SPECTROSCOPY AND DYNAMICS IN THRESHOLD ION-PAIR PRODUCTION

by

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Abstract

The high resolution photoionization technique of Threshold Ion-Pair Production Spectroscopy (TIPPS) involves VUV excitation of neutral molecules AB to the highly vibrationally excited ion-pair states $A^+(\beta^+) - B^-(\beta^-)$ just below the dissociation limit. These states behave like the high-$n$ Rydberg states used for pulsed field ionization zero kinetic energy photoelectron (PFI-ZEKE) or mass analyzed threshold ionization (MATI) spectroscopy, and can be detected by pulsed field dissociation. During the past few years TIPPS has been applied to the molecules HCl/DCl, HF/DF, HCN and (HF)$_2$. For HCl/DCl and HF/DF, the ion-pair thresholds have been precisely measured and the classical bond dissociation energies have been calculated, and therefore our results provide an experimental test of the Born-Oppenheimer breakdown in the two pairs of isotopomers. The ion-pair formation mechanisms in these molecules were discussed in light of these high resolution results. For HCN, we have precisely measured the ion-pair threshold $E_{tip}^0$ to be $122246 \pm 4$cm$^{-1}$. Our result also showed that rotationally excited instead of cold CN$^-$ fragment is favored as the ion-pair dissociation product in the threshold region. For (HF)$_2$, the total ion yield and pulsed field ionization (PFI) spectra of HFH$^+$ from (HF)$_2$ were recorded over the energy range 14.7-15.9eV. The dominant process to produce HFH$^+$ was found to be $(HF)_2 + \nu \rightarrow HFH^+ + e^- + F$, while the other energetically allowed process $(HF)_2 + \nu \rightarrow HFH^+ + F^-$ is virtually non contributing. Production of vibrationally excited HFH$^+$ fragments was observed, and assignments to different vibrational levels were performed in comparison with the calculated HFH$^+$ vibrational spacing in literature work. From the spectrum we have measured the appearance potential (AP) of HFH$^+$ to be $14.50 \pm 0.03$eV (relative to (HF)$_2$), which gives a value of $5.07 \pm 0.03$eV for the proton affinity of HF. Our result clarifies the discrepency between previous photoionization work and the results from other methods.
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1.1 Background of high-\(v\) ion-pair states and TIPPS

Threshold Ion-Pair Production Spectroscopy (TIPPS) is a high resolution threshold photoionization technique\(^1\) which can provide energetic and dynamic information associated with the process: \(A-B(\alpha) \rightarrow A^+(\beta^+) + B^-(\beta^-)\), where \(\alpha\) and \(\beta^+, \beta^-\) represent the initial and final quantum states of the system.\(^2\) TIPPS is based on the excitation of neutral molecules to highly vibrationally excited (high-\(v\)) ion-pair states \(A^+(\beta^+) - B^-(\beta^-)\) just below the dissociation limit. These states behave like the high-\(n\) Rydberg states used for pulsed field ionization-zero kinetic energy photoelectron (PFI-ZEKE) or mass analyzed threshold ionization (MATI) spectroscopy,\(^3,4\) and can be detected by pulsed field dissociation.

1.1.1 Rydberg states and ion-pair states

The quantum state of an electron orbiting an ion-core can be defined by a set of quantum numbers \(n, l, m_l\), where \(n\) is the principal quantum number, \(l\) is the angular momentum quantum number and \(m_l\) is the magnetic quantum number. If \(n\) is large enough, such as when it is larger than the principal quantum numbers of any other electrons in the same atom or molecule, the electron will spend most of the time at a large distance from the ion-core, and the interaction between the electron and ion-core is dominated by the Coulombic attraction. Such a state is called Rydberg state for which the ion-core can be considered as a frozen core of nearly spherical symmetry, with the size of a few Bohr radii.\(^5\)
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The energy levels of a Rydberg electron relative to the ionization limit can be described by:

$$E_{n,l} = -\frac{R}{(n-\delta_l)^2} = -\frac{R}{(n^*)^2}$$  (1.1)

where \(\delta_l\) is the quantum defect, and \(n^*\) is the effective principal quantum number. The magnitude of \(\delta_l\) provides an indication of the extent to which the wavefunction of the Rydberg electron penetrates into the ion-core region. Typical values of \(\delta_l\) for molecules composed entirely of first-row atoms are \(\delta_{ns}=1.0-1.5\), \(\delta_{np}=0.4-0.8\), and \(\sim 0\) for \(nd\) and higher \(l\) functions.\(^7\)

The value of \(R\) can be calculated from:

$$R = \frac{\mu}{m_e} R_\infty$$  (1.2)

where \(m_e\) is the mass of electron, \(\mu=\frac{m_e m_c}{m_e+m_c}\) is the reduced mass of the electron/ion-core system with \(m_c\) representing the mass of the ion-core, and \(R_\infty=109737.315\text{cm}^{-1}\) is the Rydberg constant.\(^8\)

From equation 1.1, the separation of successive energy levels in a Rydberg series changes approximately as the inverse third power of \(n\),\(^9\) or in other words, the state density scales as \(n^3\). On the other side, the relative cross section of optical transitions from valence state to high-\(n\) Rydberg states scales as \(n^{-3}\).\(^10\) Therefore, for transitions to high-\(n\) Rydberg states, the average transition strength per energy unit does not change. It has the same value for transitions to above and below the ionization threshold. As a result, Rydberg state yield is a direct reflection of the photoionization cross section just above the threshold.

The properties of high-\(v\) ion-pair states are similar to high-\(n\) Rydberg states in many ways. In high-\(v\) ion-pair states, the weakly bound opposite charges - anion and cation - orbit each other with a large internuclear distance, and the attraction between them can also be expressed by Coulomb potential, like the Rydberg system. This is demonstrated in Figure 1.1, in which the spectroscopically determined RKR potential\(^11\) of HF(\(B^1\Sigma\)) ion-pair state at large internuclear distance matches very well the superimposed Coulomb potential.

Due to the asymptotic attraction in the ion-pair states, there is an infinite number of quasibound vibrational levels below the ion-pair threshold (like the Rydberg series below the ionization limit).\(^12\) The energies of these vibrational levels relative to the ion-pair limit have
Figure 1.1: Coulombic attraction in HF(B^1Σ) ion-pair state. The RKR data of the B^1Σ ion-pair state and X^1Σ ground state are taken from reference 11. A Coulomb potential with the ion-pair threshold as the asymptotic energy is superimposed (solid line) and matches well with the potential of the B^1Σ ion-pair state at large internuclear distance.
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the form:

\[
E_{v,J} = -\frac{R}{(v + J + 1 - \delta J)^2}
\]

(1.3)

where \(v\) and \(J\) are the vibrational and rotational numbers of the ion-pair system, \(R = \frac{\mu}{m_e} R_{\infty}\) with \(\mu\) as the reduced mass of the ion-pair system, and \(\delta J\) is the \(J\) specific quantum defect, like the \(\delta l\) term in equation 1.1. The term \(v + J + 1\) measures the number of modes in the given ion-pair rovibrational state and replaces the principal quantum number \(n\) associated with Rydberg state. The denominator of equation 1.3 is more complicated than that of equation 1.1, since \(v\) starts from 0 and \(J\) is independent of \(v\), while in equation 1.1 \(n\) starts from 1 and \(l\) has a value between 0 and \(n-1\).

Since the reduced mass \(\mu\) of the ion-pair system is much larger (~10^3) than that of a Rydberg state, the density of high-\(v\) ion-pair states is much higher than that of Rydberg states. But both of the state densities have a similar form regarding to the state quantum number (scales as \(v^3\) for an ion-pair state and \(n^3\) for Rydberg state), and like the Rydberg system, the average cross section per energy unit is the same for transitions to ion-pair states above and below the ion-pair limit.

1.1.2 Field ionization and field dissociation

With the presence of an electric field, the long range interaction between a Rydberg electron and the ion-core is no longer Coulombic and becomes more complicated. In atomic units, it is expressed as:

\[
V_{r,z} = -\frac{1}{r} - Fz
\]

(1.4)

where \(r\) is the distance of the Rydberg electron from the ion-core, \(F\) is the applied electric field and -z is its direction. This is illustrated in Figure 1.2.

With the electric field turned on, the \(n^2\) energetic degeneracy of hydrogenic Rydberg states is partially removed, since the original spherical symmetry of the Rydberg electron is reduced to cylindrical. Consequently, the perturbation leads to a splitting of the degenerate energy levels and \(l\) is no longer a good quantum number. The energy levels are better expressed as a function of the parabolic quantum numbers \(n_1\) and \(n_2\) than a function of \(l\) because the \(|nn_1n_2m\rangle\) basis
Figure 1.2: Potential of a Rydberg electron in electric field. Solid curves are the potential when the field is off, and dashed curves are the potential when the field is on. Field strength is 100V/cm. Zero point energy is the ionization limit.
functions are adapted to the cylindrical symmetry of the problem. The $|nn_1n_2m>$ functions are superpositions of the original $|nlm>$ states. At low to moderate electric fields, $m$ remains a good quantum number as long as the potential of the Rydberg states retains cylindrical symmetry. Therefore, homogeneous and cylindrically symmetric electric fields do not induce $m$ mixing. In this case, the energy levels are given in atomic units to first order by:

$$E = -\frac{1}{2n^2} + \frac{3}{2} F(n_1 - n_2)n$$ \hspace{1cm} (1.5)

where $n_1$ and $n_2$ are non negative integers and $n_1 - n_2$ takes values ranging from $-(n - m)$ to $(n - m)$ in steps of 2.

For nonhydrogenic Rydberg atom, the situation is more complicated. The high $l$ states still can be described by the above equation, as they have little penetrating character ($\delta_1 \sim 0$). The structure of the energy levels is dominated by the linear Stark effect. The low $l$ states that have nonzero quantum defects are separated from the high $l$ hydrogenic manifold and display a quadratic Stark effect at low field strengths.

In a Stark map that shows the energy levels of a Rydberg electron in electric field, for the same principal quantum number $n$, the reddest shift (shift to lowest energy) is the edge with $n_1 - n_2 = -(n - 1)$ and $m = 0$, and the bluest shift (shift to highest energy) is the edge with $n_1 - n_2 = n - 1$ and $m = 0$.

Due to the energy splitting and shift in electric field, the blue Stark states of lower $n$ may interact with the red Stark states of higher $n$ if the electric field is strong enough that the energy levels can pass the Inglis-Teller limit. Interactions between Rydberg states with the same magnetic quantum number $m$ but different principal quantum number $n$ lead to avoided crossings for nonhydrogenic atoms. If an avoided crossing is approached quickly as the field is changed, the Rydberg electron may cross to another potential curve (diabatic process). If the crossing is approached slowly enough, the Rydberg electron will stay in the same potential curve (adiabatic process). For adiabatic process, the quantum state of the Rydberg electron is changed, which can only happen when the electron passes close to the ion-core.

The two limiting cases of diabatic and adiabatic processes correspond to very different ionization behavior. For a completely adiabatic process, the conventional saddle point model
is useful to predict the field magnitude necessary to ionize a Rydberg state. The combined Coulomb-Stark potential of the Rydberg state (equation 1.4) has the saddle point at a \( z \) value of \( 1/\sqrt{F} \) which corresponds to a potential energy of \(-2\sqrt{F}\). As a result, the ionization potential of the electron is lowered by \( 2\sqrt{F} \) (in atomic unit), or in a convenient way, the relation could be expressed as:

\[
IP = IP_0 - 6.1\sqrt{F} \tag{1.6}
\]

where \( IP \) and \( IP_0 \) are the ionization potentials with and without electric field and in cm\(^{-1}\), and \( F \) is the field magnitude in V/cm.

For a completely diabatic process, ionization of a population of Rydberg states distributed equally among all Stark states of a given \( n \) value occurs over a range of field strengths. The ionization potential is lowered by \( 4.6\sqrt{F} \) and \( 3.1\sqrt{F} \) for the bluest and reddest shifts respectively.\(^{14}\)

Experimentally, nondiabatic process which is an intermediate process between adiabatic and diabatic processes is likely to be important, and the ionization potential of a Rydberg electron is lowered by:

\[
IP = IP_0 - \alpha\sqrt{F} \tag{1.7}
\]

where the \( \alpha \) coefficient has a typical value between 3.9 and 6.1.\(^{17}\) A value very close to 3.9 or 6.1 indicates a predominantly diabatic or adiabatic behavior of the Rydberg electron in an electric field, respectively.

The lowering of the ionization threshold with electric field has been confirmed in many Rydberg systems, for example, in NO and Ar.\(^{18,19}\)

The high-\( v \) ion-pair states exhibit a similar property in an electric field, i.e., the ion-pair threshold is lowered by the application of an electric field. This was first observed by Pratt \textit{et al} for the process \( \text{H}_2 + h\nu \rightarrow \text{H}^+ + \text{H}^- \) in electric field.\(^{17}\) There, a DC field of different magnitudes on the order of a few hundred V/cm was applied to the reaction region. The \( \text{H}_2 \) molecule was excited to the \( \Sigma^+_g(v=6) \) state by two photons, and then was further excited by a tunable third photon to the ion-pair threshold. By monitoring the ion-pair yield signal as a function of the total photon energy, the energetic threshold for ion-pair formation under different electric fields could be measured. They observed that the ion-pair threshold shifts to
lower energy as the magnitude of the electric field increases according to equation 1.7, and a value of $5.7 \pm 0.2 \text{cm}^{-1}/(\text{V/cm})^{-1}$ was obtained for the $\alpha$ coefficient. Their $\alpha$ value was close to the 6.1 limit because a DC field was used for their experiment and the ionization process could be regarded as predominantly adiabatic.

### 1.1.3 PFI-ZEKE photoelectron spectroscopy

In conventional photoelectron spectroscopy, the molecules are ionized by a fixed photon energy, such as He I radiation at 21.2eV.\textsuperscript{20} Electrons are produced with different kinetic energies, leaving the parent ions in various rovibronic states. With a typical resolution of 5-25meV or 40-200cm$^{-1}$,\textsuperscript{21} the conventional photoelectron spectroscopy usually cannot resolve the rotational levels of the parent ion, except for H$_2$ and a few other small molecules with large rotational constants.\textsuperscript{22}

The resolution of photoelectron spectroscopy can be much improved by the technique of threshold photoelectron spectroscopy (TPES), in which the photon energy is scanned and only electrons with small kinetic energies are detected. The initial method employed for this purpose was to extract the electrons from the ionization region with a small electric field, and transport them as either a parallel beam, or sharply focus them onto a small aperture of an electrostatic analyzer. In this process, energetic electrons with nonzero off-axis velocities are efficiently rejected.\textsuperscript{23} An alternative method involves a waiting period ranging from several hundred $\text{ns}$ to several $\mu$s between photoexcitation and signal detection. The waiting period allows fast electrons to drift away from the ionization region and only electrons with small kinetic energies are extracted to the detection system.\textsuperscript{23} This technique can achieve a resolution of a few cm$^{-1}$.

The energy resolution is further improved by the technique of PFI-ZEKE, which from the name only detects electrons with zero kinetic energy. PFI-ZEKE takes advantage of the properties of high-$n$ Rydberg states in electric field. Instead of directly ionizing the Rydberg states using a large DC field of a few hundred V/cm, this technique uses a sequence of two electric field pulses. This is illustrated in Figure 1.3. The molecules AB are excited to high-$n$ Rydberg states or become ionized to AB$^+$ by tunable VUV photons. After a short delay time, usually a few
hundred ns, a small discrimination pulse (could be less than 1V/cm) is applied to drive away the prompt ions formed above ionization threshold. Then at a longer delay time which is about several μs, a second pulse of larger magnitude is applied to field ionize the high-n Rydberg states and extract the threshold ions into the detector. Since only threshold ions are detected, this technique can achieve very high resolution, down to laser bandwidths (<1cm⁻¹).²⁴

Besides serving as the discrimination field, the first pulse in PFI-ZEKE also ionizes the highest-n Rydberg states. From equation 1.7, the threshold signal comes from the energy range $[IP^0 - \alpha \sqrt{F}_1, IP^0 - \alpha \sqrt{F}_2]$, where $F_1$ and $F_2$ are the magnitudes of discrimination and extraction pulses. Therefore, the blue edge (high energy edge) of the signal will shift with the magnitude of the discrimination field $F_1$, and the field-free ionization potential $IP^0$ can be accurately measured by recording the spectra with a series of discrimination fields and then extrapolating to zero field.

The high resolution of PFI-ZEKE makes it an important and widespread technique to determine the molecular ionization energies, and to study the structure and rovibrational states of the molecular ions.²⁴,²⁵

A variant of PFI-ZEKE is MATI (mass analyzed threshold ionization) spectroscopy.⁴ This technique detects positive ions instead of the electrons. Since ions and electrons are the counterparts of the same ionization process, a MATI spectrum has the same structures as the one recorded by PFI-ZEKE. For MATI spectroscopy, a larger discrimination field (a few V/cm) and a longer delay time between the two field pulses need to be applied due to the much heavier mass of the ions compared to electrons. Since the blue edge of the signal gets eroded to more extent with a discrimination field of larger magnitude and Rydberg states might decay during the delay time, this technique usually has a lower signal to noise ratio than PFI-ZEKE. But since it provides mass information, MATI is useful in systems such as radicals and clusters.²⁶,²⁷

For both PFI-ZEKE and MATI, the ions can be produced in different rovibronic states. This provides a good system for studying state-selected ion-molecule reactions, such as the most fundamental one $H_2 + H^+_2 \rightarrow H_3^+ + H$.²⁸ The $H_2^+$ ions prepared in a selected rovibrational state by field ionization of high-n Rydberg states collided with a neutral H₂ molecular beam of different energies. By comparing the relative ratio of the product ion $H_3^+$ with $H_2^+$, the relative
Figure 1.3: Detection of threshold signal in PFI-ZEKE spectroscopy. Prompt signal comes from above threshold ionization process, and threshold signal is from field ionization of high-$n$ Rydberg states.
cross sections of the reaction could be determined for different states of $H_2^+$ or as a function of the collision energy.

1.1.4 TIPP spectroscopy

Molecular photodissociation into ion-pairs $AB + h\nu \rightarrow A^+ + B^-$ is a basic photofragmentation process, but not as much research has been done on it compared to photoionization or photodissociation into neutral fragments. This is due to the very high photon energies ($>10$eV for many diatomic molecules) needed to get to the ion-pair threshold, and very low cross sections from the ground state to the ion-pair continuum.

Previously ion-pair processes were studied with either fixed or tunable photon energy, both with a resolution of a few hundred cm$^{-1}$. For studies with fixed photon energy, such as the work on HF,$^{29}$ F$_2,$$^{29}$ and CH$_3$X,$^{30}$ the internal energy of the ion-pair fragments was studied from analysis of the ion fragment kinetic energy. For studies with tunable photon energy, such as the work on HCl,$^{31}$ HF,$^{32}$ HCN,$^{33}$ CF$_4,$$^{34}$ CH$_3$X and C$_2$H$_2,$$^{35,36}$ the ion-pair yield curve were recorded as a function of the photon energy, allowing the measurement of ion-pair threshold and cross sections at different energies.

Since its invention a few years ago, the high resolution technique of TIPPS has been demonstrated to be useful in obtaining energetic and dynamic information about the ion-pair dissociation processes in several different molecular systems.

Similar to the technique of PFI-ZEKE which detects the field ionization signal of high-$n$ Rydberg states, TIPPS involves the field dissociation of high-$v$ ion-pair states:

$$AB + h\nu \rightarrow A^+ - B^- \rightarrow A^+ + B^-$$

The whole process has three steps. First, the molecules AB are excited by a pulsed laser radiation from the ground state to the high-$v$ ion-pair states $A^+ - B^-$ just below threshold. Second, the prompt fragment ions produced by direct dissociation and fast predissociation are repelled out of the reaction region by a small discrimination field pulse with a magnitude of a few V/cm. Third, a larger field pulse with larger magnitude (several to tens of V/cm) is applied to field dissociate the high-$v$ ion-pair states and extract the threshold ions into the detection
system. The magnitude of the discrimination pulse and relative delay time of the two pulses can be adjusted for different molecular systems to achieve complete discrimination against the prompt ions. By only detecting the threshold ions, TIPPS can achieve a similar resolution as PFI-ZEKE. This is a great improvement over the conventional ion-pair technique.

As an illustrative example, for the ion-pair process $O_2 + h\nu \rightarrow O^+(4S) + O^-(2P_{3/2}$ or $2P_{1/2})$, the TIPP spectrum in the threshold region has two sets of clearly resolved peaks (see Figure 1.4), corresponding to fragmentation into $O^+ + O^-(2P_{3/2})$ and $O^+ + O^-(2P_{1/2})$. Each set has a sequence of peaks coming from different rotational levels of the $O_2$ molecules in the ground state. The energy separation between the peaks in each set is exactly the energy gap between $O_2$ rotational levels. The spin-orbit splitting between $O^-(2P_{3/2})$ and $O^-(2P_{1/2})$ can be determined from the energy difference between the two sets of peaks, and the intensities reflect the relative cross sections to the two ion-pair channels $O^+ + O^- (2P_{3/2})$ and $O^+ + O^- (2P_{1/2})$.

Due to the similarity between high-$n$ Rydberg state and high-$v$ ion-pair state, the blue edge of TIPPS signal also shifts with the magnitude of the discrimination field. Therefore, by recording TIPPS spectra with a series of different discrimination fields, one can measure the field-free ion-pair threshold $E_{IP}^0$ by extrapolation according to:

$$E_{IP} = E_{IP}^0 - \alpha \sqrt{F}$$

where $E_{IP}$ is usually taken as the energy corresponding to the half maximum height of the blue edge of the TIPPS signal, and $F$ is the magnitude of the discrimination field. In this way, the $E_{IP}^0$ value could be determined to an accuracy as good as a fraction of 1cm$^{-1}$.

1.1.5 Determination of bond dissociation energy

One important application of TIPPS is to determine the molecular bond dissociation energy $D_0(A-B)$. From TIPPS, the ion-pair threshold $E_{IP}^0$ can be accurately measured for the process $AB + h\nu \rightarrow A^+ + B^-$. If the ionization potential of fragment A (IP(A)) and electron affinity of fragment B (EA(B)) are also known, the bond dissociation energy $D_0(A-B)$ can be calculated
Figure 1.4: TIPP spectrum of O$_2$. Spectrum is taken from reference 1. A discrimination field of 2.1V/cm was pulsed on 0.3μs after photoexcitation. An extraction field of 60V/cm was pulsed on 4.9μs later. The field-free ion-pair thresholds for O$_2$(N) + hν → O$^+(^4S) + O^-(^3P_{3/2}, ^2P_{1/2})$ were marked above the spectrum.
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according to:

\[
D_0(A - B) = E_{IP}^0 - IP(A) + EA(B)
\]  \hspace{1cm} (1.9)

Most atomic ionization potentials are known to an accuracy better than 1 cm\(^{-1}\), as well as many atomic electron affinities.\(^{37}\) Therefore, by measuring the ion-pair threshold \(E_{IP}^0\) to a high accuracy (\(\sim 1\) cm\(^{-1}\)) using TIPPS, the bond dissociation energy \(D_0(A - B)\) of diatomic molecules can be accurately measured (\(\sim 1\) cm\(^{-1}\)).\(^{38}\) For polyatomic molecules \(ABC\), the situation is more complicated since the ionization potential or electron affinity of one or both fragments usually are not precisely known to \(\sim 1\) cm\(^{-1}\). But when the data is available, the bond dissociation energy can be determined to an accuracy of a few cm\(^{-1}\).\(^{39}\)

For diatomic molecules, the bond dissociation energy \(D_0(A - B)\) may also be obtained from extrapolation of the spectroscopically determined energy levels near the long range dissociation limit into neutral fragments \(A + B\),\(^{40,41}\) which unfortunately are not always available. This method cannot be applied to triatomic or polyatomic molecules, since the energy levels of different vibrational levels are perturbed by each other and thus make the extrapolation impossible.

Another alternative to measure the bond dissociation energy is through thermochemical reactions. For the reaction \(RH + X \rightarrow R + XH\), by measuring the equilibrium constant, \(K\), one can calculate the value of free energy change, \(\Delta G\), from which the enthalpy change, \(\Delta H\), can be extracted. If the heats of formation of \(RH\), \(X\) and \(XH\) are known, the bond dissociation energy \(D_0(R - H)\) can be derived.\(^{42}\) This method normally has an uncertainty no less than a few hundred cm\(^{-1}\).

Over the last twenty years, the technique of H(D) atom photofragment translational spectroscopy has been demonstrated to be effective to measure bond dissociation energies. This technique involves the photodissociation at fixed photon energy of molecules H-X (X is usually a free radical) into neutral fragments H and X. The translational (and, where appropriate, the angular) distribution of the fragments can be measured by recording the TOF spectrum of H atom. The TOF spectrum provides information of translational distribution of the H fragment, which is related to the translational energy of fragment X by momentum conservation. The
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Bond dissociation energy $D_0(H - X)$ can be calculated from:

$$D_0(H - X) = E_{hv} + E_{int}(HX) - E_{int}(X) - E_k(H) - E_k(X)$$  \hspace{1cm} (1.10)

where the internal energy of $HX (E_{int}(HX))$ can be ignored if the sample gas is introduced into the reaction region by a skimmed molecular beam. The internal energy of $X (E_{int}(X))$ can be obtained by analyzing the energy distribution of the fragment. This technique has been applied to measure a number of bond dissociation energies, among which are $D_0(H - NH_2)$, $D_0(HCC - H)$, $D_0(H - SH)$ and $D_0(H - CN)$. They have a typical uncertainty from $\sim 10$ to a few hundred cm$^{-1}$.

Recently, ion pair imaging spectroscopy (IPIS) was used as an efficient technique to study the ion-pair dissociation process. The molecules were dissociated into ion-pairs with fixed photon energy, and kinetic energies of the fragments were analyzed by the high resolution technique of two dimensional velocity map imaging. Fragments with the same initial velocity vector were mapped onto the same point of the image detector. This technique could be applied to study the vibrational, even rotational structure of the fragment ion, such as $CH_3^+$ from $CH_4X$. It was also used to measure the ion-pair threshold, from which the bond dissociation energy can be derived. The bond dissociation energy $D_0(F - F)$ in molecule $F_2$ was measured in this way with an uncertainty of $\sim 10$ cm$^{-1}$ ($1.606 \pm 0.001$ eV).

1.2 Recent work on TIPPS

In addition to the previous work of TIPPS on $O_2$, $HCl$, and $HF$, in the last few years TIPPS has been applied to the following molecules: $H_2/D_2$, $H_2S$, $HCl/DCI$, $HF/DF$, $HCN$ and $(HF)_2$. In this thesis, the results on $HCl/DCI$ (Chapter 3), $HF/DF$ (Chapter 4), $HCN$ (Chapter 5) and $(HF)_2$ (Chapter 6) will be presented. The work on these molecules investigated three topics: Born-Oppenheimer breakdown ($HCl/DCI$, $HF/DF$), ion-pair formation mechanism ($HCl/DCI$, $HF/DF$, $(HF)_2$), energetics and dynamics of ion-pair formation in triatomic and polyatomic molecules ($HCN$, $(HF)_2$).
1.2.1 Investigation of Born-Oppenheimer breakdown in diatomic molecules

As discussed in the previous section, the accurately measured ion-pair threshold $E_{IP}^0$ from TIPPS can be used to calculate the bond dissociation energy $D_0(A-B)$. Furthermore, since the zero point energies $E_{ZP}$ of many diatomic molecules are known to high accuracy (a fraction of $1 \text{cm}^{-1}$), the classical bond dissociation energy $D_e(A-B)$ can be determined to an accuracy of $\sim 1 \text{cm}^{-1}$ (see Figure 1.5). By measuring the $D_e(A-B)$ values of isotopomers such as HCl/DC1 and HF/DF, the phenomenon of Born-Oppenheimer breakdown can be studied for these molecules in the ground electronic state.

The Born-Oppenheimer approximation is of fundamental importance to molecular spectroscopy and provides the basis for the analysis of molecular spectra. To analyze spectroscopic data, one assumes that there is an intramolecular potential defined by the electronic state of the molecule, and solves for the motion of the nuclei in that potential to obtain the rovibrational energy levels for that electronic state. For most practical purposes, the Born-Oppenheimer approximation is a very good one, with corrections on the order of electron-nuclear mass ratio ($10^{-3}$). When the Born-Oppenheimer approximation is applied, isotopomers such as HCl and DC1 are assumed to have the same potential energy curve for a given electronic state. However, when high resolution spectroscopic data are available for different isotopomers, one cannot obtain fits to the data using the same potential function for different isotopomers, and one needs to take into account the breakdown of the Born-Oppenheimer approximation.

One useful model to take this breakdown into account was proposed by Watson. For an isotopomer $(i)$ of the diatomic molecule $(AB)$, the effective hamiltonian is expressed as:

$$
\hat{H}_{\text{eff}} = \frac{\hbar^2}{2\mu_i} \left[ -\frac{\partial}{\partial R^2} + (1 + \sum_j \frac{m_j q_j(R)}{M_j} \frac{J(J+1)}{R^2}) \right] + U_i^{\text{eff}}(R)
$$

where $\mu_i$ is the reduced mass of isotopomer $i$, the summation is over the two atomic masses for isotopomer $i$, $U_i^{\text{eff}}(R)$ is the effective potential energy function, and $q_j(R)$ is a $J$-dependent function arising from nonadiabatic coupling with other electronic states and which represents corrections for the failure of the electrons of finite mass to follow precisely the rotational and vibrational motion of the nuclei.
Figure 1.5: Born Cycle for HCl/DCl Bond Energies. The ion-pair threshold value $E_{IP}^0$ can be used to calculate the bond dissociation energy $D_0(A - B)$ and the classical bond dissociation energy $D_e(A - B)$. 
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The effective potential energy is given by:

\[ U^{\text{eff}}_i(R) = U_{BO}(R) + \frac{m_e u_A(R)}{M_A} + \frac{m_e u_B(R)}{M_B} \]  \hspace{1cm} (1.12)

where \( U_{BO}(R) \) is the Born-Oppenheimer potential function (defined with the reference \( U_{BO}(R_e) = 0 \)), and \( M_A \) and \( M_B \) are the masses of the two atoms in isotopomer \( i \). For the case where \( J=0 \), the Born-Oppenheimer breakdown terms are gathered into the \( \frac{m_e u_i(R)}{M_i} \) correction terms to the Born-Oppenheimer potential function. These correction terms for each atomic center describe the radial variation of first-order adiabatic energy and \( J \)-independent second order corrections from homogeneous interactions. The determination of the Born-Oppenheimer breakdown terms in the effective hamiltonian \( (q_A(R), q_B(R), u_A(R), u_B(R)) \) are typically done by assuming a functional form, whose terms are then fitted to available spectroscopic data.\(^{57,58}\) While this approach works for the regions of the potential where there is available data, typically for the bottom of the potential well, the extrapolation of these functions outside the range of available data may not lead to reliable results. One must extrapolate to \( R = \infty \) to determine the dissociation energy for a given isotopomer, which is outside the range of spectroscopic data.

Based on this model, the Born-Oppenheimer breakdown in the ground state of HCl/DCl and HF/DF has been studied by construction of the potential energy curves from experimental data and extrapolation to the long range dissociation limit.\(^{59,60}\) A difference of 8.8 cm\(^{-1}\) (no uncertainty quoted) and 16±9 cm\(^{-1}\) was predicted to exist between the \( D_e \) values of HCl and DCI, and of HF and DF. By applying the high resolution technique of TIPPS to these two pairs of isotopomers, we would be able to measure the small energy difference and our result would provide an experimental test to the predicted values.

1.2.2 Study of ion-pair formation mechanism

The mechanism for molecular photoion-pair formation can be either direct or indirect.\(^{61}\)

\[ A-B + h\nu \rightarrow A^+ + B^- \] (direct)
\[ A-B + h\nu \rightarrow A - B^{**} \rightarrow A^+ + B^- \] (indirect)
In the indirect mechanism, $A-B^{**}$ usually is a highly excited Rydberg state, which predissociates into the ion-pair continuum, while in the direct mechanism the continuum is excited. The indirect mechanism typically dominates, as most Franck-Condon accessible excited states have very little ionic character at $R \approx R_e$. The process of predissociation into ion-pairs is not well understood theoretically, even for simple systems.

As an example, for the ion-pair formation in HCl, single photon excitation from the $X^1\Sigma$ ground state would result in $^1\Sigma$ or $^1\Pi$ Rydberg states. The ion-core for these two Rydberg states can be either $X^2\Pi$ or $A^2\Sigma$ (see Figure 1.6). Since the $X^2\Pi$ ionization threshold is below the ion-pair threshold, and the Franck-Condon factors to the vibrationally excited levels of $X^2\Pi$ state are very low, the favorable ion-pair intermediate states are either a $^1\Sigma$ or $^1\Pi$ Rydberg state with an ion-core $A^2\Sigma$. Furthermore, it was reasoned in previous work that the coupling between $^1\Pi$ Rydberg state and $V^1\Sigma$ ion-pair state is weak, so that the ion-pair formation in HCl proceeds through $^1\Sigma$ Rydberg states with the $A^2\Sigma$ ion-core.\(^{31}\) But it remains unclear what Rydberg series converging to what rovibational levels of the $A^2\Sigma$ ion-core act as the intermediate states.

By recording the high resolution ion-pair yield and TIPP spectra of molecules, one would obtain detailed information about the energetic levels of some intermediate states. Thus the ion-pair formation mechanism could be studied.

The study of ion-pair formation mechanism is shown in the work on HCl/DCl and HF/DF. In the work on HF/DF, resonance enhancement was found to be especially important with ion-pair signals comparable to photoionization signals. Many sharp resonances were observed in the high resolution spectra. It would be interesting to attempt to understand and assign those resonant states.

Besides Rydberg states converging to ion-core $A\text{B}^+$, the excited valence states formed by the promotion of a valence electron into an excited orbital ($\pi^*$ or $\sigma^*$) could be the second type of intermediate state.\(^{62}\) The main difference between the excited valence state and Rydberg state is that the former one has a larger internuclear distance than that of the ion core in the Rydberg state.\(^{63}\) This type of mechanism is even less understood and was found to play an important role in the processes of $SF_6 + \hbar \nu \rightarrow SF_6^+ + F^- $ and $OCS + \hbar \nu \rightarrow CO^+ + S^- $.\(^{64,65}\)
Figure 1.6: Potential energy curves of HCl and HCl$^+$, from reference 31. The HCl$^+$ curves are represented by dashed curves.
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For the production of ion A$^+$ from molecule AB, besides the ion-pair process $AB + h\nu \rightarrow A^+ + B^-$, the dissociative ionization process $AB + h\nu \rightarrow A^+ + B + e^-$ can also yield the ion A$^+$. The thresholds of the two processes are different by the electron affinity of fragment B (EA(B)). Normally in our ion-pair experiments the photon energy is below the dissociative ionization threshold, and the only channel to produce A$^+$ is through the ion-pair channel. However, if the photon energy is above the dissociative ionization threshold, it would be interesting to check which process is the main channel. This is shown in the work of chapter 6 (production of HFH$^+$ from (HF)$_2$). Usually the dissociative ionization process has a much larger cross section than the ion-pair process. For example, the photodissociation of N$_2$O yields about 1000 times of N$_2$ as much as O$^-$.

1.2.3 Ion-pair formation in triatomic and polyatomic molecules

Ion-pair formation in triatomic and polyatomic molecules is even less understood than diatomic molecules for several reasons. First, the ion-pair cross sections for larger molecules (10$^{-3}$ or less compared to photoionization cross sections) are usually lower than in diatomic molecules (~10$^{-2}$ compared to photoionization cross sections). Second, the excited states of larger molecules at high energies near their ion-pair thresholds are usually not known. Thus it would be more difficult to study the ion-pair formation mechanism in larger molecules. Third, for larger molecules, one or both of the ion-pair fragments have more than one atom and they can be in different rovibronic levels, thereby making the ion-pair spectrum more complicated to interpret.

Shown in Figure 1.7 is the ion-pair formation process in HCN. The parent molecule HCN can be at different rotational levels in the ground state even for a low rotational temperature of molecular beam. After photoexcitation, the CN$^-$ fragment can also be formed in different states, and the CN$^-$ rotational number $J'$ is not necessarily related to the HCN rotational number $J''$ since there are no specific angular momentum selection rules for photodissociation into fragments. Therefore, there are many different transition combinations, and the energetic limits of all those transitions can be present in the spectrum.

Although it would be unlikely to resolve every single peak, a high resolution TIPP spectrum is expected to show the energetic pattern of ion-pair formation in triatomic and polyatomic
Figure 1.7: Ion-pair formation in HCN. The rotational energy levels HCN and CN$^-$ are shown.
molecules. From the signal intensities at different energies, it is also possible to study the relative cross sections of dissociations into fragments in different levels.

Previously TIPPS was applied to the triatomic molecule of H$_2$S. Both ion-pair channels H$^+$ + SH$^-$ and H$^-$ + SH$^+$ were studied.$^{2,6}$ The field-free ion-pair thresholds for these two channels were measured to be 122458$\pm$3cm$^{-1}$ and 109421$\pm$5cm$^{-1}$, which yielded the same value for the bond dissociation energy $D_0$(H-SH) within experimental uncertainty (31446$\pm$3cm$^{-1}$ and 31447$\pm$6cm$^{-1}$). The results revealed different dynamics between the two ion-pair channels. While the SH$^-$ fragment in the first channel was formed at low rotational levels ($J \leq$4), the SH$^+$ fragment in the second channel could be vibrationally excited with comparable cross sections to $v'$=0 and $v'$=1.

In this thesis project, TIPPS was applied to two more triatomic or polyatomic molecules (HCN and (HF)$_2$), and the results are presented in chapters 5 and 6.

References

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Chapter 2
Experimental

2.1 Introduction

The overall experimental setup is shown in Figure 2.1. It consists of three major parts: 1. A laser system to generate coherent VUV radiation which excites molecules from their ground states to high-ν ion-pair states. 2. A molecular beam and vacuum system. The sample gas is introduced by a pulsed molecular beam into the photoexcitation region under high vacuum. 3. An ion detection system. After photodissociation, the ion fragments are extracted into a Time-of-Flight mass spectrometer. Detection signals are acquired by a LabView program.

The basic components of the apparatus used in this project were moved from University of Waterloo in 2001. The original version of the apparatus was built fifteen years ago for PFI-ZEKE experiments.\(^1\) Later on some changes were made on the vacuum system and TOF spectrometer for TIPPS experiments.\(^2\) During the period of this thesis work, the ion detection system was modified, and new data acquisition software, LabView (Laboratory Virtual Instrument Engineering Workbench),\(^3\) was installed.

In this chapter all the major parts of the apparatus will be discussed.

2.2 Laser system and VUV generation

For all the molecules studied in this project, the ion-pair thresholds lie above 10eV. To pump the molecules from their ground states to their ion-pair states by single photon excitation (multiphoton excitation requires intermediate resonances and can also produce interfering neutral and ionic fragments through other reaction channels), the wavelength of the light has to be in the
Figure 2.1: Schematic of the experimental setup. Details of the TOF spectrometer are shown in Figure 2.2.
VUV region. A tunable laser that operates at such short wavelength is not yet available. On the other hand, the technology of visible dye lasers is well developed. Through the combination of nonlinear optics and the technique of four-wave mixing, a tunable VUV laser beam can be generated from dye laser outputs.

2.2.1 Nd:YAG pulsed dye lasers

Throughout this project the two dye lasers were pumped by the second and third harmonic output of a Spectra Physics Nd:YAG laser (GCR-4). The Nd:YAG laser produces very short (~8ns) laser pulses at 1064nm at a repetition rate of 10Hz. The 1064nm light is doubled by a KDP (KH2PO4) crystal to make the second harmonic at 532nm, which can then be further mixed with the fundamental in a second KDP crystal to generate the third harmonic at 355nm. The pumping scheme can be any of the possible configurations (532-355, 532-532, or 355-355) depending on the desired outputs from the dye lasers. Normally the first configuration was applied, and the energy of each pump pulse was adjusted to be around 100mJ.

Each of the two Lambda Physik dye lasers (Model FL3002) has one oscillator, one preamplifier and one amplifier. The oscillator cavity consists of one grating (600 grooves/mm), a cuvette with flowing dye solution, and an end mirror. The dye laser could be tuned by rotating the angle between the grating normal and cavity axis. The exact lasing wavelength could be calibrated to a precision of 0.005nm using a hollow cathode photogalvanic lamp of U or Fe filled with noble gas Ne or Ar.

The dye molecules are generally organic compounds with high fluorescence efficiency. The lasing wavelength for a given dye may be varied over tens of nm, depending on the dye properties and other conditions. When necessary two different dye solutions could be mixed to extend the tuning range.

After being coupled out of the oscillator cavity, the laser beam passes through the preamplifier and main amplifier. The power is amplified by a factor of about 10 by the main amplifier. Normally the output from the dye laser is about 15-30mJ/pulse.

The frequency of the dye laser output could be doubled by a KDP or BBO (β-BaB2O4) crys-
tal, depending on the wavelength.\textsuperscript{8} BBO crystals work better at shorter wavelength with the frequency-doubling limit at 205nm.\textsuperscript{9} When even shorter wavelengths (~200nm) are necessary, the second harmonic of the dye laser output can be mixed with the residual fundmental in a second BBO crystal.\textsuperscript{10} In this way the use of BBO crystal could be extended down to 197nm at room temperature, and 194.4nm in a cooled crystal.\textsuperscript{11}

After frequency doubling or even tripling the two beams are overlapped both temporally and spatially by a dichroic mirror. For effective overlapping, the two beams need to arrive at the same spot on the dichroic mirror simultaneously. This means the light path difference between the two laser beams need to be minimized, normally it is as small as a few cm. The dichroic mirror is coated for high reflection of a small range of wavelength (~20nm) and high transmission for other wavelengths. In our experiment one wavelength is fixed (2\nu_1 corresponds to one two-photon resonant state of Kr or Xe), while the other wavelength is scanned. Normally the fixed wavelength is reflected by the dichroic mirror.

After overlapping, the two laser beams are focused by a convex lens (f≈25cm for \nu_1) to interact with a pulsed jet of Kr or Xe gas to generate VUV photons.

2.2.2 Generation of VUV photons by four-wave mixing

The theory of four-wave mixing is based on the nonlinear response of nonmagnetic materials to strong laser electric fields. When an electric field is applied to a medium, the induced polarization response, \( P(\omega) \), can be expressed as a Taylor series expansion in terms of the applied field, \( E(\omega) \):\textsuperscript{12}

\[
P(\omega) = \chi^{(1)} \cdot E(\omega) + \chi^{(2)} \cdot E(\omega) \cdot E(\omega) + \chi^{(3)} \cdot E(\omega) \cdot E(\omega) \cdot E(\omega) + \ldots
\]

(2.1)

where the \( \chi^{(n)} \) tensor is the \( n \)th order susceptibility of the medium, and as \( n \) increases the \( \chi^{(n)} \) value decreases substantially. Under ordinary conditions, for example, when a cw light source is used, we only need to consider the linear term \( \chi^{(1)} \cdot E(\omega) \). However, under the strong electric fields produced by a pulsed laser, the nonlinear terms can become significant and result in the generation of frequencies at linear combinations of the applied frequencies. For media
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with a center of symmetry, such as Kr and Xe gas, the even order terms are all zero, and the first nonlinear term is the third order response. For three input frequencies \( \nu_1, \nu_2 \) and \( \nu_3 \), the output frequency \( \nu_{\text{output}} \) can be any linear combinations of the input frequencies. The output frequency, together with the three input fundamentals, oscillate in the nonlinear medium, so this type of frequency mixing is called four-wave mixing.

The specific type of four-wave mixing used in this project is two-photon resonant sum-frequency mixing, which involves two input frequencies \( \nu_1 \) and \( \nu_2 \), and the generated frequency is \( \nu_{\text{output}} \) at \( 2\nu_1 + \nu_2 \). The intensity of the output frequency is described by:

\[
I_{3\nu} = \left( \chi^{(3)} \right)^2 I_{\nu_1} I_{\nu_2} N^2 F(b\Delta k)
\]

where \( \chi^{(3)} \) has the form:

\[
\chi^{(3)} = \frac{e^4}{\hbar^3} \sum Z_{gij}^i Z_{gjk}^j Z_{kg}^k \frac{Z_{ijkl}^i Z_{klj}^j Z_{jkl}^j}{(\Omega_{ij} - \nu_1)(\Omega_{lj} - 2\nu_1)(\Omega_{kl} - 2\nu_1 - \nu_2)}
\]

Here \( I_{\nu_1}, I_{\nu_2} \) are the intensities of the input frequencies, and \( N \) is the number density of the non-linear medium. The phase matching factor \( F(b\Delta k) \) is a function of \( b\Delta k \), where \( b \) is the confocal beam parameter of the focussed light, and \( \Delta k \) is the wavevector difference between the input and output light \( (\Delta k = k(\nu_{\text{output}}) - 2k(\nu_1) - k(\nu_2)) \). The value of \( F(b\Delta k) \) is non-zero only if the refractive index at \( \nu_{\text{output}} \) is less than the refractive index at \( \nu_1 \) and \( \nu_2 \). Such behavior is called negative dispersion (in the normal case the refractive index increases with the frequency), and regions of negative dispersion are found to the blue of resonance lines and above the ionization potential in gases. Due to the pressure dependence of \( \Delta k \), one cannot simply increase \( N \) to improve the output intensity, but the \( N^2 F(b\Delta k) \) term as a whole.

For the \( \chi^{(3)} \) term, in general, the more polarizable the nonlinear medium is, the larger the value \( \chi^{(3)} \) will be, so usually rare gases such as Kr or Xe or metal vapors are used as the medium for four-wave mixing. In equation (2.3), \( Z_{xy} \) are the dipole matrix elements, \( \Omega_{xy} \) are the complex transition frequencies for the \( x \leftarrow g \) transitions. Equation shows that the \( \chi^{(3)} \) value can be greatly enhanced when the input frequency, such as \( 2\nu_1 \), is two-photon resonant with a transition in the nonlinear medium.

In this project, one input frequency \( \nu_1 \) is chosen and fixed so that \( 2\nu_1 \) corresponds to one
two-photon resonance state in the rare gas. The other input frequency $\nu_2$ is scanned so that the output frequency at $2\nu_1 + \nu_2$ is tunable. The setup of $\nu_1$ and $\nu_2$, and the energy range of the generated VUV photons for the different molecules studied in this project are tabulated in Table 2.1. To generate VUV photons in those energy ranges, a windowed gas cell does not work since no material of structural thickness is transparent at short wavelengths. Therefore, a pulsed jet of Kr or Xe was used in this project. The Kr or Xe atoms at a backing pressure of 1-2 bar are introduced into the VUV chamber from a pulsed valve (General Valve\textsuperscript{13}) with 1 mm diameter nozzle located $\sim$5 cm away from the input laser beams.

The VUV wavelength was calibrated by recording optogalvanic spectra in a hollow cathode discharge to calibrate the tunable laser $\nu_2$,\textsuperscript{6} and using the known Xe resonance energy for $2\nu_1$ in the relationship $\nu_{VUV} = 2\nu_1 + \nu_2$. The uncertainties in this calibration come from a small uncertainty in the actual value of $2\nu_1$, which can be slightly different from the tabulated value due to power broadening of the Xe resonance, and oscillations in the calibration of the dye laser due to the mechanics of the grating drive (about $\pm 0.005$ nm with a period of 1.5 nm). These effects combined give an estimated error of $\pm 0.3$ cm$^{-1}$ in our VUV calibration.\textsuperscript{2}
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After the four-wave mixing process, the generated VUV beams, together with the fundamentals, propagate into a one-meter normal incidence monochromator, which disperses and refocuses the selected VUV beam into the reaction chamber to interact with a molecular beam of the sample gas. After the interaction region the VUV intensity is recorded by a microchannel plate detector.

2.3 Molecular beam and vacuum system

In our experiments, the sample molecules are introduced into the reaction chamber in a pulsed molecular beam. One advantage of molecular beam is that it can achieve high molecular density in the reaction region with a relatively low background pressure. The sample molecules are emitted from a pulsed valve (General Valve) with a 1mm diameter nozzle located 5cm away from the VUV beam. The backing pressure is usually 1-2bar. The main chamber is pumped by a 1000L/s turbo pump and the operation pressure is on the order of 10^{-6} torr with a background of 10^{-7} torr. The VUV chamber is under 10^{-3}-10^{-2} torr with the pumping of a two-stage booster pump. The pressure in the buffer zone between VUV chamber and the monochromator is about 10^{-5} torr, and the monochromator itself is maintained at 10^{-7} torr to protect the grating installed inside from contamination.

Due to the large pressure difference between the backing gas source and the vacuum chamber, the gas molecules expand very quickly into the vacuum chamber when the nozzle is open. During the course of the expansion, the molecules collide with each other and the originally random molecular velocities become more and more aligned along the expansion axis as the molecular internal energy is converted into translational energy. At some point of the expansion, the molecular beam becomes collision free. For photoexcitation at this point, the product spatial and internal energy distribution is not perturbed by intermolecular reactions.

The average speed that the molecules finally reach, $v_\infty$, could be calculated from:

$$v_\infty = \sqrt{\frac{2k\gamma}{m\gamma - 1}T_0}$$

(2.4)
where \( \gamma = C_p/C_v \) \((C_p,C_v\) are the heat capacities of the gas species at constant pressure and volume, respectively), \( k \) is Boltzmann's constant, \( m \) is the molecular weight of the sample gas, and \( T_0 \) is the temperature of the gas reservoir. Since \( v_\infty \) is often greater than the sound velocity in the sample gas, the molecular beam is also designated as "supersonic molecular beam". By converting the internal energy into translational energy, this technique can lower the rotational energy substantially and thus the number of rotational levels occupied by the molecules is much less than at room temperature. In this way the molecular spectra of many species could be simplified and become interpretable.

The number density of sample molecules in the interaction region can be approximately calculated according to:

\[
    n = \frac{2\dot{N}}{v_\infty \pi r^2}
\]

where \( \dot{N} \) is the flow rate (number of emerging molecule per unit time), \( r \) is the distance from the nozzle orifice. The \( \dot{N} \) value can be regarded as the average pressure in the reaction chamber multiplied by the speed of the turbo pump. The typical number density in our experiment is estimated to be on the order of \( 10^{13}/\text{cm}^3 \).

If a skimmer is mounted in the expansion path, only a central portion of the molecular beam can go through. In this way the beam will become even more collimated and allow further simplification of the spectra. However, the distance between the nozzle and the reaction region will become much larger when a skimmer is mounted on the way. From equation 2.5, the gas density decreases substantially at larger distance, thus the ion signal will become even weaker. For our experiments probing ion-pair processes, the cross sections are usually at least two orders of magnitude lower than the photoionization process producing parent ions. To obtain ion-pair signals at detectable levels, no skimmer was used.

### 2.4 Detection of the ion-pair signal

Conceptually, the TIPPS experimental setup is similar to MATI (mass-analyzed threshold ionization) spectroscopy. For MATI spectroscopy, the molecules are excited through either
single-photon or multi-photon process to the highly excited Rydberg states, $AB^+ - e^-$, then a sequence of two electric pulses is applied. The first pulse discriminates against any prompt ions formed from above-threshold processes. The second pulse field ionizes the weakly bound Rydberg states and the threshold ions $AB^+$ are detected by a time of flight mass spectrometer. For TIPPS spectroscopy, the molecules are excited by single VUV photons to the highly vibrationally excited ion-pair states $A^+ - B^-$, and two electric pulses are applied to detect only the threshold ions $A^+$ (or $B^-$) formed from field dissociation of the ion-pair states.

### 2.4.1 Time-of-Flight spectrometer.

The TOF mass spectrometer used for this project is shown in Figure 2.2. This system could be used to detect both positive and negative ions, by switching the polarity of the extracting and detecting voltages. In the detection system there are four nickel mesh electrode plates (P1,P2,P3,P4). The size of each plate is $7 \times 5 \text{cm}^2$ and the distance between adjacent plates is about 2cm. The VUV laser beam crosses the molecular beam in the excitation region between P2 and P3. The two beams and the axis of the spectrometer are orthogonal to each other. For total ion-pair yield spectra, one pulsed extraction field is applied to the excitation region a few $\mu$s after photoexcitation to extract both prompt and threshold ions into the TOF spectrometer (see Figure 2.3). For a TIPP spectrum, a small pulsed discrimination field, usually about 2-10V/cm is applied at a delay time of ~300ns after photoexcitation to drive away any prompt ions formed from above threshold processes; then at a delay time of a few $\mu$s, a second electric pulse of larger magnitude (usually on the order of tens of V/cm) and opposite polarity is applied to field dissociate the long lived highly vibrationally excited ion-pair states and extract the threshold ions into the TOF tube. To collect TIPP spectra of every specific molecule studied in this project (HCl/DCI, HF/DF, HCN and (HF)$_2$), the discrimination field magnitude and relative delay time of the two pulses were adjusted to guarantee complete discrimination against the prompt ions. Furthermore, positive ions were recorded for all the molecules since they usually give relatively higher signal to noise ratio than the corresponding negative ion. For molecules HCl/DCI, HF/DF and HCN, the H$^+$/D$^+$ ion can only come from the ion-pair channel since
Figure 2.2: Time-of-Flight mass spectrometer.
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the VUV energy, scanned over a narrow range (see Table 2.1) around the ion-pair threshold was not enough to excite the molecules to the dissociative ionization channel $AB \rightarrow A^+ + B + e^-$. For $(HF)_2$, the VUV energy was scanned over a large range, and both the ion-pair channel and the dissociative ionization channel are possible. Therefore, the negative signals ($F^-$ and $e^-$) also needed to be collected to investigate which channel the positive ion HFH$^+$ originated from.

The space between P3 and P4 is the accelerating region. The voltages applied to this region were adjusted relative to the extraction field to satisfy the Wiley-McLaren condition for space focusing.\textsuperscript{16} Small voltages (a few V/cm) were applied to the steering electrodes after the acceleration region to adjust the trajectory of the ions to optimize the signal intensity from the multichannel plates at the end of the flight tube.

The next stage is the field free TOF (time-of-flight) tube. It's a rather simple design of a straight tube about 40cm long. The mass resolution of the spectrometer is about 100, which is enough to separate ions involved in the ionization and dissociation processes of small molecules in our experiments. If higher resolution is needed for larger molecules in the future, a more complex TOF arrangement such as a reflectron system could be installed.\textsuperscript{17}

Finally the ions hit the front of the MCP (microchannel plate) detector which is a stack of two pieces. Each MCP consists of a parallel array of channel electron multipliers capable of photon, ion, and electron detection and amplification. For normal operation, a high voltage of about 1000V is applied to each MCP, with the voltage of the output surface positive relative to the input surface. For such condition one MCP can generate up to $10^4$ electrons for one incident ion. When two MCPs are wired in series, an amplification factor of $10^7$ can be achieved. The electron pulse generated by the incidence of ions is collected by an anode, and the current then generates a detectable voltage through a 50Ω resistor. The signals were sent to a boxcar (SR250, Stanford Research Systems\textsuperscript{18}) where they were gated and integrated. The gate width was set at 20-50ns to match the FWHM of the TOF ion peak. The integrated signal was displayed in an oscilloscope and sent to the computer for data collection. The ion signal was recorded as a function of the VUV energy, which was tuned by scanning the wavelength of one of the dye lasers. Both laser scanning and ion signal recording were controlled by a LabVIEW program.
Figure 2.3: Detection scheme of the threshold ion-pair signal. A sequence of two field pulses is applied. The big circles represent molecules at high-$\nu$ ion-pair states, while small circles are the ion fragments.
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2.4.2 LabVIEW program

The software of LabVIEW\(^3\) is a development environment based on the graphic programming language G which uses terminology, icons and relies on graphic symbols rather than textual language to describe programming actions. LabVIEW contains comprehensive libraries for data collection, analysis, presentation and storage. All labVIEW programs have a front panel and a block diagram. The front panel is the graphic user interface which contains knobs, graphs and other controls. The block diagram contains the graphic source code of the file which is to control the inputs and outputs on the front panel. To scan the dye laser, the labVIEW command is sent through a GPIB cable to the IEEE-488 interface of the dye laser. Following the scanning of the wavelength, the angle of the doubling crystal is also rotated at the same time according to the built-in relation to give maximum power of second harmonic frequency. At each laser shot, the integrated output of ion signal from the boxcar is converted by an A/D card to a digital signal, which is then written to a data file through the LabVIEW program for further analysis.

2.4.3 Ion-counting technique

For some molecules such as HCl, although the ion-pair cross section is much lower than photoionization, there are still numerous threshold ions (H\(^+\) and Cl\(^-\)) generated for each laser shot when the VUV energy corresponds to the difference between certain levels of the ground state and the ion-pair limits. In such cases a general analogue technique could be applied; that is, the VUV energy was scanned at a speed of less than 1 cm\(^{-1}\) per step, and the threshold ions generated at each step were collected by setting the boxcar gate to the correct delay, and adjusting the boxcar sensitivity to ensure that the signal was not saturated. The averaged output voltage of the boxcar then reflected directly the number of threshold ions generated, and was plotted as a function of the VUV energy.

However, for larger molecules such as HCN, the ion-pair cross section is extremely low that there is less than one threshold ion produced per laser shot (statistically there was only one threshold ion for every one hundred laser shots at the most intense peak in HCN TIPP...
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spectrum). If general analogue detection were used, at each step there would either be just one threshold ion or no signal at all. This weak signal would be very hard to detect from the background noise, and would not reflect the relative cross sections to ion-pair states at different energies. To improve the signal level, the ion-counting technique was applied. The VUV is also scanned, but at each energy position we wait until a number of laser shots were fired (for example, 100). A threshold voltage was set for the boxcar, and only when the output voltage was above the threshold, one ion signal was counted. In this way, the signal was clearly distinguished from the noise and thus the signal to noise ratio could be highly improved. At each VUV energy, the total count of threshold ions was accumulated, and that number, which reflects the ion-pair transition strength, was plotted as a function of VUV energy.

From the above discussion, the ion-counting technique is not applicable to the situation when there are more than one ions produced for one laser shot. In such cases, the boxcar output will be above the threshold voltage as long as there is any ion. Therefore, it would not be able to tell the exact number of ions produced and reflect the transition strength.

In the work of this thesis, TIPP spectra of DCI and HCN were recorded by ion-counting technique due to their low signal levels, while TIPP spectra of other molecules and all the total ion yield spectra were recorded in the general analogue mode.

References


5. Lambda Physik, a subsidiary of Coherent, Inc., http://www.lambdaphysik.com


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Chapter 3
Threshold Ion-Pair Production in HCl/DCl

3.1 Introduction

In the work of this chapter, TIPPS was applied to two isotopomers, HCl and DCl, in an effort to measure accurately the difference between the dissociation energies of the two molecules. The HCl/DCl isotopomer pair was chosen because there has been recent work done using extensive results from high resolution spectroscopy to model Born-Oppenheimer breakdown effects in this molecule.\(^1\) Furthermore, the bond dissociation energy of HCl had been precisely measured and thus provided a good reference to the current result.\(^2\)

Based on the model in the previous chapter (section 1.2.1), Coxon and Hajigeorgiou employed all high resolution spectroscopic data for the \(X^1\Sigma^+\) and \(B^1\Sigma^+\) states of HCl and DCl in direct least-squares fits of the potential energy curves for the two states.\(^1\) By using an extensive, multi-isotopomer data set, they were able to estimate not only the Born-Oppenheimer potential for the two states, but also Born-Oppenheimer breakdown functions over a large radial range for both the hydrogen and chlorine centers. Since data was available up to \(v = 17\) for the \(X\) state of HCl, and \(v = 24\) for DCl, they were able to fit the Born-Oppenheimer breakdown terms to large R, increasing the reliability of the extrapolation to \(R = \infty\). The results of their fit indicated that the major correction term for the potential was \(\mu_H(R)\), and the difference in \(D_e\) for HCl and DCl was 8.8cm\(^{-1}\) (they found 37194cm\(^{-1}\) for \(D_e(\text{HCl})\)).

Given these very extensive spectroscopic results for HCl and DCl, where the highest vibrational levels were within 1500cm\(^{-1}\) of the dissociation limits, this is a perfect test case for comparing the results of the spectroscopic analysis with our highly accurate determinations of
bond dissociation energies for this system. Previous TIPPS results \( (37232.1 \pm 0.6 \text{cm}^{-1}) \)^2 indicated a small inaccuracy in the \( D_e(\text{HCl}) \) value determined by Coxon and Hajigeorgiou, but it is interesting to compare the predicted difference between the two isotopomers. With the high-resolution capabilities of our TIPPS spectroscopic technique, it is possible to observe the predicted small difference of \( 8.8 \text{cm}^{-1} \), therefore, the present work provides an experimental result that should be a rigorous test for the theoretically predicted Born-Oppenheimer breakdown in HCl. This is the primary goal of this work.

As TIPPS is based on photoion-pair formation, the present work also investigated the detailed dynamics of photoion-pair formation in HCl/DCl. For the hydrogen halides, the process of photon-pair formation was observed first for HF by Berkowitz et al., but was not observed for any other hydrogen halides until Yencha et al. published the results of a synchrotron radiation study on HCl and DC1. These authors characterized the ion-pair production process by monitoring the total Cl\(^-\) ion signal as a function of wavelength from 75 to 86 nm. They found that in the threshold region, the photoion-pair yield spectrum showed a strong resonance structure, similar to what had been previously observed in HF photoion-pair yield. In addition to the experimental work, Yencha et al calculated the cross section for ion-pair production in HCl and DC1 by multichannel quantum defect theory (MQDT). The agreement between the theoretical results and the experimental measurements was good. A striking feature in their spectra are the intense, sharp peaks, just above the threshold in both HCl and DC1. The results of the MQDT calculation were that the cross sections for photoion-pair formation for HCl and DC1 were quite similar in the threshold region, while experiment showed photoion-pair formation to be somewhat less likely in DC1. We looked at the total photoion-pair yield spectra for HCl and DC1 in the threshold region as part of the current study. Our results are somewhat different from the previous work. In addition to the obvious resolution improvement, we find the spectra different between HCl and DC1, particularly with regard to cross sections, which we find to be much lower in DC1. Unlike in the case of HF/DF (see chapter 4), the lack of resolved rotational structure in the current results makes a definitive assignment of the resonant structure problematic, but using the previous calculations of Rydberg resonances as a guide, we have successfully assigned much of the observed structure in the threshold region. Our current
assignment is in basic agreement with the previous work, although the details are different, particularly with respect to intensity of the resonances.

3.2 Experimental

For the present work on HCl and DCl, the tunable, pulsed VUV radiation was generated through resonant four-wave mixing of dye laser radiation (Lambda-Physik FL 3002 dye lasers pumped by a Spectra Physics GCR4 Nd:YAG laser) in a pulsed supersonic Xe beam. Two different four-wave mixing schemes were used to generate the 14.4eV (86nm) light necessary for these experiments. One of the input wavelengths was fixed either at 222.57nm or 249.63nm corresponding to a two-photon resonance in Xe (5p6p'5p6p'[1/2,0] at 89860.538cm⁻¹ or 5p6p[1/2,0] at 80119.474cm⁻¹). The other wavelength was scanned either from about 360nm to 380nm or from 265nm to 280nm for the two different fixed wavelengths, resulting in tunable VUV light at approximately 86 nm, with a bandwidth of ~1cm⁻¹.

The VUV light was separated from the fundamental by a one meter focal length normal incidence monochromator, which also focused the VUV beam into the uncollimated HCl/DCl gas jet. The VUV crossed the pulsed molecular beam of HCl or DCl expanded from a pulsed source with a 1mm diameter nozzle (General Valve, Series 9), at about 5 cm downstream from the pinhole. Both HCl (research purity, 99.999%, Matheson) and DCl (99%, C/D/N Isotopes Inc.) gases were used directly with a backing pressure of ~20psi. The pressure in the reaction chamber was ~2.0x10⁻⁶torr with the beam on, with a background pressure of ~2.0x10⁻⁷torr.

For the ion-pair yield spectra, an extraction field pulse of 35V/cm was applied to the interaction region 2μs after the photodissociation, and the positive ion signal was recorded using gated integration (Stanford Research Systems SR250). For the TIPP spectra, a discrimination field pulse of duration 1μs and magnitude 2V/cm was applied 300ns after the VUV pulse to discriminate against any prompt ions formed upon VUV excitation. After a delay time of 2.0μs after the VUV pulse, a pulsed field of 7V/cm was applied to field dissociate those long-lived weakly bound ion-pair states and extract the resulting protons and deuterons into the TOF.
By using gated detection, we were able to completely discriminate against prompt ions, and only detect threshold signals.

Due to the different ion intensities of H$^+$ and D$^+$, the TIPP spectra of HCl and DCI were recorded in different ways. For HCl, the H$^+$ ions were recorded by gated integration of the analogue signal from the channel plates. For DCI, because the D$^+$ signal was weaker (about one order of magnitude lower than the H$^+$ signal from HCl), the TIPP spectra were recorded using gated ion counting. This was done by using the gated integrator as a discriminator, with the LabView signal collection software recording a count if the output of the gated integrator exceeded a fixed threshold on a shot by shot basis.

We found that it was never possible to eliminate the HCl$^+$ and H$^+$ signals even when pure DCI was allowed to flow through the gas handling system for several days. This signal came from proton exchange with the walls of the gas handling system, as we did not take the time necessary to fully deuterate the system, since we changed gases often in our experiments, and used a very low flow of DCI through the system. However, this had an advantage for the present work in that it was possible to record both TIPP and total photoion-yield spectra for both isotopes under identical conditions. To determine relative cross sections for total ion-pair yield, we could use the HCl$^+$/DCI$^+$ signals to normalize the H$^+$/D$^+$ yields.

3.3 Results and Discussion

3.3.1 TIPP spectra

The TIPP spectra of HCl and DCI are shown in Figure 3.1. For both molecules, the spectra cover the excitation range of HCl/DCI($X^1\Sigma, v''=0, J'' \leq 6$) + hν → H$^+$/D$^+$ + Cl$^-(^1S_0)$. The spectra shown in figure 3.1 were collected using both Xe resonances as described in the previous section, and two spectra have been overlapped for both HCl and DCI. For the HCl TIPPS, spectra were recorded at several different discrimination fields, and an extrapolation to zero field yielded the same result as in our previous work, within the error limits. However, the reduced signal to noise for the DCI TIPPS made this procedure less reliable, so a different
Figure 3.1: TIPP spectra of DC1 and HC1. The field-free ion-pair thresholds for \( \text{HCl/DCI}(J'') + h\nu \rightarrow H^+ + D^+ + Cl^- (^1S_0) \) were marked above the spectrum. In both cases, two different spectra have been superimposed. Both were recorded under the same conditions in terms of beam conditions and electric fields. The difference between the two spectra is that different Xe resonances are used in the four-wave mixing process used to generate the tunable VUV (see text).
Table 3.1: Results from HCl/DCI TIPP spectra. Energies in cm$^{-1}$. $D_0$ is the bond dissociation energy from $v = 0$, $D_e$ is the classical BDE. The uncertainty in the zero point energy is less than 10$^{-3}$ cm$^{-1}$.\(^8\) Notations: a, $^{35}$Cl isotopomer value (see reference 2). b, Reference 2. c, Reference 8, for $^{35}$Cl isotopomer. The published value much more accurate, so uncertainty is not given here. d, Result of fit including B-O breakdown (reference 1). Error is statistical error of fit. See reference 1 for discussion of overall uncertainty.

<table>
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<tr>
<th></th>
<th>HCl</th>
<th>DCI</th>
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<tr>
<td></td>
<td>current</td>
<td>literature</td>
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<td>2V/cm</td>
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<td>116726.4±0.6</td>
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<td>116288.7±0.6(^b)</td>
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<tr>
<td>$D_0$</td>
<td>35746.9±1.1</td>
<td>35748.2±0.8(^b)</td>
</tr>
<tr>
<td>$G_0$</td>
<td>1483.88(^c)</td>
<td></td>
</tr>
<tr>
<td>$D_e$</td>
<td>37230.8±1.1</td>
<td>37194.0±0.7(^d)</td>
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</table>

approach was taken to determine the relative thresholds for HCl and DCI. The four spectra shown in figure 3.1 were recorded under the same pulsed field conditions, so the blue edges of all of the peaks in these spectra should be shifted by the same amount from the field free thresholds. To get the value of the 2V/cm thresholds for $J''=0$ HCl or DCI, the half height positions of the blue edges were measured for all the peaks that were clearly resolved. Since the threshold energy for a given $J''$ state is given by:

$$E_{\text{threshold}} = E_{J''=0} - E_{\text{rot}} = E_{J''=0} - B_0(J + 1) + D_0(J(J + 1))^2$$  \(3.1\)

the data could be fitted to a straight line to determine $E_{J''=0}$, the field-shifted threshold energy for $J'' = 0$, and $B_0$, the rotational constant (the literature value of $D_0$ was used\(^8\)). This plot of the threshold data is shown in figure 3.2, and resulted a 2V/cm ion-pair dissociation threshold of 116282.2 ± 0.8 cm$^{-1}$ for HCl, which is in good agreement with the value determined by extrapolation when the $3.9\sqrt{F} = 5.5$ cm$^{-1}$ field shift is taken into account. The results of this data analysis are given in table 3.1.

The value obtained for $D_0$(H-Cl) in the present study is in good agreement with previously
Figure 3.2: Determination of ion-pair thresholds for HCl and DCl. The blue edge of the TIPPS peaks for $J''=0-5$ are plotted for HCl (squares) and DCl (triangles) for the spectra shown in figure 3.1. The DCl thresholds have all been shifted upwards by 400 cm$^{-1}$. 
published result, \( \text{which was obtained by the more accurate method of extrapolation to zero field.} \) Since what matters in the present work is the comparison between HCl and DCl, we have not attempted to improve on our previous value for \( D_0(\text{H-Cl}) \), and still recommend that it be used. The uncertainty in the determination of \( D_0 \) comes from three sources: the determination of the ion-pair dissociation threshold from the data shown in figure 3.2: ±0.8\( \text{cm}^{-1} \) for HCl, ±0.6\( \text{cm}^{-1} \) for DCl; the electron affinity of Cl: 29138.3±0.5\( \text{cm}^{-1} \); the calibration of VUV: ±0.3\( \text{cm}^{-1} \), and the model dependence of obtaining the H\( ^{35} \text{Cl}/\text{D}^{35} \text{Cl} \) threshold from the TIPPS of the mixture: 0.1\( \text{cm}^{-1} \).

The result of this analysis gives the difference in classical bond dissociation energy to be \( D_e(\text{H-Cl}) - D_e(\text{D-Cl}) = 2.9±1.1\text{cm}^{-1} \) (the error due to EA(Cl) does not matter to the difference in \( D_e \)), which is smaller than the value of 8.8\( \text{cm}^{-1} \) obtained by Coxon and Hajigeorgiou. In the data shown in figure 3.1, there is a spectrum of HCl and one of DCl that were recorded on the same day under identical conditions, taking advantage of the mixture of HCl and DCl present in the molecular beam. If we consider only these data, which would minimize errors due to wavelength calibration, field strengths and ion density, we obtain a somewhat different value for the difference in \( D_e \): \( D_e(\text{H-Cl}) - D_e(\text{D-Cl}) = 3.7±1.5\text{cm}^{-1} \). The increased error in this determination is caused by the difficulty in determining the threshold energies, and the reduced amount of data. The two different analyses do produce a number that is in agreement within the uncertainty of each determination. Our recommendation for the value of \( D_e(\text{H-Cl}) - D_e(\text{D-Cl}) \) is the error-weighted average of these two determinations: 3.2±1.0\( \text{cm}^{-1} \).

There is also a disagreement of 37\( \text{cm}^{-1} \) and 43\( \text{cm}^{-1} \) in the values of \( D_e \) obtained by analysis of the spectroscopic data, although that is not surprising given that the least bound levels considered in the analysis were still 1500\( \text{cm}^{-1} \) below the dissociation limit. However, given the extensive high quality spectroscopic data available for HCl/DCl, this difference does highlight the limitations of obtaining precise bond dissociation energies from spectroscopic data. Of course, one can obtain more accurate values for \( D_0 \) from spectroscopic measurements if it is possible to observe levels at or just above the dissociation threshold, as was the case in HF.

In a recent study carried out by Michel \textit{et al}, a precise value was obtained for the dissociation energy of HCl\(^+\) by analysis of the lineshape of individual rotational lines in the
Chapter 3. Threshold Ion-Pair Production in HCl/DCl

$A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ spectrum.\textsuperscript{10} These lines correspond to transitions to $A^2\Sigma^+$ rotational levels just above the $X^2\Pi_{3/2}$ dissociation limit, and allowed for a determination of the HCl$^+$ dissociation energy that had an uncertainty of $\pm 0.5\text{cm}^{-1}$. Through a Born cycle, Michel et al were then able to derive a value for $D_0(\text{H-Cl})$ in excellent agreement with our previously published value. We can, of course, use the current results in a Born cycle to obtain the bond dissociation energies of both HCl$^+$ and DC1$^+$, thus probing the Born-Oppenheimer breakdown in an ionic system.

Combining our results with the ionization energy of Cl (104590$\pm 0.3\text{cm}^{-1}$),\textsuperscript{11} and the ionization energies of HCl and DC1 (102801.5$\pm 1\text{cm}^{-1}$ for HCl and 102836.1$\pm 1\text{cm}^{-1}$ for DC1)\textsuperscript{12} we can calculate the bond dissociation energies of HCl$^+$ and DC1$^+$ for the dissociation processes HCl$^+$/DC1$^+$(X$^2\Pi_{3/2}$, $J^+=3/2$) $+$ h$\nu \rightarrow \text{H/D} + \text{Cl}^+(^3\text{P}_2)$. The results of these calculations are given in table 3.2. As would be expected, there is good agreement between our value for $D_0(\text{H-Cl}^+)$ and that obtained by Michel et al, although their accuracy is much better since they directly determined the dissociation energy for the ion in their experiments. In this case, the definition of $D_0$ for the ion is the energy required to dissociate the ground rotational level in the $^2\Pi_{3/2}$ spin-orbit state into H(D) + Cl$^+$. Using the known spectroscopic constants for HCl$^+$ and DC1$^+$, one can calculate the zero-point energies for these ions (including the Dunham correction) and derive the classical bond dissociation energies. The difference in classical bond dissociation energies has the opposite sign to the difference found for the neutral pair: $D_e(\text{H-Cl}^+) - D_e(\text{D-Cl}^+) = -7.5 \pm 2.0\text{cm}^{-1}$.

There have been relatively few systems for which an attempt has been made to determine the effect of Born-Oppenheimer approximation breakdown on bond dissociation energies, as there have been relatively few systems for which sufficiently accurate determinations of these energies have been made. Thus, while the effects of B-O approximation breakdown on the high resolution spectrum has been studied in detail for a number of diatomic systems, such as BeH$^+$,\textsuperscript{15} LiH,\textsuperscript{16} HBr,\textsuperscript{8} and HI,\textsuperscript{8} there are only a few systems where it has been possible to look at the effect of B-O approximation breakdown on $D_e$. These data are summarized in table 3.3. For the H$_2$ isotopomers, the bond energies used were the recommended values from a review.
### Table 3.2: Data for determining the bond dissociation energies of HCl$^+$ and DCI$^+$. Energies are in cm$^{-1}$. Notations: a, Reference 2. b, Reference 12. c, Reference 10. d, Calculated from spectroscopic constants given in reference 13 using formulae in reference 14.

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</tr>
<tr>
<td>$D_e$(HCl$^+$/DCI$^+$)</td>
<td>38861.2±1.5</td>
<td></td>
<td>38868.6±1.4</td>
<td></td>
</tr>
</tbody>
</table>

Paper by Stoicheff,$^{17}$ with the zero-point energy calculated from spectroscopic constants. For HeH$^+$, the results of a thorough analysis by Coxon and Hajigeorgiou was used.$^{18}$ Since this analysis included data from quasi-bound rotational levels just above the dissociation limit, the $D_e$ values should be accurate. In all cases, the $D_e$ value for the hydride was larger than the corresponding deuteride for all the neutral, while the reverse was true for the cations.

#### 3.3.2 Ion-pair yield spectra

The ion-pair yield spectra of HCl and DCI (normalized by VUV intensity) are shown in Figure 3.3. The spectra were recorded with an extraction field pulse of 35V/cm applied to the reaction region 2.0μs after the photodissociation. For yield spectra, there was no discrimination field pulse applied, so both threshold and prompt ions were collected, and therefore the ion intensities reflect the total cross section for the ion-pair production processes.

For both molecules, the spectra cover the range just above the ion-pair dissociation threshold. Since H$^+$ and D$^+$ were collected in the same energy range under the same experimental conditions, and we could normalize for relative HCl and DCI densities using the HCl$^+$ and DCI$^+$
Table 3.3: Summary of classical bond energies $D_e(H-X)$ for hydrides.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Isotopomer</th>
<th>$D_e(H-X)/cm^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>HCl</td>
<td>37230.8±1.1</td>
<td>Current</td>
</tr>
<tr>
<td></td>
<td>DC1</td>
<td>37227.9±0.9</td>
<td>Current</td>
</tr>
<tr>
<td>HCl$^+$</td>
<td>HCl$^+$</td>
<td>38861.2±1.5</td>
<td>Current</td>
</tr>
<tr>
<td></td>
<td>DC1$^+$</td>
<td>38868.6±1.4</td>
<td>Current</td>
</tr>
<tr>
<td>H$_2$</td>
<td>H$_2$</td>
<td>38297.25</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>38295.93</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>D$_2$</td>
<td>38294.77</td>
<td>16</td>
</tr>
<tr>
<td>$^4$HeH$^+$</td>
<td>$^4$HeH$^+$</td>
<td>16448.8</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$^4$HeD$^+$</td>
<td>16456.2</td>
<td>17</td>
</tr>
<tr>
<td>HeH$^+$</td>
<td>$^3$HeH$^+$</td>
<td>16451.2</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$^3$HeD$^+$</td>
<td>16458.6</td>
<td>17</td>
</tr>
</tbody>
</table>
Figure 3.3: Total photoion-pair yield spectra for DCI (top) and HCl (bottom). Both spectra have been normalized by VUV intensity and are on the same relative scale. Note that the relative scale for the DCI spectrum is expanded by a factor of five compared with HCl. The thresholds for a field of 35V/cm are indicated above the spectra for different initial rotational levels.
signals, the relative cross sections for the ion-pair channels were measured. The higher signal level for the HCl spectrum makes it somewhat more reliable than the DCl spectrum, but it is clear that the cross section for photoion-pair formation is significantly higher for HCl than DCl in the threshold region, in contrast with the earlier published work. Although the resonances are relatively sharp for both HCl and DCl, there is no clearly resolved rotational structure in any of the observed resonances, although the resonances do show an unresolved rotational contour, and some hints of rotational structure can be seen in a few of the resonances.

In the analysis of their data, Yencha et al relied on \textit{ab initio} calculations and multichannel quantum defect theory to assign the features they observed.\textsuperscript{4} The mechanism proposed for photoion-pair formation was a predissociation of \( ^1\Sigma^+ \) Rydberg states with an \( A^2\Sigma^+ \) ion core by the continuum of the \( V^1\Sigma^+ \) ion-pair state, and all resonances observed were assigned to this type of Rydberg states. They identified three Rydberg series in their spectra: \( n\sigma, n\rho \sigma \) and \( nd\sigma \), with the \( n\sigma \) and \( nd\sigma \) states dominating. Although \( ^1\Pi \) Rydberg states are observed in the absorption and autoionization spectra of HCl,\textsuperscript{5} Yencha et al\textsuperscript{4} argued that the heterogeneous coupling between these states and the \( V^1\Sigma^+ \) ion-pair state will be weak, and thus one would not expect to observe \( n\lambda\pi \) Rydberg states in the photoion-pair yield spectrum. To simulate the observed spectra, Yencha et al used quantum defects of 1.90, 1.55, and 0.83 for the \( so, pr\sigma \) and \( ds\sigma \) Rydberg series, which were close to the \textit{ab initio} values reported by Lefebvre-Brion et al,\textsuperscript{5} \textit{ab initio} transition moments for transitions to the \( n\lambda\sigma \) states,\textsuperscript{5} and couplings between the Rydberg states and the \( V^1\Sigma^+ \) and ionization continua estimated based on \textit{ab initio} values. The repulsive wall of the \( V^1\Sigma^+ \) state was adjusted to enhance the intensities of the higher \( v'n\sigma \) Rydberg resonances, which have small Franck-Condon factors with the \( V^1\Sigma^+ (v'=0) \) ground state. As a result, the most prominent peak in the experimental spectrum was assigned to the \( 4s\sigma(v=9) \) state, with the adjacent resonances, even the \( 4s\sigma(v=8 \text{ or } 10) \) ones, having a much lower intensity. While we agree with the general dynamics proposed by Yencha et al, our detailed assignments are somewhat different from theirs.

In the HCl spectrum shown in figure 3.3, there are several resonances that might be assigned. To come up with the assignments given for four of the possible resonances, we used the following methodology. The ionization limits for the various vibrational levels of the \( A^2\Sigma^+ \)
Chapter 3. Threshold Ion-Pair Production in HCl/DCI

state of HCl$^+$ could be calculated using the accurate value for the HCl ionization energy$^{12}$ and the term values for the vibrational levels of the $A^2\Sigma^+$ state of HCl$^+$,$^{13}$ for the levels from $v^+=0$ to 6. To extrapolate to higher levels, spectroscopic constants derived from the high resolution data were used. The rotational constants for the various Rydberg states were assumed to be the same as the constants for the corresponding ionic states, and these were derived from the spectroscopic data. Assignments were made such that the effective quantum defects for the various Rydberg states were as close as possible to those quoted in Yencha et al: 1.90 for the $s\sigma$ states, 1.56 for the $p\sigma$ states, and 0.84 for the $d\sigma$ states. To simulate the spectrum shown in figure 4.4, we assumed a linewidth of 25 cm$^{-1}$ for the $4s\sigma(8)$ and $3d\sigma(7)$ bands, and 50 cm$^{-1}$ for the $4p\sigma(3)$ and $4s\sigma(9)$ bands, and a rotational temperature of 150 K. The quantum defects given in table 3.4 were calculated from the band origins: \( \mu = n \sqrt{R/(IE - E)} \), where $IE$ is the limit for the Rydberg series determined from spectroscopy, $E$ is the fitted band origin, and $n$ is the principal quantum number of the Rydberg state. The relative intensities of the bands shown in figure 3.4 were adjusted to provide good agreement with the measured spectra. If all four Rydberg states had the same coupling with the $V^1S^+$ ion-pair state, the $3d\sigma(7)$ resonance would be the strongest, based on the \textit{ab initio} results\footnote{4} and calculated Franck-Condon factors. We had to assume an enhanced coupling (relative to that for the $3d\sigma(7)$ state) of 100x for the $4s\sigma(9)$ state, 40x for the $4s\sigma(8)$ state, and 8x for the $4p\sigma(3)$ state. This enhanced coupling is in qualitative agreement with the \textit{ab initio} results\footnote{4}, which had the coupling between the $4s\sigma$ state about 13 times stronger than the $3d\sigma$ state. Presumably, the rest of the enhancement results from larger Franck-Condon factors between the high $v$ $4s\sigma$ states and the $V^1S^+$ state, or a reduced coupling with the ionization continuum.

The agreement between the simulated and the measured spectrum in figure 3.4 is reasonable. Most of the features are reproduced, and the band contours agree with the measured spectrum. There are still features in the spectrum that are not accounted for in our simulation, to the blue of the assigned bands. The signal/noise of the spectrum makes drawing conclusions about these extra features somewhat difficult, but it would appear that other Rydberg states are contributing to the photoion-pair yield. The other possible $1\Sigma$ Rydberg state would be a $3f\sigma$ state, which has a calculated transition moment comparable to that for the $3d\sigma$ state.$^5$
Figure 3.4: Simulation (bottom) of HCl total photoion-pair yield spectrum (top). Assignments are as described in the text. The number in brackets after the Rydberg state designation is the vibrational quantum number.
Chapter 3. Threshold Ion-Pair Production in HCl/DCl

Since the quantum defect for such a state would have to be close to zero, it would have to be a highly vibrationally excited series, \( v^+ = 9 \) or higher. Other possibilities would be \( ^1\Pi \) Rydberg states, such as \( np\pi \) and \( nd\pi \) states, which have strong calculated transition moments in HCl, although they are expected to couple weakly to the ion-pair continuum.

The situation with DCl is less clear. While resonance structure is evident in the spectrum shown in figure 3.3, problems with baseline fluctuations caused by the lower signal level make it difficult to draw conclusions about the detailed structure. Within these limitations, some possible assignments for these resonances are also provided in table 3.4. The lowest energy resonance is fairly well defined, and we simulated its structure using literature spectral constants,\(^1\) a linewidth of 25 cm\(^{-1}\), and a rotational temperature of 150 K (see figure 3.5). The resulting quantum defect is the same as that for the HCl \( 4s\sigma(9) \) state, and ratio of intensities DCl[\( 4s\sigma(11) \)]/HCl[\( 4s\sigma(9) \)] was the same as the ratio of Franck-Condon factors. For the other possible resonances, there is a good indication that the bands are red-shaded, as one would expect, but again there would appear to be some extra structure beyond the four bands we have tentatively assigned. Within the limitations of this assignment, it would appear that the DCl resonances are consistent with the HCl ones.

Beyond assigning the resonances, there is a significant difference between the cross sections for HCl and DCl in the threshold region. This is at odds with the calculated results, where the cross sections at threshold were found to be nearly equal, and is also at odds with the previous experimental results, where the cross section for DCl was described as being about one-half that for HCl. The results shown in figure 3.3 indicate that there is roughly one order of magnitude difference between the maximum photoion-pair yield cross sections just above threshold for HCl and DCl. We have no explanation for this discrepancy, other than to note that in the previous experiment, there was a possibility that the Cl\(^-\) signal attributed to DCl could have been coming from the unavoidable HCl contamination. We presume that the previous work did not look at H\(^+\) or D\(^+\) signal because of the problem of higher energy second order light coming from the synchrotron, which is not a problem in our experiments.

Our assignments for HCl are also somewhat different from the previous work in that we chose to keep the quantum defects for the Rydberg resonances in a given series as close as
Figure 3.5: Simulation (bottom) of lowest energy resonance in the DCI photoion-pair yield spectrum (top).
Table 3.4: Assignment of Rydberg resonances in HCl/DCl photoion-pair yield spectra. Energies are in cm\(^{-1}\). Notation: a, Reference 4.

<table>
<thead>
<tr>
<th>Resonance</th>
<th>Assignment</th>
<th>(\mu)</th>
<th>Calculated(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>116330</td>
<td>4s(\sigma)((v=8))</td>
<td>1.8978</td>
<td>116500</td>
</tr>
<tr>
<td>117220</td>
<td>4s(\sigma)((v=9))</td>
<td>1.8962</td>
<td>117250</td>
</tr>
<tr>
<td>117100</td>
<td>4p(\sigma)((v=3))</td>
<td>1.5602</td>
<td>NA</td>
</tr>
<tr>
<td>116680</td>
<td>3d(\sigma)((v=7))</td>
<td>0.8400</td>
<td>NA</td>
</tr>
<tr>
<td>116720</td>
<td>4s(\sigma)((v=11))</td>
<td>1.8962</td>
<td>116620</td>
</tr>
<tr>
<td>116830</td>
<td>3d(\sigma)((v=9))</td>
<td>0.825</td>
<td>NA</td>
</tr>
<tr>
<td>116830</td>
<td>4p(\sigma)((v=9))</td>
<td>1.583</td>
<td>NA</td>
</tr>
<tr>
<td>117135</td>
<td>3d(\sigma)((v=10))</td>
<td>0.846</td>
<td>NA</td>
</tr>
<tr>
<td>117135</td>
<td>4p(\sigma)((v=4))</td>
<td>1.562</td>
<td>NA</td>
</tr>
<tr>
<td>117340</td>
<td>4s(\sigma)((v=12))</td>
<td>1.900</td>
<td>117320</td>
</tr>
</tbody>
</table>
possible to one another. This choice resulted in the assignment of the largest resonance to the 4pσ Rydberg state, with an \( A^2Σ^+(v=3) \) core. We should again stress that we used effective quantum defects, and did not carry out a full MQDT calculation. While some other 4pσ states were assigned in the previous work, their cross sections were small compared with the 4sσ and 3dσ resonances. However, we do not regard these differences in assignment as significant, and feel that our work points to the same basic mechanism proposed in the earlier work.

References

11. NIST Chemistry webbook: http://webbook.nist.gov/chemistry
Chapter 3. Threshold Ion-Pair Production in HCl/DCl

13. Saenger K L, Zare R N and Mathews C W 1976 J. Mol. Spectrosc. 61 216


Chapter 4
Threshold Ion-Pair Production in HF/DF

4.1 Introduction

In this chapter, the total ion-pair yield and TIPPS spectra of HF and DF will be presented. Similar to the work of HCl/DCl, TIPPS was applied to HF/DF in an attempt to investigate the Born-Oppenheimer breakdown in the ground electronic state, and to study in detail the mechanism of photoion-pair formation in HF/DF.

To investigate the Born-Oppenheimer breakdown, it is necessary to know the \( \text{D}_e \) values of both HF and DF to high accuracy. While the HF value is available from previous TIPPS work (which measured the ion-pair threshold to be 129557.7±1cm\(^{-1}\) and thus the \( \text{D}_e \) value to be 49362.2±1cm\(^{-1}\)),\(^1\) the DF value is not exactly known. In the earlier work performed by Zemke \textit{et al.}\(^2\) new hybrid potential energy curves based on experimental potentials were constructed for the \( X^1\Sigma^+ \) ground state of HF/DF. For the molecule of HF, some quasibound rotational states were observed near the dissociation threshold. The energies and linewidths of these quasibound states were calculated from the hybrid potential for three different \( \text{D}_e \) values: 49355, 49363 and 49371cm\(^{-1}\). By comparing the calculated and observed line positions and widths, the \( \text{D}_e \) value of HF was given as 49362±5cm\(^{-1}\). This value is almost the same as the one calculated from reference 1 and the current TIPPS result (49361.6±0.9cm\(^{-1}\)). For the molecule of DF, no such quasibound states was observed, and the \( \text{D}_e \) value given by Zemke \textit{et al.} (49346±8cm\(^{-1}\)) is slightly different from the result presented here (49349.2±0.9cm\(^{-1}\)).

For the mechanism of ion-pair production in HF/DF, it has been demonstrated that the ion-pair cross section in the threshold region is comparable to the photoionization cross section,
while usually the ion-pair cross section is at least two orders of magnitude lower. The high ion-pair cross section in the threshold region is due to strong resonance enhancement, which was observed in the previous work of Berkowitz et al\textsuperscript{9} and Yencha et al\textsuperscript{4}, and was confirmed in previous TIPPS work on HF.\textsuperscript{1} In the work of both Berkowitz et al and Yencha et al, the experiments were carried out at significantly lower resolution than this work, and over a broader range of photon energies. These lower resolution studies showed that for both HF and DF, the photoion-pair yield spectra are dominated by a sharp resonance just above the ion-pair threshold, followed by a series of weaker resonances at higher energies, with the cross section at 17eV about two orders of magnitude smaller than that of the initial resonance at 16.07eV. Berkowitz et al proposed an indirect mechanism,\textsuperscript{3} with ion-pairs formed through predissociation of Rydberg states converging to low vibrational levels of the HF\textsuperscript{+}/DF\textsuperscript{+}(X^2\Pi) state. In the photoionization work by Guyon et al,\textsuperscript{5} Rydberg states converging to low vibrational levels, such as $v = 1$ and 2 of both components $1/2$ and $3/2$ of the $X^2\Pi$ state were also found to contribute to the formation of HF\textsuperscript{+}/DF\textsuperscript{+}(X^2\Pi, v = 0) ion signal through resonant autoionization. Yencha et al proposed a different mechanism of ion-pair formation based on MQDT calculations,\textsuperscript{4} with the most important resonances assigned to the Rydberg states with highly vibrationally excited $A^2\Sigma^+$ ion cores. In recent work carried out at CRYRING,\textsuperscript{6} a high resolution study on resonant ion-pair formation in HF ($e^- + HF \rightarrow H^+ + F^-$) found the same resonance structure as was observed in the earlier photoionization experiments, and so no refinement of the assignments or mechanism was proposed. By applying TIPPS to HF/DF, the current study would reveal detailed information about the dynamics and mechanism about photoion-pair formation in this prototypical system.

4.2 Experimental

In this work, the molecules of HF/DF were excited by a pulsed coherent VUV light source in the photon energy range corresponding to the threshold for forming ion-pairs (15.97 to 16.16eV). The coherent VUV radiation was generated through resonant four-wave mixing $\nu = 2\nu_1 + \nu_2$ in
a pulsed supersonic Kr beam.\textsuperscript{7} One input wavelength $\nu_1$ was fixed at the 212.55nm so that $2\nu_1$ corresponds to the $4p^5p[1/2,0]$ resonance at 94093.662cm\textsuperscript{-1} in Kr.\textsuperscript{8} The other wavelength $\nu_2$ was scanned roughly from 276nm to 288nm, resulting in tunable VUV light at approximately 16eV, with a bandwidth of $\sim$1cm\textsuperscript{-1}. The VUV wavelength was calibrated by using optogalvanic spectroscopy in a hollow cathode discharge to calibrate $\nu_2$,\textsuperscript{9} and using the known Kr resonance energy for $2\nu_1$.

The VUV light was separated from the fundamental by a one meter focal length normal incidence monochromator, which also focused the VUV into an uncollimated pulsed jet of HF or DF (from a General Valve Series 9 pulsed source) about 5cm downstream from the nozzle. Both HF (U.H.P. grade, Matheson) and DF (99%, Cambridge Isotope Laboratories, Inc.) gases were used directly without further purification, and the stagnation pressure in the source was about 1bar. The pressure in the reaction chamber is $\sim$2.0x10\textsuperscript{-6}torr with the molecular beam on, with a background of $\sim$2.0x10\textsuperscript{-7}torr.

For the total ion-pair yield spectra, an extraction field pulse of 35V/cm was applied to the interaction region $2\mu$s after the laser pulse, and the positive ions were detected in a time of flight mass spectrometer. For the TIPP spectra, a discrimination field pulse of 2-6 V/cm and 1$\mu$s duration was applied 300ns after the laser to repel any ions formed from above threshold processes. At a delay time of $2\mu$s after the laser, an extraction field pulse of 35V/cm was applied to field dissociate long-lived Rydberg-like ion-pair states and extract the resulting $\text{H}^+$ or $\text{D}^+$ ions into the mass spectrometer.

4.3 Results and Discussion

4.3.1 TIPPS spectra and Bond dissociation energies of HF/DF

The TIPP spectrum of HF is shown in Figure 4.1. The spectrum covers the excitation range of $HF(X^1\Sigma_g, v'' = 0, J'' \leq 5) + h\nu \rightarrow H^+ + F^-(1\Sigma_0)$. The DF spectrum for the excitation range $DF(X^1\Sigma_g, v'' = 0, J'' \leq 6) + h\nu \rightarrow D^+ + F^-(1\Sigma_0)$ is shown in Figure 4.2.

As stated in the introduction, the primary motivation of this work is to investigate the Born-Oppenheimer breakdown in HF/DF ground state. To achieve this goal, the exact val-
Figure 4.1: TIPP spectrum of HF. A discrimination field of 2V/cm magnitude and 1μs duration was pulsed on 300ns after photoexcitation. The extraction field of 35V/cm was pulsed on 2μs after photoexcitation. Field dissociation ranges for different $J''$ are indicated on the spectrum.
Figure 4.2: TIPP spectrum of DF. A discrimination field of 2V/cm magnitude and 1μs duration was pulsed on 300ns after photoexcitation. The extraction field of 35V/cm was pulsed on 2μs after photoexcitation. Field dissociation ranges for different $J''$ are indicated on the spectrum.
ues of the ion-pair thresholds need to be measured, and then the dissociation energies can be calculated. To measure the ion-pair thresholds, a similar technique to the HCl/DCI case was applied; that is, TIPP signals were collected with different magnitudes of discrimination pulses and then extrapolation was applied to get the field-free ion-pair threshold. However, during the course of this experiment, big differences were found to exist between HF/DF and HCl/DCI. In the TIPP spectra of HCl/DCI, there is one clearly resolved peak observed for each rotational level of the ground state, and the blue edge of each peak shifts with the magnitude of the discrimination field according to expected Stark ionization behaviour (Ion-Pair Threshold \( E_{IP} = E_{IP}^0 - \alpha \sqrt{F} \), with \( 3.9 < \alpha < 6.1 \)).

The TIPP spectra of HF/DF on the other hand are dominated by strong resonance peaks, and direct transitions to the ion-pair quasi-continuum were weak. Resonance signals can be identified from the fact that their blue edges do not shift with the discrimination field. To be observed in TIPP spectra, the resonance states have to be within the narrow detection window \([E_{IP}^0 - \alpha \sqrt{F_1}, E_{IP}^0 - \alpha \sqrt{F_2}]\), where \( F_1 \) and \( F_2 \) are the magnitudes of discrimination and extraction pulses. With the current set up of pulse fields, the detection window has a range of about 30cm\(^{-1}\) and the upper edge of the window lies about 8cm\(^{-1}\) below the ion-pair threshold.

Although not obvious in the HF/DF TIPP spectra, there might be contribution of direct transition to the total TIPPS signal. To get the exact values of ion-pair thresholds, it was necessary to find those direct transitions. Figure 4.3 shows HF TIPP spectra for \( J'' = 0, 1 \) and 3 with discrimination pulses of 2, 4 and 6V/cm (direct transition is too weak compared to resonance signal for \( J'' = 2 \)). To optimize the signal-to-noise ratios, each spectrum was scanned seven times under the same field to give an average signal. Shift in the blue edge was observed for the peak that comes from direct transition. This is clearly demonstrated in the \( J'' = 1 \) spectrum: while resonance peaks are always at the same energetic positions, there is shift with electric field for signal coming from direct transition to ion-pair states. This is similar to what we observed in the TIPP spectra of H\(_2\)/D\(_2\).\(^{11}\)

From the shift of TIPPS signal, the field-free ion-pair threshold \( E_{IP}^0 \) of HF was extrapolated to be 129557.1 ± 0.9, 129557.3 ± 0.9, and 129556.9 ± 0.9cm\(^{-1}\) for \( J'' = 0, 1 \) and 3 (see Figure 4.4). An average value of 129557.1 ± 0.9cm\(^{-1}\) was obtained for the ion-pair threshold of HF. Similar
Table 4.1: Energetic results from HF/DF TIPP spectra. Energies are in cm$^{-1}$. There are two major uncertainties for the $E_{IP}^0$ values: ±0.3cm$^{-1}$ for wavelength calibration and ±0.8cm$^{-1}$ for extrapolation to zero electric field. $D_0$ is the bond dissociation energy from $v'' = 0$, and $D_e$ is the classical BDE.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>DF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{IP}^0$</td>
<td>129557.1 ±0.9</td>
<td>130135.0 ±0.9</td>
<td>Current</td>
</tr>
<tr>
<td>$D_0$</td>
<td>47310.8 ±0.9</td>
<td>47858.8 ±0.9</td>
<td>Current</td>
</tr>
<tr>
<td>$D_e$</td>
<td>49361.6 ±0.9</td>
<td>49349.2 ±0.9</td>
<td>Current</td>
</tr>
<tr>
<td>$D_e$</td>
<td>49362 ±5</td>
<td>49346 ±8</td>
<td>2</td>
</tr>
</tbody>
</table>

measures were taken for DF (see Figures 4.5 and 4.6), and the ion-pair threshold value was determined to be 130135.0 ± 0.9cm$^{-1}$. These results are given in Table 4.1. The HF ion-pair threshold agrees with the previous measurement, while the DF value is reported for the first time.

Combined with the ionization energy of H(D)$^{12}$ and electron affinity of F,$^{13}$ the bond dissociation energies $D_0$ of HF/DF could be determined. Furthermore, with the zero point energies being available (2050.771cm$^{-1}$ for HF and 1490.304cm$^{-1}$ for DF),$^{14}$ we can also determine the classical bond dissociation energies of these two molecules. Our $D_e$ value for HF is very close to the fitting result of Zemke et al, while the $D_e$ value for DF is a few wavenumbers higher than their result.$^2$

To provide a more accurate measurement of Born-Oppenheimer breakdown effects, a comparison of HF and DF TIPPS recorded under identical conditions using a mixed beam of HF and DF gave the difference in classical bond dissociation energy of $D_e(H-F) - D_e(D-F) = 12.4±0.5$cm$^{-1}$, with the error limit coming from the ±0.3cm$^{-1}$ uncertainty in VUV calibration of the two spectra. Our result provides a benchmark for studying these effects in this simple system.
Figure 4.3: HF TIPP spectra for $J''=0$, 1 and 3 with discrimination fields of 2 (red), 4 (green) and 6V/cm (blue).
Figure 4.4: Extrapolation to determine the field-free ion-pair threshold for HF. The $J''=1,3$ data has been shifted up in energy by $BJ''(J'' + 1) - D(J''(J'' + 1))^2$. 

Chapter 4. Threshold Ion-Pair Production in HF/DF
Figure 4.5: DF TIPP spectra for $J''=0$ and 2 with discrimination fields of 2 (red), 4 (green) and 6V/cm (blue).
Figure 4.6: Extrapolation to determine the field-free ion-pair threshold for DF. The $J''=2$ data has been shifted up in energy by $BJ''(J'' + 1) - D(J''(J'' + 1))^2$. 
4.3.2 Total ion-pair yield spectra and mechanism of ion-pair formation

The total ion-pair yield spectra of HF/DF covering the same energy ranges as the TIPP spectra (Figure 4.1 and 4.2) are shown in Figures 4.7 and 4.8. As can be seen, both spectra are dominated by some sharp resonances. At energy positions where the ion-pair yield signal is strong, such as 129560cm$^{-1}$ for HF and 130120cm$^{-1}$ for DF, the yield of H$^+$/D$^+$ is comparable with that of parent ion HF$^+$/DF$^+$. This contrasts with the normal case, where ion-pair yield is orders of magnitude smaller than the parent ion yield.

Although they cover much shorter energy ranges than the literature work\textsuperscript{4} (15.97-16.09eV compared to 16.0-16.9eV for HF), our high-resolution spectra show much more detail of the signal in the threshold region (roughly 16.0-16.1eV). While there is only one single intense peak in the threshold region in the previous published work,\textsuperscript{4} there are tens of sharp resonance peaks observed in our current spectrum. By analyzing the positions of those sharp resonances, the mechanism of HF/DF ion-pair formation in the threshold region could be studied in detail.
Figure 4.7: Total ion-pair yield spectrum of HF. An extraction field of 35V/cm was pulsed on 2μs after photoexcitation. No discrimination field was applied. Assignments of the resonances are labelled as $N^+ - J'' (J'')$. 
Figure 4.8: Total ion-pair yield spectrum of DF. An extraction field of 35V/cm was pulsed on 2μs after photoexcitation. No discrimination field was applied. Assignments of the resonances are labelled as $N^*$.J$^\prime$ (J$^\prime$).
4.3.2.1 Assignment of resonance peaks

By using the resonances observed in the TIPP spectra, we can determine the energy levels of some resonance peaks observed in the total ion-pair yield spectra. Because our current work provides an accurate energy for the ion-pair dissociation threshold, we can provide definitive assignments for the \( J'' \) for any resonances that are observed in TIPPS. This is based on the fact that any resonances observed in TIPPS result from optically allowed transitions to states which then couple to the pseudo-continuum of the ion-pair states lying just below the dissociation limit. Since the ion-pair threshold for HF (or DF) is at a fixed energy, the excitation energy range that reaches this fixed energy band is distinct for all \( J'' \) levels above \( J''=1 \) (there is a small overlap between \( J''=0 \) and \( J''=1 \) ranges for the field strengths used). From the resonances observed in TIPPS, one can obtain the energies of the upper states relative to \( J''=0 \) simply by adding the initial rotational energy to the photon energy for the observed resonance. These energies are given in Table 4.2. Due to the asymmetric shape and relatively large width (FWHM up to 5cm\(^{-1}\)) of the resonance signal, and the \( \pm 0.3 \)cm\(^{-1}\) uncertainty in VUV calibration, the values given in Table 4.2 have an uncertainty of about \( \pm 0.5 \)cm\(^{-1}\). Therefore, final states within a difference of less than 1cm\(^{-1}\) are regarded as the same resonance.

To proceed further with the assignment, we can start with the DF spectrum, which has fewer resonances than that of HF. One can immediately see that there are two levels in DF that are seen in several transitions in Table 4.2: one at 130104cm\(^{-1}\), the other one at 130123cm\(^{-1}\). Combining with some other resonance peaks in the total ion-pair yield spectrum, we obtained a sequence of excited state levels with energies of 130104, 130123, 130154, 130198 and 130253cm\(^{-1}\). This sequence of levels corresponds closely to what one would expect for the five lowest rotational levels of one DF\(^+\)\(X^2\Pi_{1/2}\) state, with core rotational number \( N^+ \) equals 0 to 4. This is based on the approximation that Rydberg states have the same rotational energy pattern as the pure ion-core.

For an electronic state of \( ^2\Pi_{1/2} \), the rotational energy levels could be expressed as:\(^{15}\)

\[
E_{1/2} = -\frac{A_{eff}}{2} + B_{1/2eff}(J + \frac{1}{2})^2 - 1 
\]  

(4.1)
Table 4.2: Resonances seen in TIPP spectra of HF and DF, and corresponding final state energies. Energies are in cm\(^{-1}\). Error in position is about ±0.5 cm\(^{-1}\). Final state energy is relative to \(J''=0\). Notation: \(ov\) indicates a resonance that lies in the energy range of overlap between \(J''=0\) and \(J''=1\).

<table>
<thead>
<tr>
<th>(J'')</th>
<th>Resonance (\text{cm}^{-1})</th>
<th>Final State (\text{cm}^{-1})</th>
<th>(J'')</th>
<th>Resonance (\text{cm}^{-1})</th>
<th>Final State (\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>130123.6</td>
<td>130123.6</td>
<td>0</td>
<td>129526.9</td>
<td>129526.9</td>
</tr>
<tr>
<td>(0^v)</td>
<td>130104.0</td>
<td>130104.0(^v)</td>
<td>1</td>
<td>129485.0</td>
<td>129526.1</td>
</tr>
<tr>
<td>(1^v)</td>
<td>130104.0</td>
<td>130125.7(^v)</td>
<td>1</td>
<td>129471.6</td>
<td>129512.7</td>
</tr>
<tr>
<td>1</td>
<td>130081.4</td>
<td>130103.1</td>
<td>2</td>
<td>129416.9</td>
<td>129540.2</td>
</tr>
<tr>
<td>2</td>
<td>130058.8</td>
<td>130123.9</td>
<td>2</td>
<td>129403.3</td>
<td>129526.6</td>
</tr>
<tr>
<td>2</td>
<td>130039.0</td>
<td>130104.1</td>
<td>3</td>
<td>129292.8</td>
<td>129539.2</td>
</tr>
<tr>
<td>3</td>
<td>129989.5</td>
<td>130119.7</td>
<td>3</td>
<td>129284.0</td>
<td>129530.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>129131.4</td>
<td>129541.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>129126.5</td>
<td>129536.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>129119.8</td>
<td>129530.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>129112.1</td>
<td>129522.4</td>
</tr>
</tbody>
</table>
where $A_{e ff} = A - 2B$ is the effective spin-orbit splitting between the two spin components $^{2}\Pi_{3/2}$ and $^{2}\Pi_{1/2}$, $B_{1/2 e ff} = B(1 - B/A)$ is the effective rotational constant, and $J$ has the value of $N^+ + 1/2$ for $^{2}\Pi_{1/2}$ state. Therefore, the energy gap between adjacent rotational levels has a pattern of $3:5:7:9\ldots$ (the corresponding $^{2}\Pi_{3/2}$ state has a pattern of $5:7:9:11\ldots$ starting from $N^+ = 0$).

Theoretically the rotational structure for a Rydberg state with a $^{2}\Pi_{1/2}$ core should be described in Hund’s case (c) or (e).\textsuperscript{16} But if we approximate the low $N^+$ rotational structure of the Rydberg state to be similar to that of the ion core, the Rydberg states converging to $^{2}\Pi_{1/2}$ ion core would also have the pattern of $3:5:7:9\ldots$. That is why the sequence of $130104\text{cm}^{-1}$ etc. was assigned as Rydberg states with $^{2}\Pi_{1/2}$ ion core.

As can be seen in Figure 4.8 a consistent assignments can be arrived at for a number of observed resonances as transitions to the above sequence, with two strong peaks at $130123$ and $130133\text{cm}^{-1}$ each assigned to two different possible transitions. The overall results are also tabulated in Table 4.3.

For the spectra of HF, similar measures were taken to do the analysis, but the assignment is more complicated due to the presence of more structure in both the TIPP and total yield spectra. Furthermore, due to the relatively large rotational constant of HF$^+$ ion ($B_e = 17.577\text{cm}^{-1}$ for $X^2\Pi_{1/2}$ electronic state)\textsuperscript{17}, it is unlikely that there are two resonances observed in TIPP spectrum belonging to the same rotational sequence of the ion, considering the narrow detection window ($\sim 30\text{cm}^{-1}$) used in the experiment. From the resonances listed in Table 4.2, we can pick up the two values of $129526\text{cm}^{-1}$ and $129540\text{cm}^{-1}$, both of which were observed for a few transitions in TIPP spectrum. However, when looking for corresponding peaks at the same positions in the total ion-pair yield spectrum, for the resonance of $129526\text{cm}^{-1}$, only a transition from $J'' = 2$ was found at $129404\text{cm}^{-1}$. This renders a lot of uncertainty for the assignment of this resonance. For the resonance of $129540\text{cm}^{-1}$, a few transitions from different $J''$ levels were observed in the total yield spectrum ($129417\text{cm}^{-1}$ from $J'' = 2$, $129294\text{cm}^{-1}$ from $J'' = 3$, and $129130\text{cm}^{-1}$ from $J'' = 4$). To assign this resonance to one rotational sequence of Rydberg states converging to a certain vibrational level of HF$^+$ ion, one can assume that the $129540\text{cm}^{-1}$ resonance has core rotational number $N^+$, then one looks for higher rotational lev-
Table 4.3: List of predicted and observed resonances in DF ion-pair yield spectrum. Energies are in cm$^{-1}$, with predicted values followed by observed resonances in brackets. Notation: $sh$ indicates observed line is a shoulder.

<table>
<thead>
<tr>
<th>$J''\backslash N^+\cdot J''$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>130104</td>
<td>130123</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(130104)</td>
<td>(130123)</td>
</tr>
<tr>
<td>-1</td>
<td>130082</td>
<td>130101</td>
<td>130132</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(130081)</td>
<td>(130104$sh$)</td>
</tr>
<tr>
<td>0</td>
<td>130039</td>
<td>130058</td>
<td>130089</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(130038)</td>
<td>(130059)</td>
</tr>
<tr>
<td>1</td>
<td>129993</td>
<td>130024</td>
<td>130068</td>
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<tr>
<td></td>
<td></td>
<td>(129992)</td>
<td>(130024)</td>
</tr>
<tr>
<td>2</td>
<td>129937</td>
<td>129981</td>
<td>130036</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(129938)</td>
<td>(129981)</td>
</tr>
</tbody>
</table>
levels of \( N^++1, N^++2 \) etc. (lower rotational levels such as \( N^+-1 \) cannot be observed since they lie below the detection window). The energetic values of these higher levels could presumably be calculated based on the already known \( B_e \) value of HF\(^+\) ion. Then we can look for transitions to those higher levels. The idea is that since a few transitions were observed corresponding to the resonance at 129540 cm\(^{-1}\), it is reasonable to expect similar transitions to the next resonance \( N^++1 \). From this another rotational level was derived, with energy at 129669 cm\(^{-1}\) (with transitions of 129424 cm\(^{-1}\) from \( J''=3 \), 129259 cm\(^{-1}\) from \( J''=4 \), and 129054 cm\(^{-1}\) from \( J''=5 \)). There are no resonances with even higher core rotational number obtained, perhaps due to the low cross sections associated with those higher resonances, or relaxation from those high rotational resonances. If the two levels at 129540 cm\(^{-1}\) and 129669 cm\(^{-1}\) were assumed to belong to the same rotational sequence, they would have core rotational numbers of 3 and 4 according to their energy gap.

Since only two resonances were found in the above sequence, the assignments are not as convincing as the DF sequence. The other issue is that many strong transitions in HF ion-pair yield spectrum remain unassigned. To go further with the assignment, one need to look for resonances not observed in the TIPP spectrum (refer to Table 4.2). With careful calculation which started from the attempt to assign some of the most intense resonance peaks, such as 129579, 129560 and 129495 cm\(^{-1}\) as transitions to the same sequence, another sequence of resonances was derived, with energy levels as 129579, 129618, 129683 and 129774 cm\(^{-1}\) (\( N^+=0, 1, 2 \) and 3). Many of the strong peaks in the total yield spectrum can be assigned as transitions to this sequence, with 129579 cm\(^{-1}\) identified as transition Q(0) or Q(1), 129560 cm\(^{-1}\) as Q(2), 129495 cm\(^{-1}\) as P(2) and so on. The detailed assignment can be seen in Figure 4.7 and the results are also given in Table 4.4. Some other strong peaks in HF yield spectrum which are not related to this sequence can be identified as transitions to resonances listed in Table 4.2, with the peak 129472 cm\(^{-1}\) identified as 129513 cm\(^{-1}\) \( \leftarrow J''=1 \), 129389 cm\(^{-1}\) as 129513 cm\(^{-1}\) \( \leftarrow J''=2 \), 129404 cm\(^{-1}\) as 129527 cm\(^{-1}\) \( \leftarrow J''=2 \).

So far three rotational sequences of HF\(^+\)/DF\(^+\) Rydberg states have been assigned. They all have ion core at the \( X^2\Pi_{1/2} \) state (energies of corresponding Rydberg states with an \( X^2\Pi_{3/2} \) core are \(~290 \) cm\(^{-1}\) lower\(^5\) and thus below threshold for producing ion-pairs, see Table 4.5).
Table 4.4: List of predicted and observed resonances in HF ion-pair yield spectrum. Energies are in cm$^{-1}$, with predicted values followed by observed resonances in brackets. Notation: $sh$ indicates observed line is a shoulder.

<table>
<thead>
<tr>
<th>$J'' \backslash N'^+ - J''$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>129579</td>
<td>129618</td>
<td>129683</td>
</tr>
<tr>
<td></td>
<td>(129579)</td>
<td>(129616$sh$)</td>
<td>(129682)</td>
</tr>
<tr>
<td>1</td>
<td>129538</td>
<td>129577</td>
<td>129642</td>
</tr>
<tr>
<td></td>
<td>(sh)</td>
<td>(129579$sh$)</td>
<td>(sh)</td>
</tr>
<tr>
<td>2</td>
<td>129456</td>
<td>129495</td>
<td>129560</td>
</tr>
<tr>
<td></td>
<td>(129456)</td>
<td>(129495)</td>
<td>(129560)</td>
</tr>
<tr>
<td>3</td>
<td>129372</td>
<td>129437</td>
<td>129528</td>
</tr>
<tr>
<td></td>
<td>(129371)</td>
<td>(129436)</td>
<td>(sh)</td>
</tr>
<tr>
<td>4</td>
<td>129273</td>
<td>129364</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(129274)</td>
<td>(129364)</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4. Threshold Ion-Pair Production in HF/DF

The overall agreement between calculated and observed peak positions is very good; therefore we believe it is reasonable to have the above sequences, especially the two that involve 4 or 5 energy levels. It is the first time that such kind of rotational sequences have been derived as the intermediate resonance states in ion-pair formation processes. At the same time we are aware that at this point it is impossible to calculate every resonance level and assign it to one sequence, due to the large number of resonances present in our spectrum and the lack of enough high resolution data for the HF/DF excited states. But as our purpose is to understand the mechanism for ion-pair formation in HF/DF, the current tentative assignment will be useful in providing some insight about this process.

From the energetic pattern of $^2\Pi_{1/2}$ state (refer to equation 4.1), the values of effective rotational constants $B_{\text{eff}}$ of the three rotational sequences could be calculated. For the two sequences with 4 or 5 levels, $B_{\text{eff}}$ values were calculated to be $6.3\pm0.1\text{cm}^{-1}$ (DF sequence) and $13.0\pm0.1\text{cm}^{-1}$ (HF sequence), respectively.

Furthermore, if the effective rotational constant of the Rydberg states is assumed to be about the same as the ion core, one can calculate the vibrational level of the ion core. For HF sequence, the closest effective rotational constant of HF$^+$ ion core is $12.9\text{cm}^{-1}$ ($v^+=6$). For DF sequence, the closest effective rotational constant of DF$^+$ ion core is $6.2\text{cm}^{-1}$ ($v^+=10$). The spectroscopic constants of HF$^+$ are available in literature,\textsuperscript{18} while those of DF$^+$ were derived from HF$^+$ and corrected for the change in reduced mass.\textsuperscript{15}

From Table 4.5 one can see that for both HF and DF sequences identified in our ion-pair spectra, very similar $B_{\text{eff}}^+$ values could be found and those $B_{\text{eff}}^+$ values correspond to HF$^+$/DF$^+$(X$^2\Pi_{1/2}$) at high vibrational levels. However, it is not certain whether or not we can simply assign those identified sequences to Rydberg states with HF$^+$/DF$^+$(X$^2\Pi_{1/2}$) ion at those high vibrational levels. At this moment it is not clear how close the effective rotational constants are for Rydberg states and pure ion core, especially when the Rydberg electron has a low principal quantum number. Actually if the value of $B_{\text{eff}}^+$ is not that close to $B_{\text{eff}}$, one would get a very different match. For HF, if $\pm2\text{cm}^{-1}$ difference exists between the two values, the vibrational level of the pure ion core can vary from $v^+=4$ ($B_{\text{eff}}^+=14.5\text{cm}^{-1}$) to $v^+=8$ ($B_{\text{eff}}^+=11.4\text{cm}^{-1}$).
Table 4.5: Energetics of HF/DF and assignment of Rydberg sequences in the total ion-pair yield spectra. Energies are in cm$^{-1}$ and relative to HF/DF($X^1\Sigma, v'' = 0, J'' = 0$). The HF ionization energy to form HF$^+X^2\Pi_{1/2}$ was calculated from the $X^2\Pi_{3/2}$ limit. DF ionization energies were derived from HF energetics using the Born-Oppenheimer approximation for the HF/DF($X^1\Sigma$) and HF$^+/DF^+(X^2\Pi)$ potential curves, and therefore are not so precise.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>DF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$$-$F$^-$ / D$^+$$-$F$^-$</td>
<td>129557.1 ± 0.9</td>
<td>130135.0 ± 0.9</td>
<td>Current</td>
</tr>
<tr>
<td>HF$^+$/DF$^+(X^2\Pi_{3/2}, v^+=0, N^+=0)$</td>
<td>129422.4 ± 1</td>
<td>129567</td>
<td>19</td>
</tr>
<tr>
<td>HF$^+$/DF$^+(X^2\Pi_{1/2}, v^+=0, N^+=0)$</td>
<td>129700.7</td>
<td>129825</td>
<td></td>
</tr>
<tr>
<td></td>
<td>129579</td>
<td>130104</td>
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</tr>
<tr>
<td></td>
<td>129618</td>
<td>130123</td>
<td></td>
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<tr>
<td>Observed Rydberg sequence</td>
<td>129683</td>
<td>130154</td>
<td></td>
</tr>
<tr>
<td></td>
<td>129774</td>
<td>130198</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>130253</td>
<td></td>
</tr>
<tr>
<td>Assigned ion core</td>
<td>$X^2\Pi_{1/2}$, $N^+=0$</td>
<td>$X^2\Pi_{1/2}$, $N^+=0$</td>
<td></td>
</tr>
<tr>
<td>$B_{eff}$</td>
<td>13.0±0.1</td>
<td>6.3±0.1</td>
<td></td>
</tr>
<tr>
<td>Closest $B_{eff}^+$</td>
<td>12.9</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Ion core with closest $B_{eff}^+$</td>
<td>$X^2\Pi_{1/2}$, $v^+$ = 6</td>
<td>$X^2\Pi_{1/2}$, $v^+$ = 10</td>
<td></td>
</tr>
<tr>
<td>$n^*$</td>
<td>2.71</td>
<td>2.51</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.6: Franck-Condon factors for transitions $\text{HF}^+/\text{DF}^+(X^2\Pi_{1/2}, v^+) \leftarrow \text{HF/DF}(X^1\Sigma, v''=0)$.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$v^+=0$</th>
<th>$v^+=1$</th>
<th>$v^+=2$</th>
<th>$v^+=3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.674</td>
<td>0.253</td>
<td>0.060</td>
<td>0.011</td>
</tr>
<tr>
<td>DF</td>
<td>0.589</td>
<td>0.294</td>
<td>0.090</td>
<td>0.022</td>
</tr>
</tbody>
</table>

If it is true that Rydberg states with $\text{HF}^+/\text{DF}^+(X^2\Pi_{1/2})$ at high vibrational levels are more favorable than low vibrational levels ($v^+=0$ or 1) as the resonance states, it would be similar to the resonance assignment in HCl/DC1 ion-pair yield spectra. It could also explain the difference between HF ion-pair yield spectrum and the HF photoionization spectrum in the same energy range (see Figure 4.9). While most of the strong resonances in ion-pair spectrum could be found in the ionization spectrum, the latter spectrum also has many other resonances which may come from Rydberg states with ion core at low vibrational levels.

Unfortunately, the above analysis is not supported by calculations. To illustrate this point and to further understand the ion-pair dynamics of HF/DF, two calculations were performed to see what kind of vibrational levels of $\text{HF}^+/\text{DF}^+(X^2\Pi_{1/2})$ are favored as the intermediate states, i.e., what vibrational levels of $\text{HF}^+/\text{DF}^+$ ion are more easily accessed from the HF/DF ground states and strongly coupled to the ion-pair states. The first calculation used the computation program Level 7.5\textsuperscript{20} to calculate the Franck-Condon factors to $\text{HF}^+/\text{DF}^+$ ion at different vibrational levels. The results show that for both HF and DF, the relative cross section drops quickly as $v^+$ increases. This agrees with experimental results in HF/DF photoionization spectra.\textsuperscript{5,19}

A second calculation was performed to see which vibrational levels cross the ion-pair curve. The spectroscopically determined RKR data\textsuperscript{21} of $\text{HF}(B^1\Sigma)$ ion-pair state was fitted with a Rittner model potential and extended to shorter internuclear distance using equation:\textsuperscript{22}

$$V_{MX}^{\text{Ritt}}(R) = A_M X e^{R/\rho_M X} - R^{-1} - [(a_M + a_X)/2R^4] - (a_M a_X/R^7) - (C_M X/R^6)$$ (4.2)

The fitting result (see Figure 4.10) shows that the ion-pair curve is likely to cross the $\text{HF}^+/\text{DF}^+ X^2\Pi$ curve at low vibrational levels, such as $v^+=0$ or 1. While not certain, such
Figure 4.9: Comparison of H+ and HF+ in the threshold region.
crossing indicates that low vibrational states of HF$^+/DF^+(X^2\Pi)$ have better chance to couple to the ion-pair states.

If it is true that Rydberg states with ion core HF$^+/DF^+(X^2\Pi)$ at low vibrational levels are critical in making ion-pairs, it would explain the high intensity of the ion-pair signal. As mentioned earlier, the ion-pair signal of HF/DF is comparable to the parent ion near the threshold while usually ion-pair signals are orders of magnitude lower. This might be due to the very close values of ion-pair thresholds and ionization thresholds (for HF, the ion-pair threshold is 16.06eV while the ionization threshold is 16.04eV$^{19}$). Within such a close energy range, there would be a large number of Rydberg resonances of HF$^+/DF^+(X^2\Pi)$ ion at low vibrational levels available to couple to the ion-pair states and thus greatly enhance the ion-pair signal.

It would also give us some hints about the relatively different pattern between the total ion-pair yield spectra of HF and DF (see Figures 4.7 and 4.8). The HF ion-pair yield spectrum has some rotational branches, i.e., the yield signal seems to appear at the energy roughly corresponds to the detection window for each ground rotational state in TIPP spectrum. This is obvious for $J'' \geq 3$ (signal is strong and overlapped for $J''=0, 1$ and 2). There is no such pattern shown in DF ion-pair yield spectrum. This is interesting and possibly indicates that HF and DF do not follow exactly the same mechanism in making ion-pairs. One explanation is that while HF ion-pair threshold lies roughly halfway between the energy limits of HF$^+(X^2\Pi_{3/2},v^+=0)$ and HF$^+(X^2\Pi_{1/2},v^+=0)$, the DF ion-pair threshold is about 300cm$^{-1}$ above the DF$^+(X^2\Pi_{1/2},v^+=0)$ limit (see Table 4.5). This means that while energetically Rydberg states converging to HF$^+(X^2\Pi_{1/2},v^+=0)$ can couple to ion-pair states, corresponding states in DF cannot. This would explain the different patterns between HF and DF ion-pair yield spectra if Rydberg states with HF$^+/DF^+(X^2\Pi)$ ion at low vibrational levels are favored as the intermediate states in making ion-pairs. If high vibrational levels ($v^+ \geq 3$) are favored, we would not expect such big difference between the HF and DF spectra.
Figure 4.10: HF Potential curves. The dashed vertical lines represent the Franck-Condon region for transitions from the HF ground vibrational state. The star symbols are the RKR data of the $B^{1}\Sigma^{+}$ ion-pair state and the imposed solid line is the fitted Rittner potential.
4.3.2.2 Comparison with previous assignments

While our total ion-pair yield spectra agree with previous work, in that the ion-pair formation in HF/DF is greatly enhanced by resonance states, there was no indication of anything but a single resonance at threshold in any of the previous work. As a result, all previous analyses were based on a single Rydberg resonance dominating the ion-pair yield spectrum.

In the initial work by Guyon et al of almost thirty years ago, two resonances were observed near HF ion-pair threshold. The two low resolution (about 20 meV, or 160 cm\(^{-1}\)) resonances roughly correspond the energy ranges [129100, 129350] cm\(^{-1}\) and [129400, 129650] cm\(^{-1}\) in our spectrum. They were assigned to Rydberg states with ion core at \(X^2\Pi_{3/2}, v^+ = 1\) and \(X^2\Pi_{1/2}, v^+ = 1\), respectively, and principal quantum number of Rydberg \(n=6\). The separation between those two resonances matches well with HF\(^+\) spin-orbit splitting which is about 290 cm\(^{-1}\). But their assignment would not be able to explain the better resolved resonance structures in our high resolution spectrum. For example, there are many sharp resonance peaks in the range of [129400, 129650] cm\(^{-1}\). If they were all from transitions to some resonances converging to the same vibronic state, all those peaks in that 250 cm\(^{-1}\) range would have to be related to each other by the same rotational sequence. This is not what we observed. Since the present results show many sharp resonances in the threshold region, one can hope to provide a more definitive assignment for the Rydberg states involved in photoion-pair formation through an analysis of the observed rotational structure.

In the work by Yencha et al, the strongest resonances near ion-pair threshold were assigned to Rydberg states with \(A^2\Sigma^+\) ion core at high vibrational levels (\(v^+ = 17, 18\) for HF and \(v^+ = 22, 23, 24\) for DF). This is different from our assignment. Actually, the \(\omega_{e\chi_e}\) value used in their work (20 cm\(^{-1}\)) is rather different from the value given in reference 5 (88.4 cm\(^{-1}\)) and this would lead to some miscalculation of the vibrational levels of the \(A^2\Sigma^+\) state. Furthermore, Rydberg sequence with \(A^2\Sigma^+\) ion-core has a rotational pattern of 2:4:6:... , and that is not what was observed in the current study.

To summarize the discussion on HF/DF ion-pair production mechanism, we have observed strong resonances in both TIPP and total yield spectra, and the energy levels of many resonances
were calculated and three rotational sequences were derived from those resonances. All of them were assigned to Rydberg states with HF$^+/DF^+(X^2\Pi_{1/2})$ ion cores. The effective rotational constants of those sequences were found to be close to that of pure HF$^+/DF^+(X^2\Pi_{1/2})$ ion core at high vibrational levels. However, other calculations show that Rydberg states with HF$^+/DF^+(X^2\Pi)$ ion core at low vibrational levels are more favored as the intermediate states in HF/DF ion-pair production.

References

Chapter 4. Threshold Ion-Pair Production in HF/DF


Chapter 5
Threshold Ion-Pair Production in HCN

5.1 Introduction

In the work of the last two chapters, it has been demonstrated that by applying TIPPS to diatomic molecules, the ion-pair thresholds could be accurately measured and the ion-pair formation mechanism in the threshold region could be investigated in detail. It is therefore interesting to know whether this technique can also be applied to more complex system, such as triatomic molecules. For triatomic molecules, the ion-pair product has one fragment containing two atoms, and this fragment could be in different rovibronic states. Therefore, the spectra of triatomic molecules are expected to be more complicated than diatomic molecules. In the work of this chapter, TIPPS was applied to the molecule of HCN.

Previously TIPPS has been applied to another triatomic molecule H₂S, for both channels H⁺ + SH⁻,¹,² and H⁻ + SH⁺.² Ion-pair thresholds in both processes have been measured, and they yielded the same value for the bond dissociation energy $D_0$(H-SH). The results revealed different dynamics between the two ion-pair channels. While the SH⁻ fragment in the first channel was formed at low rotational levels ($J \leq 4$), the SH⁺ fragment in the second channel could be vibrationally excited with comparable cross sections for $v'=0$ and $v'=1$.

For photoion-pair production in HCN, the first yield spectrum was measured by Berkowitz et al almost forty years ago.³ Their work was carried out at significantly lower resolution (~0.01eV or 100cm⁻¹) and over a much broader range of photon energies (70-83nm or 14.94-17.71eV). Both H⁺ and CN⁻ ion signal were monitored, and the two spectra showed the same structure within experimental uncertainty. As photon energy increases the ion intensity rises to the max-
Chapter 5. Threshold Ion-Pair Production in HCN

imum roughly at 78nm (or 15.9eV) and then gradually decreases. From the offset of the spectra they obtained the value of HCN ion-pair threshold: 15.18±0.02eV. Their spectra also indicated a mechanism of predissociative ionization, i.e., the ion-pair process goes through excited states of HCN, rather than direct transition to the ion-pair continuum.

Although there is no recent work performed on the ion-pair production process in HCN, there has been a large number of work done on the dissociation of HCN into neutral products with CN fragment in ground or excited electronic states. The work most related to us are those giving the value of bond dissociation energy $D_0$(H-CN). Using the technique of H(D) atom photofragment translational spectroscopy, Morley et al have measured the $D_0$(H-CN) value. They recorded the translational energy spectra of the H atoms resulting from photolysis of jet-cooled HCN molecules at 121.6nm. Their spectra displayed structure which provided information about the energy disposal into the rovibrational states of the CN fragment. They found out that fragmentation into H + CN(A, $v' = 0$) is the dominant dissociation channel, while there was no CN(X) product observed. Their spectra showed the energetic pattern of the CN(A, $v' = 0$) fragment for different rotational levels. From that they measured the dissociation energy of HCN into H + CN(A, $v' = 0$, $N' = 0$), which was then used to calculate the dissociation energy into H + CN(X, $v' = 0$, $N' = 0$). They reported the $D_0$(H-CN) to be 43740 ± 150cm$^{-1}$, with the uncertainty related mainly to the uncertainty in the measured TOF distance. Later on this value was improved by Cook et al using similar technique. They reported a value of 43710±70cm$^{-1}$. By applying our high resolution technique of TIPPS to the HCN molecule, we were hoping to provide a more accurate value of $D_0$(H-CN), and some insight into ion-pair formation in the threshold region.

5.2 Experimental

The HCN molecules were excited by a pulsed coherent VUV light source in the photon energy range corresponding to the threshold for forming ion-pairs (15.18±0.02eV). The coherent VUV radiation was generated through resonant four-wave mixing $\nu = 2\nu_1 + \nu_2$ in a pulsed supersonic
Kr beam. One input wavelength $\nu_1$ was fixed at $\sim 212.55$ nm so that $2\nu_1$ corresponds to the $4p^55p[1/2,0]$ resonance at $94093.662$ cm$^{-1}$ in Kr. The other wavelength $\nu_2$ was scanned around $350$ nm, resulting in a tunable VUV light beam at approximately $15.2$ eV, with a bandwidth of $\sim 1$ cm$^{-1}$. The VUV wavelength was calibrated by using optogalvanic spectroscopy in a hollow cathode discharge to calibrate $\nu_2$, and using the known Kr resonance energy for $2\nu_1$. The actual value of $2\nu_1$ can be slightly different from the tabulated value $94093.662$ cm$^{-1}$ due to power broadening of the Kr resonance. There is also a small uncertainty in the calibration of $\nu_2$ due to the oscillations of the grating drive in the dye laser. These combined uncertainties give an estimated error of $\pm 0.3$ cm$^{-1}$ in the VUV calibration.

The VUV light was separated from the fundamental by a one meter focal length normal incidence monochromator, which also focused the VUV into an uncollimated pulsed jet of HCN (from a General Valve Series 9 pulsed source) about $5$ cm downstream from the nozzle. The HCN gas (CP grade, Tex-La Gases Inc.) was used directly without further purification, and the stagnation pressure in the source was about $1$ bar. The pressure in the reaction chamber was $\sim 2.0 \times 10^{-6}$ torr with the molecular beam on, with a background of $\sim 2.0 \times 10^{-7}$ torr.

For the total ion-pair yield spectrum, an extraction field pulse of $7$ V/cm was applied to the interaction region $2\mu s$ after the laser pulse and the H$^+$ ions were detected with a time of flight mass spectrometer. For the TIPP spectrum, a discrimination field pulse of $2$ V/cm and $1\mu s$ duration was applied $300$ ns after the laser was fired to repel any ions formed from above threshold processes. At a delay time of $2\mu s$ after the laser, an extraction field pulse of $7$ V/cm was applied to field dissociate long-lived Rydberg-like ion-pair states and extract the resultant H$^+$ ions into the mass spectrometer.

### 5.3 Results and Discussion

The total ion-pair yield spectrum of HCN normalized by the VUV intensity is shown in Figure 5.1. The spectrum covers the energy range roughly from $121800$ to $123200$ cm$^{-1}$, corresponding to the rising edge of HCN ion-pair yield spectrum in reference 3. There are no sharp resonances
present in this spectrum, but it does show some relatively broad structures, which according to reference 3 might be due to some vibrational bands of excited states of HCN. At energy positions where the ion-pair yield signal is strong, such as 122600cm⁻¹, the yield of H⁺ is about 0.015% of the parent ion HCN⁺ (in the case of H₂S → H⁺ + SH⁻, the H⁺:H₂S⁺ ratio is ~0.1%)\(^1\). Within the energy range of Figure 5.1 are the thresholds corresponding to excitation to different ion-pair limits H⁺ + CN⁻(X¹Σ⁺, v' = 0, J') from the initially populated rotational levels of HCN(X¹Σ, v'' = 0, J''). Therefore it was impossible to determine where these ion-pair limits exactly lie since this spectrum does not show any apparent rovibrational pattern of either HCN molecule or the CN⁻ fragment.

The TIPP spectrum of HCN is shown in Figure 5.2, also normalized by VUV intensity. The spectrum covers the energy range from 121840 to 122840cm⁻¹. The overall TIPP signal starts to increase at about 122200cm⁻¹, becomes more or less steady for a few hundred wavenumbers and then decreases slightly at higher energy. Due to the very low intensity of the ion-pair signal, the H⁺ ions were recorded using boxcar detection in ion-counting mode. The VUV energy was scanned at steps of 0.4cm⁻¹, and at each step, the signal was accumulated for one thousand laser shots. It was estimated that at the most intense peak the average number of threshold ions produced for one thousand laser shots was about 10 counts (compared to 200 counts of threshold H⁺ ions for H₂S → H⁺ + SH⁻)\(^1\). To confirm that we were counting the 'real' ion shots at such low level of signal, we repeated scanning the TIPP spectrum in the range from 122300 to 122800cm⁻¹ (see Figure 5.3), almost every single peak was reproducible although the relative intensity of each peak might vary (within a factor of 2). This makes us confident about the peak positions in the TIPP spectrum.

Figure 5.2 shows that the TIPP spectrum is complicated and full of structure. There are more than 50 not clearly resolved peaks in the range from 122200 to 122800cm⁻¹. This is understandable, taking into account the relatively small rotational constants of both HCN molecule and CN⁻ fragment (≤2cm⁻¹\(^{16,17}\)). A spectral range of 500cm⁻¹ could cover many transitions to different ion-pair limits H⁺—CN⁻(v' = 0, J') from HCN at different initial rotational levels J''. Each peak in Figure 5.2 is likely to be a combination of a few such transitions. With the setup of the two field pulses in this work, most peaks have a typical width (FWHM)
Figure 5.1: a, Ion-pair yield spectrum of HCN from reference 3. The horizontal axis was converted from Å to cm$^{-1}$ and therefore is not evenly spaced. b, Total ion-pair yield spectrum of HCN from the current work. An extraction field of 7V/cm was pulsed on 2µs after photoexcitation. No discrimination field was applied.
Figure 5.2: TIPP spectrum of HCN. A discrimination field of 2V/cm magnitude and 1\(\mu\)s duration was pulsed on 300ns after photoexcitation. The extraction field of 7V/cm was pulsed on 2\(\mu\)s after photoexcitation.
Figure 5.3: TIPP spectra of HCN with two different VUV intensities. The intensity of the strong VUV is about twice that of the weak VUV. Both spectra are normalized by the relative VUV intensities. The TIPP spectrum with the strong VUV is shifted up for comparison. For both spectra, a discrimination field of 2V/cm magnitude and 1μs duration was pulsed on 300ns after photoexcitation. The extraction field of 7V/cm was pulsed on 2μs after photoexcitation.
of 3cm$^{-1}$, which is about half of the field detection window $\alpha(\sqrt{F_2} - \sqrt{F_1})$ with 2 and 7V/cm for $F_1$ and $F_2$, respectively, and $\alpha$ values between 3.9 and 6.1.$^{18}$

It has been suggested in the previous work that the HCN ion-pair process goes through the Rydberg states of HCN$^+$ which couple to the ion-pair states.$^3$ To test whether the TIPP signal is dominated by resonance enhancement or mainly comes from direct transition to the ion-pair pseudo continuum, several peaks in Figure 5.2 with above average intensity were randomly selected and scanned with different discrimination fields of 2, 4 and 6V/cm. However, likely due to the extremely low intensity of the threshold signals, it was very difficult to tell whether there was shift of the blue edges expected for ionization behaviour.$^{18}$
Figure 5.4: Simulation I of the HCN TIPP spectrum. The bottom trace is the experimental spectrum, while the top one is the result of simulation 1.
Figure 5.5: Simulation II of HCN TIPP spectrum. The bottom trace is the experimental spectrum, while the top one is the result of simulation 2.
To obtain useful energetic and dynamic information, similar measures were taken to analyse and simulate the TIPP spectrum similar to our previous work on H$_2$S. To do the simulation, a Gaussian line shape function was assumed for each transition from HCN molecule at ground state to the ion-pair states. The rotational energy levels of HCN were calculated from its precisely known rovibrational constants$^{16}$ ($B=1.478221840$ cm$^{-1}$, $D=2.91047$ x $10^{-6}$ cm$^{-1}$, and $H=3.40$ x $10^{-12}$ cm$^{-1}$ for H$^{12}$C$^{14}$N which was the only isotopomer considered in our simulation), the relative population distribution could also be calculated by assuming an approximate rotational temperature. For CN$^-(X^1\Sigma^+)$, a rotational constant of $1.87158\pm0.00090$ cm$^{-1}$ was taken from the recent work of T J Lee et al$^{17}$, although the results of different theoretical approaches can vary from 1.86 to 1.89 cm$^{-1}$ while experimental result of a few decades ago gave the value of 1.89107 cm$^{-1}$. The centrifugal distortion constant of CN$^-$ is not available but was assumed to be $6\times10^{-6}$ cm$^{-1}$ based on the values of CN$^+$ ion and CN free radical. To match the peak positions in the TIPP spectrum, which is our first consideration and priority in doing the simulation, one tentative value of ion-pair threshold $E_{ip}^0$ (for transition from HCN$(X^1\Sigma, v''=0, J''=0)$ to ion-pair H$^+$ + CN$^-(X^1\Sigma^+, v'=0, J'=0)$) was assumed and then adjusted to give the best agreement. The results are shown in Figures 5.4 and 5.5.

From the fitting we obtained the rotational temperature of HCN as 200K which is reasonable for the beam conditions in the experiment. The best fitting of the TIPP spectrum gave a value of 122238.3 cm$^{-1}$ for the HCN ion-pair threshold in an electric field of 2 V/cm. Corrected by the field shift term $\alpha\sqrt{2}$ (with $3.9 < \alpha < 6.1$)$^{18}$, the field-free HCN ion-pair threshold $E_{ip}^0$ was determined to be 122246±4 cm$^{-1}$. There is an uncertainty of $\pm1.5$ cm$^{-1}$ from the $\alpha\sqrt{2}$ term and $\sim0.3$ cm$^{-1}$ in VUV calibration; the rotational constant of CN$^-$ has an uncertainty of $\sim0.015$ cm$^{-1}$ and could contribute an error of $\sim2.7$ cm$^{-1}$ (for $J'=12-14$) to the final value. Our result agrees with the one given in reference 3, but has a much improved precision.

To calculate the bond dissociation energy $D_0$(H-CN) from the ion-pair threshold $E_{ip}^0$, one needs to know the ionization energy of H atom and the electron affinity of CN radical. While the IP(H) value is precisely known$^{21}$, there is relatively large uncertainty in the value of EA(CN)$^{22,23}$ If one uses the result of EA(CN)=3.862±0.004 eV determined in reference 23 using the technique of photoelectron spectroscopy of the negative ion, the $D_0$(H-CN) value can
be obtained as $43717\pm32\text{cm}^{-1}$, with the uncertainty mainly from the EA(CN) value. This value agrees with the result from reference 10 ($43710\pm70\text{cm}^{-1}$) and has a smaller uncertainty. When in the future a more precise value of EA(CN) is measured, one will be able to calculate the $D_0(\text{H-CN})$ value to even better accuracy from our $E_{IP}^0$ value.

Furthermore, from the simulation one can also obtain dynamical information about the relative branching ratio into different rotational levels of the CN$^-$ product. The CN$^-$ fragment produced in our experiment has to be vibrationally cold due to its relatively large fundamental vibrational frequency ($2035\pm40\text{cm}^{-1}$), but it would be interesting to look into its rotational distribution. In our simulations a set of parameters which represent the relative strengths of different transitions were included so that the fitting would agree with the overall shape of the spectrum. To fit those parameters, two different approaches were applied. In the first approach (Figure 5.4), consecutive CN$^-$ rotational levels $J'$ were grouped in threes (012, 345, 678 and so on), and one cross strength was assumed for each group regardless of the initial HCN rotational level $J''$. The second approach (Figure 5.5) was to assume one cross strength for each $\Delta J$ ($J'-J''$) from -10 to 10. The two approaches gave the same value for HCN ion-pair threshold $E_{IP}^0$ and similar pattern of branching ratio into CN$^-$ fragments at different rotational levels (see Figure 5.6). Both approaches show that HCN ion-pair process has a maximum transition strength at about $J'=12-14$. Such pattern is close to the population distribution of CN$^-$ fragment with a rotational temperature of 900K.

The relative fragmentation ratio of HCN into H + CN$^-(J')$ is different from the two ion-pair channels of H$_2$S ($\text{H}^+ + \text{SH}^-$ and $\text{H}^- + \text{SH}^+$). As what mentioned in the introduction, the SH$^-$ fragment is mainly rotationally cold and the SH$^+$ fragment can be vibrationally excited. While in the current study it was observed that the formation of rotationally excited CN$^-$ fragment is favored in the ion-pair process of HCN.

The distribution of CN$^-$ rotation indicates that the ion-pair process goes through bending excited states. The excitation of the bending mode will induce an increase in the rotational excitation of the CN fragment which eventually manifests itself in the production of CN$^-$ at high rotational levels. Similar rotational patterns have been observed in neutral HCN dissociation.$^7$ In the work of reference 7, the relative transition strength to CN$(A)_{v'=0}$ at
Figure 5.6: Relative branching ratio into CN$^-$ fragment at different rotational levels. The star symbols are the fitting results of the first approach while the triangles are from the second approach. The solid line is the calculation of population distribution of CN$^-$ based on a rotational temperature of 900K.
different rotational levels was found to resemble the population distribution of CN with a rotational temperature of \(700 \pm 150\text{K}\). The rotationally excited CN radical was reasoned to be the predissociation product of bent HCN at electronic state \(3^1A'\), for which the potential energy surface is available from \textit{ab initio} calculation.\textsuperscript{24} The HCN ion-pair dissociation process is expected to follow similar mechanism, although further understanding would require more knowledge of HCN excited states, especially the multidimensional potential energy surfaces in the high energy region that produce ion-pairs (15.2eV).

To summarize, we have recorded the high resolution ion-pair yield and TIPP spectra of HCN in this work. Although the ion-pair signal is very low, the TIPP spectrum has a lot of structure. Simulations were performed to match the TIPP spectrum. From the simulations we have derived the precise value of the ion-pair threshold of HCN, which was then used to calculate the bond dissociation energy \(D_0(\text{H-CN})\). The simulations also demonstrate that rotationally hot CN\(^-\) fragment is favored as the product with the cross strength peaks at about \(J'=12-14\).

\textbf{References}


Chapter 5. Threshold Ion-Pair Production in HCN


Chapter 6
Production of HFH$^+$ from (HF)$_2$

6.1 Introduction

As the last part of this thesis project, TIPPS was applied to a hydrogen bonded dimer — (HF)$_2$, initially aimed to study the ion-pair process (HF)$_2$ → HFH$^+$ + F$^-$. Like the work on HCN, by recording the high resolution total yield and threshold spectra of the HFH$^+$ ion, it is possible to obtain the energetic threshold of the above process, and the rovibrational distribution of the HFH$^+$ fragment.

The dissociation energy of (HF)$_2$ into two HF monomers ($D_0$) is 1038 cm$^{-1}$. The stationary geometry of the dimer has been investigated by ab initio calculations$^2$ and microwave experiments$^3,4$. The (HF)$_2$ dimer at equilibrium is planar (see Figure 6.1). The bond length of H-F in the two HF units are very close to that of HF monomer (0.917 Å),$^5$ and the hydrogen bonded H atom is slightly off the F-F axis. There are relatively large uncertainties in the six fundamental vibrational frequencies of (HF)$_2$, with differences up to 200 cm$^{-1}$ between theoretical and experimental results.$^2$ The rotational structures in the two H-F stretching bands of (HF)$_2$ have been investigated by infrared and microwave absorption experiment,$^6$ and laser-induced fluorescence.$^7$

Since the frequencies of the stretching modes ($\nu \approx 3900$ cm$^{-1}$)$^2$ of both HF monomers in (HF)$_2$ are greater than the dissociation energy of (HF)$_2$ into two HF monomers, excitation of those two modes can result in states well above the dissociation limit of (HF)$_2$. During the past two decades, a lot of theoretical$^8-10$ and experimental$^6,11-16$ work have been performed to study the predissociation rates, the photofragment rovibrational distribution, as well as tunnel-
Figure 6.1: (HF)$_2$ energetics and molecular structures of (HF)$_2$ and HFH$^+$. Bond lengths are in Å. Shaded area represents the tuning range of the VUV energy.
ing between the two equivalent conformers of (HF)$_2$ (labelled as H$_a$F$_a$-H$_b$F$_b$ and F$_a$H$_a$-F$_b$H$_b$)$^{17}$.

The equilibrium structure of HFH$^+$ ion in the $^1A_1$ ground electronic state is available from different work,$^{18-20}$ with $R_{HF} = 0.97\pm 0.01\text{Å}$ and $\angle HFH = 114\pm 2^\circ$. The two stretching mode frequencies have been accurately measured by high resolution infrared absorption spectroscopy ($v_1 = 3348.7078\pm 0.36\text{cm}^{-1}$, $v_3 = 3334.6895\pm 0.26\text{cm}^{-1}$),$^{18}$ and the bending mode frequency is about $v_2 = 1390\pm 15\text{cm}^{-1}$.$^{19}$ The potential energy surface up to 1.5eV above the zero point energy are also available by variational calculations performed in Jacobi coordinates.$^{19,21}$ These discrete vibrational levels have an estimated uncertainty of tens of cm$^{-1}$.

It was shown in the work of Ng and Tiedemann et al that (HF)$_2$ and other higher clusters could be formed in the expansion of HF molecular beam.$^{22,23}$ Photoionization of the HF beam could yield ion species HFH$^+$, (HF)$_2$H$^+$ etc., while the parent ions (HF)$_n^+$ (with $n > 1$) were not observed. For HFH$^+$ ion, the yield curve is smooth and shows very little structure. From the onset of the yield curve the appearance potential of HFH$^+$ was measured to be 15.65±0.04eV. This value was regarded as the dissociation threshold to form products HFH$^+$ + e$^-$ + F, and was then used to calculate the proton affinity of HF (the enthalpy change $\Delta H$ for the process HF + H$^+$ $\rightarrow$ HFH$^+$). They obtained a value of 95.5±1.4kcal/mol.

However, a much higher value for HF proton affinity was reported by Foster and Beauchamp,$^{24}$ who studied the proton exchange reaction CH$_3^+$ + HF $\rightarrow$ CH$_4$ + HFH$^+$. By measuring the equilibrium constant $K$, they were able to calculate the free energy change $\Delta G$ for this reaction. With an estimated value of entropy change $\Delta S$, the enthalpy change $\Delta H$ could be obtained. The $\Delta H$ value is the difference between the proton affinities of HF and CH$_4$. Using the known proton affinity of CH$_4$, the proton affinity of HF was obtained as 112±2kcal/mol.

There are also some $ab$ initio calculation results about HF proton affinity. By using the method of MRD-CI (multireference single- and double- excitation configuration interaction), Petsalakis et al gave a proton affinity of 116.5kcal/mol for HF (no uncertainty quoted),$^{19}$ which is very close to SCF (self-consistent-field) calculation results (116.3$^{25}$ and 116.9kcal/mol$^{26}$). All these calculation results agree reasonably well with the value obtained by Foster and Beauchamp.$^{24}$

If the proton affinity value for HF obtained from thermochemical reaction and $ab$ initio cal-
Chapter 6. Production of HFH$^+$ from (HF)$_2$

culations is correct, the dissociation threshold of (HF)$_2$ into HFH$^+$ + e$^-$ + F would be about 14.52eV, and the ion-pair threshold of (HF)$_2$ (to form HFH$^+$ + F$^-$) would be about 11.22eV (EA(F)=27432.440±0.025cm$^{-1}$ or ~3.40eV)$^{27}$. These thresholds are also shown in Figure 6.1.

In the current work, the (HF)$_2$ dimer was excited with tunable VUV photons in the energy range from 14.7 to 15.9eV. Initially the goal was to study the ion-pair channel HFH$^+$ + F$^-$, although the HFH$^+$ ion could also be produced from the dissociative ionization channel HFH$^+$ + e$^-$ + F. Another goal of this work was to study the mechanisms of these two dissociation channels and compare their cross sections. Since the VUV energy is above the two dissociation thresholds, the HFH$^+$ could be produced at high vibrational levels, which would allow the study of fragmentation ratio into products in different vibrational states. Furthermore, since the potential surface of HFH$^+$ has been calculated,$^{19,21}$ one could assign the different vibrational bands in HFH$^+$ spectrum recorded by the high resolution technique of TIPPS/PFI-ZEKE. Our results would resolve the discrepancy between the HF proton affinity values from previous photoionization technique and other methods.

6.2 Experimental

The dimers of (HF)$_2$ were excited by a pulsed coherent VUV light source which was generated through resonant four-wave mixing $\nu = 2\nu_1 + \nu_2$ in a pulsed supersonic Kr or Xe gas beam.$^{28}$ One input wavelength $\nu_1$ was fixed so that $2\nu_1$ corresponds to either Kr $4p^55p[1/2,0]$ resonance at 94093.662cm$^{-1}$ or Xe $5p^56p'[1/2,0]$ resonance at 89860.538cm$^{-1}$. The other wavelength $\nu_2$ was scanned over 100nm (590-720nm) to tune the final VUV energy in the long range (14.7-15.9eV) necessary for this experiment. The tabulated resonance value was used for $2\nu_1$, while the wavelength of $\nu_2$ was calibrated in two short ranges (with each range ~10nm) using optogalvanic spectroscopy in a hollow cathode discharge.$^{30}$ The optogalvanic calibration was then extrapolated to the whole range and was found to agree with the reading given by a Burleigh WA4500 wavemeter to ±0.01nm. The final absolute VUV energy was estimated to have an uncertainty of ±1.5cm$^{-1}$, with a bandwidth of ~1cm$^{-1}$.

The VUV light was separated from the fundamental by a one meter focal length normal
incidence monochromator, which also focused the VUV into an uncollimated pulsed jet of HF from a General Valve Series 9 pulsed source about 5 cm downstream from the nozzle. The HF gas (CP grade, Matheson Gas Products, Inc.) was used without further purification, and the stagnation pressure in the source was about 1 bar. The pressure in the reaction chamber was ~8 x 10^{-6} torr with the molecular beam on, with a background pressure of ~2.0 x 10^{-7} torr.

For the total ion yield spectrum, an extraction field pulse of 35 V/cm was applied to the interaction region 5 μs after the laser pulse and the HFH^+ ions were detected with a time of flight mass spectrometer. For the PFI spectrum, a discrimination field pulse of 10 V/cm and 1 μs duration was applied 300 ns after the laser to repel any ions formed from above threshold processes. At a delay time of 5 μs after the laser, an extraction field pulse of 35 V/cm was applied to field dissociate long-lived Rydberg states and extract the resultant HFH^+ ion into the mass spectrometer.

6.3 Results and Discussion

The interaction of a molecular beam of HF with VUV photons at 15.90 eV yields the time-of-flight spectrum in Figure 6.2. Both HF^+ and HFH^+, together with ions from larger complexes were observed. The ionization potential of HF is 16.04 eV,\(^{31}\) therefore the HF^+ signal in Figure 6.2 was from rotationally excited HF molecules (J'' ≥ 7).

The relative intensity of HF^+ against HFH^+ is shown in Figure 6.3. As VUV energy decreases from 16.02 to 15.87 eV, the HF^+ signal drops quickly. Since the ion yield and PFI spectra were recorded in the energy range from 14.7 to 15.9 eV, there was no contamination of the HFH^+ signal from HF^+ considering the relative narrow width (~30 ns) of the boxcar detection gate.

There are no peaks corresponding to the species of (HF)_2^+ in Figure 6.2, which is consistent with the observation in previous photoionization works.\(^{22,23}\) This was confirmed by the TOF spectrum recorded from a HF molecular beam mixed with Ar (see Figure 6.4). When the VUV energy was below the ionization potential of Ar (127109.80 cm\(^{-1}\) or ~15.76 eV)\(^{32}\), there was no
Figure 6.2: Ion species produced from photoionization of HF molecular beam at 15.90eV.
Figure 6.3: Relative ion intensities of HF$^+$ and HFH$^+$ at different VUV energies.
Chapter 6. Production of HFH\textsuperscript{+} from (HF)\textsubscript{2}

peak of $m/e = 40$. When the VUV energy was above Ar ionization potential, a peak of mass 40 was observed. Since both (HF)\textsubscript{2}\textsuperscript{+} and Ar\textsuperscript{+} have $m/e = 40$, Figure 6.4 showed that there was no (HF)\textsubscript{2}\textsuperscript{+} produced.

The total ion yield spectrum of HFH\textsuperscript{+} normalized with VUV intensity is shown in Figure 6.5. The ion signal increases substantially as VUV energy rises above 15.65eV. It confirms the observation in previous photoionization work\textsuperscript{22,23} and why they gave a value of 15.65±0.04eV for the appearance potential of HFH\textsuperscript{+}. However, our yield spectrum clearly shows that there is also ion signal at VUV energies as low as 14.8eV. This indicates that the appearance energy of HFH\textsuperscript{+} is actually much lower than the value given in previous work, and that the high intensity of HFH\textsuperscript{+} signal above 15.65eV probably comes from the Frank-Condon favored vertical transitions from the molecular ground state into closely spaced high vibrational levels of the ion. Another noticeable point is that while the yield curve in previous work is smooth and shows no structure, there are many very sharp peaks in our high resolution spectrum. These well resolved sharp peaks have a typical width (FWHM) of ~2cm\textsuperscript{-1}.

To check whether the sharp peaks present in the yield spectrum are from transitions to resonance states, a short range of the spectrum was collected with different amplitudes of discrimination pulses of 6, 10 and 16V/cm (see Figure 6.6), no shift was observed for the blue edges of the signal expected for Stark behavior\textsuperscript{33}. Therefore, it is certain those peaks are due to resonant transitions to predissociating states.

To further understand those resonance peaks in the HFH\textsuperscript{+} yield spectrum, there are a few issues need to be clarified. First, is (HF)\textsubscript{2} the only source for production of HFH\textsuperscript{+} ion? Second, among the two competitive processes that can produce HFH\textsuperscript{+} from (HF)\textsubscript{2}: the dissociative ionization process and the ion-pair process, which is dominant? Third, what is the detailed mechanism for HFH\textsuperscript{+} production?

To produce HFH\textsuperscript{+} ion from a HF molecular beam, there are a few possible sources. Beside (HF)\textsubscript{2}, some other clusters such as (HF)\textsubscript{3} are also generated in the expansion of HF beam. Photoexcitation of (HF)\textsubscript{3} could yield different ion products through (HF)\textsubscript{3}→ (HF)\textsubscript{2}H\textsuperscript{+} + e\textsuperscript{-} + F and (HF)\textsubscript{3}→ HFH\textsuperscript{+} + e\textsuperscript{-} + F + HF. The threshold to make HFH\textsuperscript{+} ion from (HF)\textsubscript{3} is higher than the threshold from (HF)\textsubscript{2} by the binding energy of (HF)\textsubscript{2} and HF (~0.1eV). But since
Figure 6.4: TOF spectrum from HF beam mixed with Ar.
Figure 6.5: Total ion yield spectrum of HFH$^+$. An extraction field of 35V/cm was pulsed on 5$\mu$s after photoexcitation. No discrimination field was applied.
Figure 6.6: PFI signal of HFH\(^+\) with different discrimination fields.
HFH\(^+\) could be produced in different vibrational levels and there are relatively large uncertainties in the energetics of the vibrational levels, one would not be able to tell which peak in the spectrum is from which parent neutral. However, if it is assumed that (HF)\(_3\) could be the common source to make (HF)\(_2\)H\(^+\) and HFH\(^+\), one would expect that at certain photon energies corresponding to specific resonances of (HF)\(_3\), both (HF)\(_2\)H\(^+\) and HFH\(^+\) could be produced as the product of unimolecular dissociation of (HF)\(_3\). As the result, some peaks in (HF)\(_2\)H\(^+\) and HFH\(^+\) yield spectra would overlap. Figure 6.7 shows the yield signal of (HF)\(_2\)H\(^+\) and HFH\(^+\) in the energy range from 15.80 to 15.87eV. While the HFH\(^+\) spectrum shows many resonances, the (HF)\(_2\)H\(^+\) curve is rather smooth. Therefore, the (HF)\(_3\) complex is very unlikely to produce HFH\(^+\).

On the other hand, it is necessary to check whether HFH\(^+\) is produced from collision through the process HF\(^*\) + HF \rightarrow HFH\(^+\) + e\(^-\) + F. If this collision process is important, one would expect that HFH\(^+\) intensity increases substantially with the collision time. This phenomenon was not observed, while actually the ion intensity seemed to be stable during the waiting period of a few \(\mu\)s after photoexcitation. This is shown in Figure 6.8. The intensity of the HFH\(^+\) ion signal stays more or less stable as the delay time of the extraction pulse varies from 400ns to 4 \(\mu\)s.

Another way to check the collision effect is to compare the spectrum of HFH\(^+\) with that of HF\(^+\). Since HF\(^*\) is the source to make HF\(^+\) ion, one can collect HF\(^+\) and HFH\(^+\) signal at the same time. Figure 6.9 shows that there is no clear correspondence between the spectra of HF\(^+\) and HFH\(^+\).

For the production of HFH\(^+\) from (HF)\(_2\), there are two competitive channels. One is the dissociative ionization channel (HF)\(_2\) \rightarrow HFH\(^+\) + e\(^-\) + F. The other one is the ion-pair channel (HF)\(_2\) \rightarrow HFH\(^+\) + F\(^-\), for which the threshold is 3.40eV (EA value of F atom)\(^27\) lower than the first channel. To test which channel is the major one to produce HFH\(^+\), the polarity of the extraction field and detection voltage were inverted to check the negative signal (e\(^-\) or F\(^-\)). There was no observation of F\(^-\), while detecting of e\(^-\) signal gave the same spectrum as HFH\(^+\) positive ion (see Figure 6.10). Similar comparisons were performed in two other short energy regions and led to the same conclusion. Therefore, the dissociative ionization is the dominant
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Figure 6.7: Comparison of yield spectra of HFH\(^+\) and \((HF)_2H^+\).
Figure 6.8: TOF spectrum of HFH$^+$ ion with different delay time of the extraction pulse.
Figure 6.9: Comparison of the yield spectra for $HF^+$ and $HFH^+$. 

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channel to produce HFH$^+$ from (HF)$_2$ over the photon energy range studied.

The very weak transition to the ion-pair states is at least partly due to the very few number of (HF)$_2^+$ resonance states available. Since the ion-pair potential is 3.40eV lower than the corresponding dissociative ionization potential, there are many fewer resonance states coupled to the ion-pair channel than to the dissociative ionization channel.

The PFI spectrum of HFH$^+$ in the same energy range as the total ion yield spectrum is shown in Figure 6.11, also normalized to the VUV intensity. The overall structure of the PFI spectrum shows similar pattern to the total yield spectrum, and every peak observed in PFI spectrum was also seen in the total yield spectrum. To make sure that we were not recording some prompt HFH$^+$ ions for the PFI spectrum, a MATI spectrum of Ar was recorded under similar gas pressure with even smaller discrimination fields (see Figure 6.12). It was confirmed that such experimental conditions guaranteed complete discrimination against prompt HFH$^+$ ion. Actually since resonance enhancement is a big factor in both the yield and PFI signals, it is not surprising that some peaks appear at the same positions in both spectra. At the same time, there are some peaks present in the yield spectrum that are missing in the PFI spectrum. This is better shown in Figure 6.13 where the total yield and PFI spectra of shorter energy range are compared. That is because those resonances lie above the thresholds of certain dissociation limits and therefore do not couple to make PFI signal. The resonances observed in the spectra are listed in Table 6.1.
Figure 6.10: Comparison of the HFH$^+$ and $e^-$ signals.
Figure 6.11: PFI spectrum of HFH\textsuperscript{+}. A discrimination field of 10V/cm magnitude and 1\,\mu s duration was pulsed on 300\,ns after photoexcitation, and an extraction field of 35V/cm was pulsed on 5\,\mu s after photoexcitation. The star signs are the calculated vibrational levels of HFH\textsuperscript{+}.\textsuperscript{19,21}
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To produce PFI signals, besides the necessity for the resonance states of (HF\(_2\))\(^+\) to couple to the dissociation channel, energetically the resonance states have to be just (about 12 to 24 cm\(^{-1}\)) below certain dissociative ionization limits with HFH\(^+\) product in different rovibronic states. Therefore, the peak positions in the PFI spectrum also reflect various dissociative ionization limits although some limits may be unaccessible due to the lack of coupling resonance states at the corresponding energy. From this point a comparison of the PFI spectrum with the energetic spacing of the HFH\(^+\) ion is necessary to obtain any energetic information.

In the PFI spectrum (Figure 6.11) the vibrational levels of HFH\(^+\) from theoretical calculations are labelled with star symbols. They are shifted in energy to match to the best with the energetic pattern of PFI spectrum. But since both (HF\(_2\))\(^+\) and HFH\(^+\) could be rotationally excited, it is not possible to exactly determine the vibrational band heads. Therefore, if an uncertainty of ±200 cm\(^{-1}\) is allowed for assignments of PFI signal to different HFH\(^+\) vibrational levels, the match is reasonable. From this, the HFH\(^+\) appearance potential is given as 14.50 ± 0.03 eV for the process (HF\(_2\))\(^-\) → HFH\(^+\) + e\(^-\) + F. The proton affinity of HF was then calculated to be 5.07 ± 0.03 eV (or 116.9 ± 0.7 kcal/mol), which agrees well with the result in references 19, 25 and 26, and thus resolve the discrepancy between the results from previous photoionization work and other literature values.

Regarding the mechanism of the dissociative ionization process, the following process is proposed:

1. photoexcitation H-F—H-F + h\(\nu\) → (H-F)*—H-F
2. intramolecular reaction (H-F)*—H-F → (H-F-H—F)*
3a. dissociative ionization (H-F-H—F)* → HFH\(^+\) + F + e\(^-\)
3b. dissociation (H-F-H—F)* → HFH\(^*\) + F

The first step is the absorption of the VUV photon by one H-F monomer in the dimer complex. The hydrogen bond is relatively weak and would easily get broken if it is the one getting excited. The second step is through intramolecular reaction, one H atom is transfered from the originally strongly bonded F atom to the other F atom. This step is necessary to produce the final fragments of HFH\(^+\) and F. The third step is the dissociation of (H-F-H—F)*. For the yield
Figure 6.12: MATI spectra of Ar with different discrimination fields. The discrimination field of 1μs duration was pulsed on 300ns after photoexcitation, and an extraction field of 35V/cm was pulsed on 5μs after photoexcitation.
Figure 6.13: Comparison of total yield and PFI spectra for HFH$^+$. 

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Chapter 6. Production of HFH\(^+\) from \((\text{HF})_2\)

Table 6.1: Resonances seen in HFH\(^+\) total yield spectrum Figure 6.5. Energy levels of corresponding final states are not known. Energies are in cm\(^{-1}\) and relative to 120000 cm\(^{-1}\) with an uncertainty of \(\pm 1.5 \text{cm}^{-1}\) from calibration. Notation: * indicates a resonance also observed in PFI spectrum Figure 6.11.

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signal, prompt HFH$^+$ ions are generated directly via reaction 3a. For the PFI signal, Rydberg HFH$^*$ states are generated by reaction 3b which are then field ionized to make threshold HFH$^+$ ion. In 3b, F atom has to leave the system before e$^-$ to make Rydberg HFH$^*$. But for step 3a, it is hard to tell whether the F atom leaves before or at the same time as the e$^-$. One might argue that if they were produced at the same time, they would combine to form the F$^-$ ion which is much more stable. However, considering the fairly large distance of between the F atom and the e$^-$ in (H-F-H—F)$^*$, there is not much chance that F atom would capture the e$^-$. 

References

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Chapter 7
Concluding Remarks and Future Work

In the work of this thesis, TIPPS has been applied to HCl/DC1, HF/DF, HCN and (HF)₂. It was demonstrated that as a high resolution photoionization technique, TIPPS can provide useful information about energetics, mechanism and dynamics in ion-pair formation processes.

For energetics, the ion-pair thresholds could be measured to an accuracy of ~1cm⁻¹ for diatomic molecules (HCl/DC1, HF/DF), and a few cm⁻¹ for triatomic molecules (HCN). From the ion-pair threshold one can calculate bond dissociation energies to an unprecedented accuracy, and investigate the Born-Oppenheimer breakdown in isotopomers of diatomic molecules (HCl/DC1, HF/DF).

The ion-pair formation mechanism can be studied. Resonance enhancement can play an important role in the production of ion-pairs. For HCl/DC1, some relatively broad structures were observed in the ion-pair yield spectrum, which were assigned to Rydberg states converging to some vibronic states of HCl⁺/DC1⁺(A²Σ⁺). For HF/DF, sharp resonances were observed in both the TIPP and ion-pair yield spectra. The energetic levels of some resonances could be determined, thus allowing detailed analyses of those resonances. Three rotational sequences of Rydberg states converging to HF⁺/DF⁺(2Π₁/₂) were derived as the intermediate states in ion-pair formation. For (HF)₂, detailed mechanism about the production of HFH⁺ has been investigated. Sharp peaks in both ion yield and threshold spectra were assigned to resonance states of (HF)₂.

The ion-pair formation dynamics can be studied, as shown in the work on HCN. The CN⁻(ν', J') fragments were found to be rotationally hot with a J' maximum near 12-14. The ion-pair formation process of HCN is likely to go through a bent electronic state, with the
excitation of the bending vibrational mode inducing the production of CN$^-$ in high rotational levels.

However, this technique does have some difficulties. First, the ion-pair cross sections are usually very low compared to those for photoionization process. For diatomic molecules, it is about two orders of magnitude lower (HF/DF is an exception in which the ion-pair signal is greatly enhanced by resonance states). For larger molecules, the ion-pair signal is even weaker (for HCN, the ion-pair signal H$^+$ is about 0.015% of the parent ion HCN$^+$). For (HF)$_2$, the ion-pair signal is negligible compared to the dissociative ionization process. One has to use the ion-counting technique when the ion-pair signal is very low (DCl and HCN) to accumulate the threshold ion signal over thousands of laser shots, which takes a long time.

Second, in order to study ion-pair formation mechanisms, one needs to know the potential energies of the resonance states at high energies. Unfortunately this usually is not clearly known, especially for triatomic and polyatomic molecules. Therefore, there are some uncertainties in determining the ion-pair formation mechanism, even for diatomic molecules.

Third, for triatomic and polyatomic molecules, TIPP spectra become more complicated since one or both of the ion-pair fragments can be in different energy levels (HCN). This can lead to difficulty in determining the exact ion-pair threshold. It would be even more difficult if the energetic levels of the fragment are not well known. Furthermore, the presence of resonances would make exact measurement of the energetic limits to an accuracy of a few cm$^{-1}$ almost impossible (such as (HF)$_2$).

Future work could be performed in the following aspects.

For diatomic molecules, there are many molecular systems where the ion-pair formation processes have not been studied. Therefore, there is still a lot of work one can do.

For triatomic or polyatomic molecules, there exists many interesting systems that one can study, and there might be some ways to improve the signal level. First, since the ion-pair signal is usually much weaker than the parent ion, the MCP detector would get saturated with the parent ion when one tries to increases the ion-pair signal. One possible way to solve this problem is to use a quadrupole mass spectrometer which can select the ion species to detect. If only the ion-pair signal is detected, it would be difficult to saturate the MCP and therefore
Chapter 7. Concluding Remarks and Future Work

would allow ample room to improve the ion-pair signal (which of course requires higher VUV intensity). Second, to collect the signal by ion-counting technique, one needs to fire many laser shots (for example, one thousand) at each energy. Right now the Nd:YAG laser used for this project has a repetition rate of 10Hz and laser pulses of about 8ns wide. This means that there is about 100ms duration between two successive laser shots. Since it only takes tens of μs for photoexcitation and data collection, a lot of time is wasted between two laser pulses. If in the future, a laser system with a higher repetition rate is installed, it would take shorter time to collect a TIPP spectrum.

Furthermore, for large molecules and ion fragments, although it is hard to resolve the rotational energy levels, one would expect to get information about vibrational levels, which currently are not known for many ionic species.

Finally, it would be interesting to do state-selected ion-ion or ion molecule reactions. Since TIPP can produce ion fragments in certain rovibronic states, one might like to study the reactivity of ions in those specific states.