molecule, a van der Waals complex, or a negative ion. These experiments can be divided into time-domain and frequency-domain studies. Since the transition state by its nature is short-lived, with passage through a transition state typically occurring on a time scale of 10–100 fs, experiments with ultrafast lasers would seem to be a natural way to probe reacting or dissociating systems, and this has indeed been the focus of “femtochemistry” experiments in the Zewail laboratory^{4,5} and

elsewhere. While most of these studies are pump-probe experiments with two laser pulses, success has recently been achieved using ultrafast electron diffraction⁶ as a probe, in which one can directly probe the geometries of the transient species produced by the pump pulse.

The most successful frequency-domain TSS experiments have been the negative ion photodetachment experiments performed in our laboratory and by Lineberger and co-workers.^{7–9} In these experiments, one photodetaches a stable negative ion similar in structure to a neutral transition state, and the resulting photoelectron spectrum can yield resolved vibrational structure characteristic of the transition state. In many cases, these experiments have revealed vibrational frequencies characteristic of nuclear motion perpendicular to the reaction coordinate. These are clearly of interest, since, for example, these are the frequencies one would use in the calculation of the transition state theory rate constant of a chemical reaction. The intensity distribution in the photoelectron spectra is also of interest, as it reflects the change in geometry between the anion and neutral.

A more elusive goal in TSS experiments has been the detection of dynamical resonances, loosely defined as levels of the transition state complex that are bound or quasi-bound along the reaction coordinate. Resonances have been predicted in reactive scattering calculations on model potential energy surfaces for many years,¹⁰ and are a very appealing target for TSS because they can be quite narrow and precisely located, thereby providing a particularly sensitive probe of the transition state. Thus far, however, the only TSS experiment that has definitively revealed the existence of resonances was the zero-electron kinetic energy (ZEKE) spectrum of IHI^- ,¹¹ which showed clear evidence for quasi-bound IHI levels and not just the broader vibrational structure characteristic of motion perpendicular to the reaction coordinate. The only other definitive observation of reactive resonances to date comes from scattering experiments on the $\text{F} + \text{H}_2$ and $\text{F} + \text{HD}$ reactions by Liu and co-workers,^{12–14} in which structure in the total reaction cross section and rapid changes in the differential cross section as functions of collision energy provided an unambiguous signature of FH_2 resonance states.

There are several promising new directions in the area of TSS. In the time-domain, the development of increasingly shorter laser pulses¹⁵ and the recent implementation of time-dependent photoelectron spectroscopy¹⁶ in several laboratories

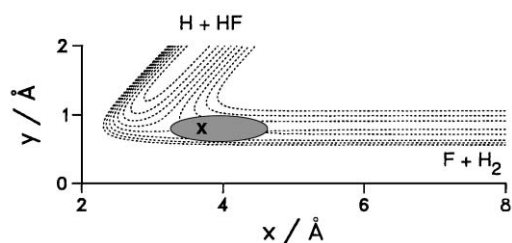


Fig. 1 Photodetachment of FH_2^- probes the $\text{F} + \text{H}_2$ transition state region. The ground state vibrational wavefunction for FH_2^- (shaded region) is superimposed on a model collinear potential energy surface for $\text{F} + \text{H}_2$ reaction. The saddle point on the reactive surface is marked with an X. (Adapted from ref. 34).

holds considerable promise for probing more rapid transition state dynamics in greater detail, as does further development of ultrafast electron and X-ray light sources.^{17,18} Negative ion photodetachment on mass-selected cluster anions has been used recently to probe the effects of solvation on transition state spectroscopy and dynamics,^{19,20} and as such provides a key link between gas phase and condensed phase reaction dynamics. Finally, the recent observation of pre-reactive van der Waals states of the $\text{OH} \cdot \text{H}_2$ and $\text{OH} \cdot \text{CO}$ complexes^{21,22} points out the importance of studying a relatively neglected region of reactive potential energy surfaces, the shallow van der Waals well between reactants. The interplay between this well and the transition state may have a significant effect on transition state geometry as well as the overall reaction dynamics, so characterization of this well may be of comparable importance to the transition state itself.

The main body of this perspective focuses on TSS using negative ion photodetachment. Results on several benchmark bimolecular reactions are summarized, followed by a description of recent work on TSS in cluster anions and possible future experiments on reactant van der Waals wells.

TSS of benchmark chemical reactions

The promise of TSS using negative ion photodetachment is exemplified by our studies of transition states for the $\text{F} + \text{H}_2$ and $\text{OH} + \text{H}_2$ reactions by photoelectron spectroscopy of

FH_2^- and H_3O^- , respectively. These are benchmark reactions that have been studied extensively by experiment and theory. The $\text{F} + \text{H}_2$ reaction, in particular, has defined the state-of-the-art in experimental reactive scattering studies, with increasingly sophisticated crossed molecular beams experiments yielding progressively more detail on the dependence of the integral and differential cross sections on collision energy, the partitioning of product translational, vibrational, and rotational energy, and the possible reactivity of spin-orbit excited F atoms.^{12,13,23-29}

Although some features of the differential cross section, namely state-selected forward scattering of the $\text{HF}(v=3)$ product, were originally attributed to dynamical resonances,²³ these features could be largely reproduced by classical trajectory calculations^{30,31} on potential energy surfaces with bent as opposed to linear transition states. We therefore hoped to address the issue of the FH_2 bend potential by photoelectron spectroscopy of FH_2^- .

As shown in Fig. 1, this reaction is ideal from the TSS perspective, because electronic structure calculations indicate that the geometry of FH_2^- is similar to that of the FH_2 transition state,^{32,33} in both, the distance from the F atom the H_2 center-of-mass is relatively long, and the H-H bond distance is similar to that in diatomic H_2 . These geometries reflect the fact that FH_2^- is essentially F^- weakly bound to H_2 ($D_0 \cong 0.20$ eV), while the $\text{F} + \text{H}_2$ reaction has an early barrier. The calculations indicate FH_2^- is linear, so the existence or extent of bend progressions in the anion photoelectron spectrum would provide a direct probe of the bend potential at the neutral transition state.

The FH_2^- photoelectron spectrum^{34,35} shown in Fig. 2 indeed shows progressions in the two vibrational modes perpendicular to the reaction coordinate: the H-H stretch and the F-H-H bend, which is more like an H_2 internal rotor. The bend progression is quite extended, indicating that the FH_2 transition state is bent rather than linear. This conclusion is supported by quantum mechanical simulations of the spectrum performed on a high level potential energy surface for the $\text{F} + \text{H}_2$ reaction.³⁵ This system thus represents an example in which TSS resolved a key issue in a benchmark chemical reaction.

The FH_2^- photoelectron spectrum shows no clear evidence for resonances, *i.e.* states of the FH_2 complex bound along as opposed to perpendicular to the reaction coordinate. The

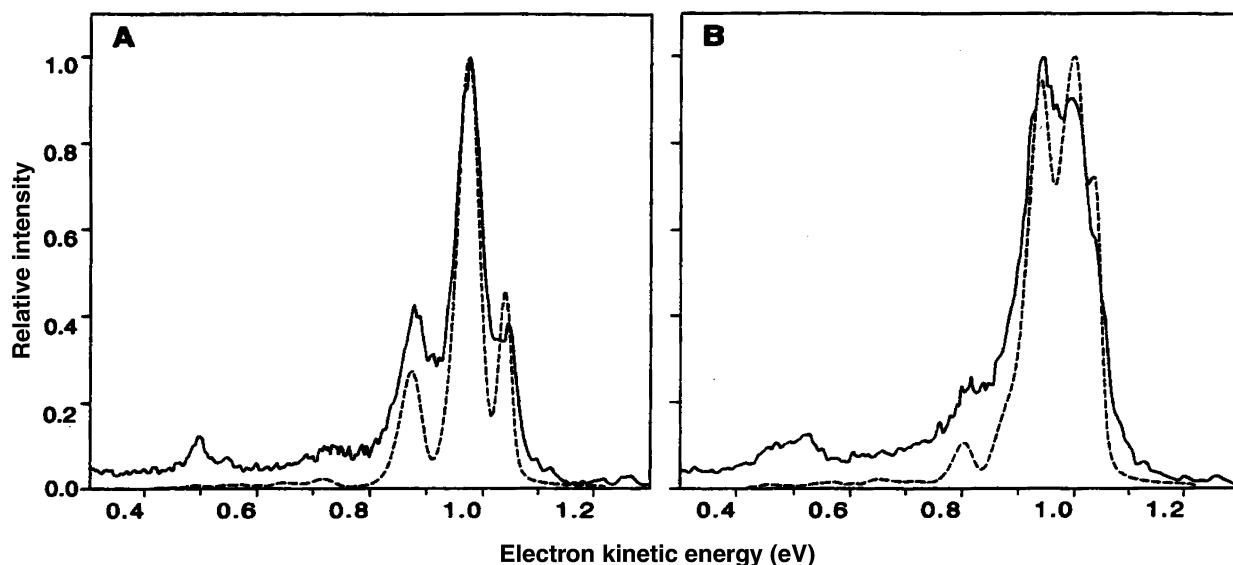


Fig. 2 Solid lines are experimental photoelectron spectra of $\text{F}^- \cdot \text{para-H}_2$ (left) and $\text{F}^- \cdot \text{n-H}_2$ (right). Dashed lines are exact simulations using anion surface from ref. 32 and $\text{F} + \text{H}_2$ surface from ref. 33. The peaks around 1 eV are a progression in FH_2 internal rotor states, while the smaller peaks around 0.5 eV involve H_2 stretch excitation. (Adapted from ref. 35).

signature for resonances would be additional, low frequency vibrational progressions corresponding to either $F \cdots H_2$ or $HF \cdots H$ vibrational motion, depending on whether the resonance wavefunction is localized on reactant or product region of the potential energy surface. Calculations by Manolopoulos³⁶ indicate that these progressions should be observable at higher resolution, and experiments of this type are planned in our laboratory in the near future.

While the $F + H_2$ reaction is one of several three-atom benchmark reactions, along with $H + H_2$, $O + H_2$, and $Cl + H_2$, the $OH + H_2 \rightarrow H_2O + H$ reaction is unique as a prototypical four atom reaction, since the presence of three hydrogen atoms makes both electronic structure calculations of potential energy surfaces and the execution of scattering calculations on these surfaces tractable. As a consequence, high quality surfaces have been constructed and scattering calculations on these surfaces have been performed by several groups.^{37–41} Scattering experiments by Casavecchia³⁷ and Davis⁴² have yielded product angular distributions and detailed vibrational energy distributions for the H_2O product. These experiments are complemented by studies of the $OH \cdots H_2$ van der Waals complex by Lester and co-workers.^{21,43}

TSS of the $OH + H_2$ reaction *via* photoelectron spectroscopy of H_3O^- is complicated by the existence of two anion structures:^{44–47} $H^- \cdots H_2O$, which has good Franck–Condon overlap with the neutral $H_2O + H$ product valley, and $OH^- \cdots H_2$, which overlaps the neutral transition state. As shown in Fig. 3, the $H^- \cdots H_2O$ structure is calculated to lie ~ 0.08 eV lower in energy, which might appear problematic from the perspective of TSS. Nonetheless, the anion photoelectron spectrum⁴⁸ was quite revealing.

The top spectrum in Fig. 4 is dominated by photodetachment from $H^- \cdots H_2O$, showing a resolved vibrational progression in which the peak spacing was slightly lower than the H_2O antisymmetric stretch frequency. This progression was assigned to transitions to the $H + H_2O$ exit valley, with the lowered frequency a signature of non-negligible interaction between the separating products in the Franck–Condon region. An even lower frequency progression was seen in simulations^{48,49} on the best surface available at the time of the experiment.^{50,51} This discrepancy indicates that the barrier on the model surface was too “late” along the reaction coordinate (*i.e.* the $OH \cdots H_2$ distance is too small at the saddle point), resulting in an overly large effect on the peak spacings in the Franck–Condon region. In fact, the saddle points on more recent $OH + H_2$ surfaces occur at larger $OH \cdots H_2$ distances (by 0.14 Å, on average³⁹), and a simulation of the $H^- \cdots H_2O$ photoelectron spectrum on one of these new surfaces⁴⁷ is in better agreement with experiment. Hence, even though the

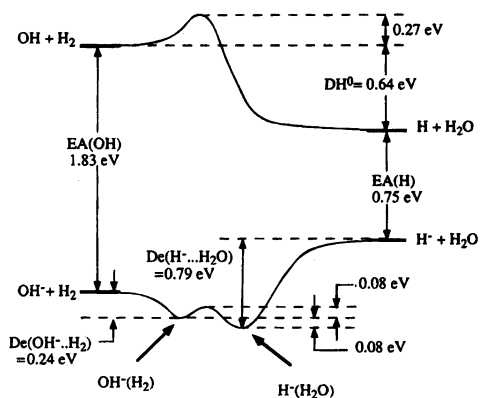


Fig. 3 Reaction coordinates for $OH^- + H_2$ and $OH + H_2$ reactions, showing energetics of the $H^-(H_2O)$ and $OH^-(H_2)$ minima. (Adapted from ref. 48).

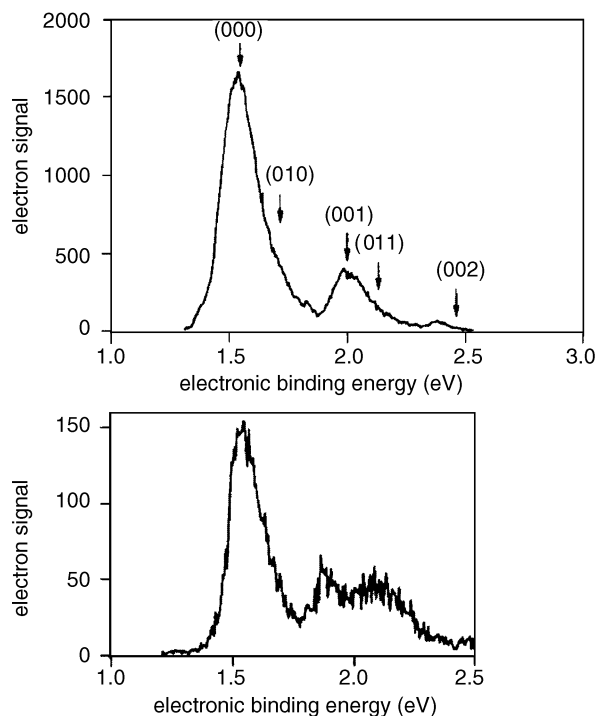


Fig. 4 Photoelectron spectra of H_3O^- at laser polarization angles $\theta = 0^\circ$ (top) and 90° (bottom). Top spectrum is dominated by photodetachment of $H^-(H_2O)$ structure. Vibrational level spacings of free H_2O are shown in parentheses ($\nu_1\nu_2\nu_3$). Broad peak in lower spectrum around 2.1 eV is from $OH^-(H_2)$ structure. (Adapted from ref. 48).

$H^- \cdots H_2O$ vibrational wavefunction has little or no overlap with the $OH + H_2$ saddle point, the nature of the vibrational structure in the photoelectron spectrum is quite sensitive to the location of the saddle point and therefore provides important information regarding the transition state of the reaction.

What about the $OH^- \cdots H_2$ structure? The H_3O^- photoelectron spectra show a strong angular dependence, with a broad feature appearing at high electron binding energy (bottom spectrum, Fig. 4) when the laser polarization angle is perpendicular to the direction of photoelectron detection. This feature becomes more intense when the ion source temperature is raised, suggesting it might be from the higher energy $OH^- \cdots H_2$ structure and therefore corresponding to photodetachment to the $OH + H_2$ transition state. We constructed a two-dimensional potential energy surface for the H_3O^- anion and determined the 2-D vibrational wavefunctions and energy levels supported by this surface. While the $\nu = 0$ wavefunction was localized in the $H^- \cdots H_2O$ well, as expected, the $\nu = 2$ wavefunction showed significant amplitude in the $OH^- \cdots H_2$ well, and simulations of the photoelectron spectrum from the $\nu = 2$ wavefunction approximately reproduced the broad experimental feature. Hence, vibrational excitation of the anion results in considerably better overlap with the $OH + H_2$ entrance valley and transition state, a result supported in more sophisticated simulations of the photoelectron spectrum.^{47,49,52}

It also appears that vibrational excitation of H_3O^- results in a marked change in the photoelectron angular distribution, a rather unusual observation in negative ion photoelectron spectroscopy. This effect can be understood in terms of the nature of the orbital from which detachment occurs; near threshold, H^- undergoes *p*-wave detachment, because an *s*-electron is being detached,^{53,54} whereas OH^- undergoes *s*-wave detachment. The photoelectron angular distributions therefore reflect the dominance of the $H^- \cdots H_2O$ structure in the $\nu = 0$ wavefunction and the dominance of the $OH^- \cdots H_2$ structure in the $\nu = 2$ wavefunction.

Transition state spectroscopy of clustered TS precursors

One of the more intriguing new directions for TSS *via* anion photoelectron spectroscopy is the investigation of clustered transition state precursors. It is straightforward to generate mass-selected cluster anions of the type $ABC^-(S_n)$, where ABC^- is a transition state precursor anion and S is a solvent atom or molecule. The photoelectron spectroscopy of clusters of this type can probe the effects of solvation on the neutral transition state spectroscopy and dynamics, thereby providing an important link between gas phase and condensed phase reaction dynamics. We have recently initiated experiments of this type using the bihalide transition state precursors $BrHI^-$ and IHI^- clustered to one or more Ar atoms.^{19,20} Photo-detachment of the bare ions accesses the transition state region of the $Br + HI$ and $I + HI$ heavy + light-heavy reactions, and the photoelectron spectra of these anions^{55,56} are dominated by progressions in the antisymmetric H-atom stretch. In addition, the higher resolution ZEKE spectrum of IHI^- showed lower frequency progressions in IHI hindered rotor states and symmetric stretch states;¹¹ the latter represent a definitive observation of reaction resonances as defined above. In any case, the rich vibrational structure seen for both bihalide species provides a suitable template for determining the effects of solvation.

Our PE spectra of $BrHI^-(Ar)$ and $IHI^-(Ar)$, displayed in Fig. 5, showed that even a single weakly bound solvent species such as Ar induced significant changes in the photoelectron spectrum of the bare anion.²⁰ These changes are primarily due to cooling effects, since a cluster in which an Ar atom is clustered to a vibrationally excited bihalide anion will undergo predissociation before it passes through our mass spectrometer, leaving only those clusters in which the anion chromophore is vibrationally cold; similar effects have been seen in the PE spectrum of $I_2^-(Ar)$ and in the infrared spectrum of clustered halide anions.^{57,58} As a consequence, the vibrational features in the $BrHI^-(Ar)$ PE spectrum are considerably narrower than in the $BrHI^-$ spectrum,⁵⁶ enabling a more detailed comparison with theory. While the bare IHI^- spectrum shows a well-resolved progression in the relatively high frequency IHI antisymmetric stretch,⁵⁵ the $IHI^-(Ar)$ PE spectrum shows additional structure from progressions in low frequency hindered rotor states of the IHI complex.

The PE spectra of $IHI^-(Ar)_n$ ($n = 1-15$) clusters, shown in Fig. 6, exhibit several trends that reflect the effects of solvation on the anion and the neutral, and sorting these out is perhaps the most challenging aspect in the interpretation of the spectra.¹⁹ We observe shifts with EA as a function of cluster size that are very similar to those seen for $I_2^-(Ar)_n$ clusters,⁵⁷ implying that the first six Ar atoms cluster around the waist of the IHI^- , where they can interact with the partial negative charges on the two I atoms. Subsequent Ar atoms bind primarily to a single I atom. We also observe a change in the spacing of the IHI antisymmetric stretch frequency as a function of cluster size, an effect attributed to solvent-induced distortion of the IHI^- geometry. However, the most intriguing effect is that the low-frequency hindered rotor structure seen in the binary $IHI^-(Ar)$ cluster becomes more pronounced for the largest clusters we studied, an unusual result since clustering generally obscures vibrational structure in photoelectron spectra. This effect is attributed to caging of the neutral IHI complex by the surrounding Ar atoms, resulting in a longer lifetime and hence sharper structure than seen in the smaller clusters. It represents a remarkable demonstration of the effect of clustering on transition state dynamics, with clear analogies to the caging of photoexcited chromophore molecules such as I_2 and I_2^- in cryogenic matrices and clusters seen in several laboratories.^{59,60}

The Ar cluster experiments also provided evidence for an additional structural isomer of the form $I^-(Ar)_nHI$,¹⁹ suggesting that even a weakly interacting solvent species such as Ar can result in structural perturbations of the anion chromophore. These results point the way toward future studies aimed at the effects of more strongly solvating species such as water on the photoelectron spectrum of symmetric (XHX^-) and asymmetric (XHY^-) bihalides. Photoelectron spectra of size-selected anions $XHY(X)^-(H_2O)_n$ will provide a novel probe of the effects of hydration in the negative ion. As water molecules are added, we expect vibrational structure to reflect structural changes induced by hydration. We might, for example, expect the first few water molecules to asymmetrically hydrate one of the halogen atoms, resulting in partial localization of the charge on the more hydrated atom in analogy to predicted and observed effects in $I_2^-(CO_2)_n$ and $I_2^-(Ar)_n$ clusters,⁶¹⁻⁶⁴ with the addition of further waters possibly resulting in dissociation of the bihalide within the cluster to a hydrated halide anion clustered to HX .

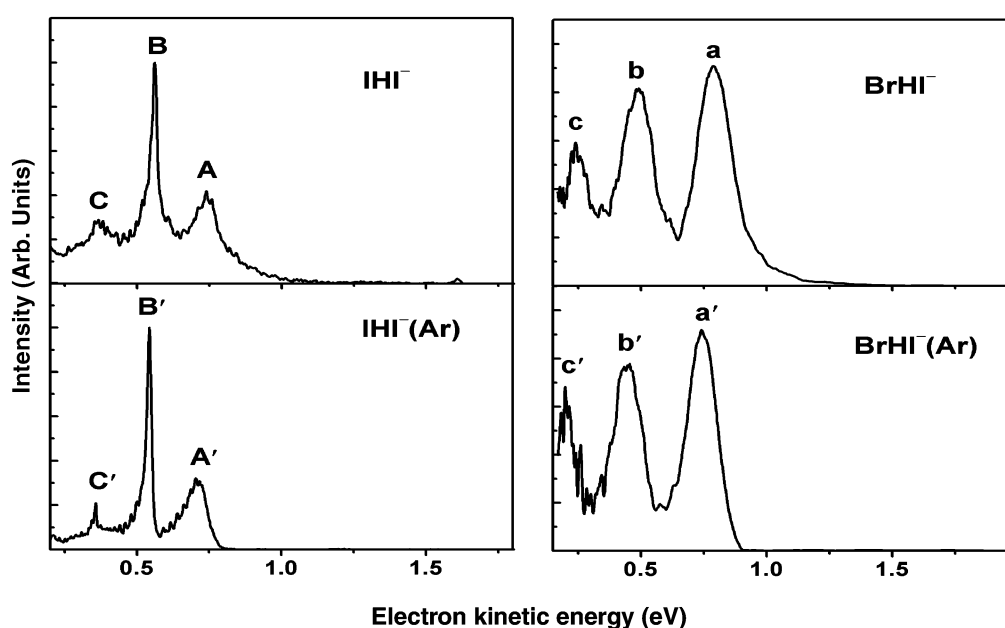


Fig. 5 Effect of complexation of single Ar atom on photoelectron spectra of IHI^- (a) and $BrHI^-$ (b). Addition of an Ar atom results in narrower peaks and, for IHI^- , the observation of additional fine structure from progressions in IHI hindered rotor states. (Adapted from ref. 20).

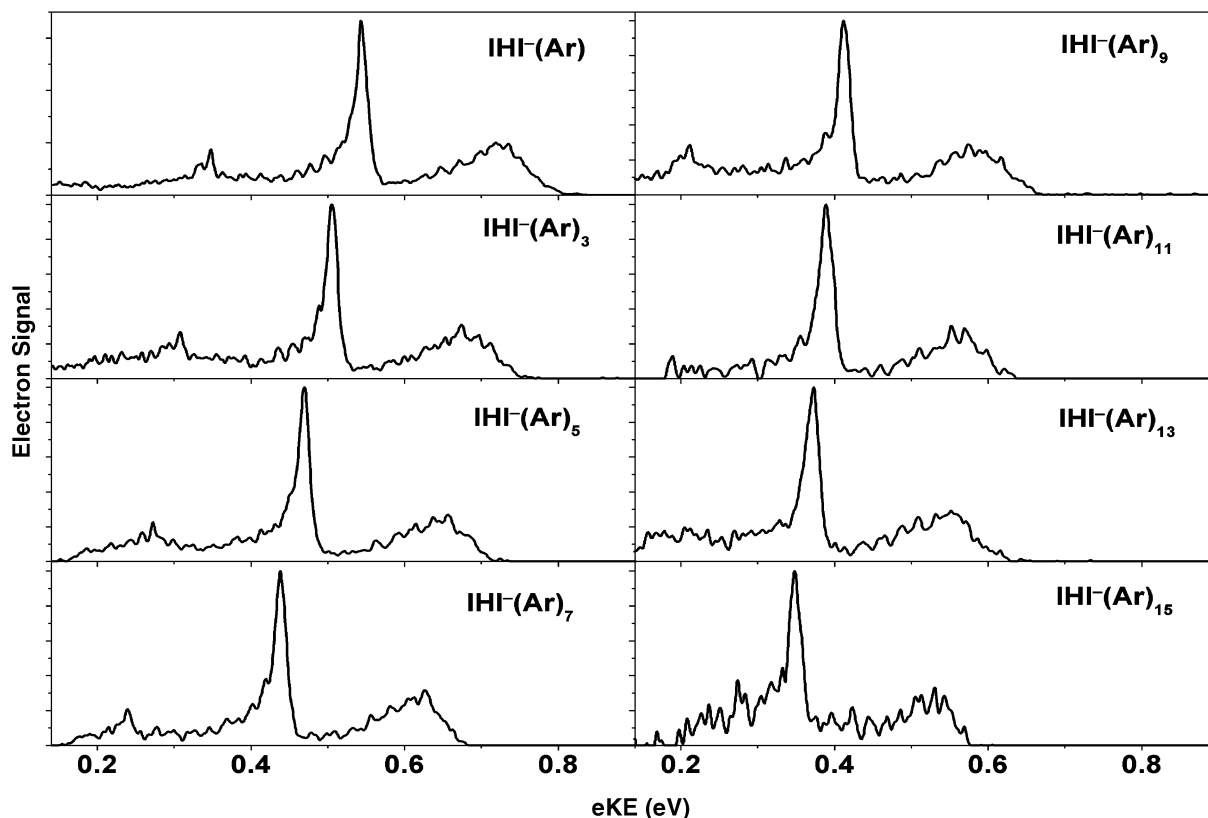


Fig. 6 Photoelectron spectra of $\text{IHI}^-(\text{Ar})_n$, $n \leq 15$. (Adapted from ref. 19).

Probing the van der Waals reactant well

Transition state spectroscopy is most generally defined as an experiment that yields spectroscopic information on the reaction complex, as opposed to separated products or reactants. The conventional wisdom in reaction dynamics is that a successful transition state spectroscopy experiment is one that probes the classical transition state, *e.g.* the barrier region for a direct reaction. However, for any direct reaction between neutral species, one expects shallow wells along the reaction coordinate on either side of the barrier due to the attractive van der Waals interaction between reactants or products. These wells have often been used to launch bimolecular reactions through either electronic excitation⁶⁵ or photodissociation^{66,67} of one of the reactants constituting the complex. For example, photoexcitation of the metal atom in HgH_2 or NaFH complexes initiates an excited state chemical reaction,^{68,69} and by probing the product yield as a function of excitation energy one can essentially perform transition state spectroscopy of the excited state potential energy surface.

The possible role of vdW wells on ground state dynamics is an issue of considerable interest. Even though these wells occur at considerably larger internuclear distances than are characteristic of transition states, they can play an important role in the ground state reaction dynamics. For example, recent experiments and calculations on $\text{Cl} + \text{HD}$ by Liu and co-workers⁷⁰ showed that the presence of a reactant vdW well was necessary to reproduce the experimental $\text{HCl} : \text{DCI}$ product branching ratio. This effect arises because the vdW minimum is T-shaped, whereas the transition state geometry is linear, so the shallow vdW well results in a torque on the reactants en route to the transition state. In the $\text{F} + \text{H}_2$ reaction, the vdW well is also T-shaped,³³ and occurs at only a slightly larger $\text{F} \cdots \text{H}_2$ distance than the transition state geometry. The barrier for $\text{F} + \text{H}_2$ is much lower than that for $\text{Cl} + \text{H}_2$, $1.9 \text{ kcal mol}^{-1}$ vs. $7.6 \text{ kcal mol}^{-1}$,^{71,72} so one can speculate that the bent nature of the transition state in $\text{F} + \text{H}_2$ arises in part from its

proximity to the T-shaped well. Hence, experiments that probe the spectroscopy of ground state complexes between reactants may be quite important for gaining a global picture of the corresponding reaction.

The reactant vdW well has been probed in an elegant series of experiments by Lester and co-workers.^{21,22} In these studies, open-shell, “pre-reactive” vdW complexes such as $\text{OH} \cdot \text{H}_2$ and $\text{OH} \cdot \text{CO}$ are formed in a free jet expansion, and their infrared and Raman predissociation spectra are measured by action spectroscopy through detection of the OH radical. These complexes lie to the reactant side of small barriers for the $\text{OH} + \text{H}_2$ and $\text{OH} + \text{CO}$ reactions. One question underlying these studies is whether vibrational excitation of the complexes can actually drive the chemical reaction; there is strong indirect evidence for this, although reaction products have yet to be observed experimentally. Regardless, these rotationally-resolved spectra provide a detailed probe of the van der Waals well and therefore provide new experimental insight into what now appears to be a very important region of the reactive potential energy surface.

Experiments of this type can also be carried out with negative ion photoelectron spectroscopy, so long as there is good overlap between the anion and neutral vdW well. This condition favors reactions with relatively “late” barriers; otherwise the reactants will be too far apart in the vdW well to be accessed by photodetachment. The slightly endothermic $\text{Cl} + \text{H}_2$ reaction is an excellent candidate for this experiment. Based on the rotationally resolved IR spectrum of ClH_2^- by Bieske⁷³ and electronic structure calculations of the $\text{Cl} + \text{H}_2$ surface,⁷² photodetachment of ClH_2^- should have poor overlap with the transition state but excellent overlap with the van der Waals well in the $\text{Cl} + \text{H}_2$ reactant valley. The anion has a linear equilibrium geometry, while the vdW well is lowest for a T-shaped, C_{2v} structure. Hence, the ClH_2^- photoelectron spectrum should reveal progressions in the vdW low-frequency stretch and hindered rotor levels, providing a

detailed characterization of the vdW well. These experiments are currently underway in our laboratory.

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