Final Closeout Report for DOE Contract: DE-FG02-02ER15306

High-Resolution Photoionization, Photoelectron and Photodissociation Studies: Determination of Accurate Energetic and Spectroscopic Database for Combustion Radicals and Molecules

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Scope of DOE supported project:

The main goal of this research program was to obtain accurate thermochemical and spectroscopic data, such as ionization energies (IEs), 0 K bond dissociation energies, 0 K heats of formation, and spectroscopic constants for radicals and molecules and their ions of relevance to combustion chemistry. Two unique, generally applicable vacuum ultraviolet (VUV) laser photoion-photoelectron apparatuses have been developed in our group, which have used for high-resolution photoionization, photoelectron, and photodissociation studies for many small molecules of combustion relevance.

1. Results of DOE support: DE-FG02-02ER15306

1.1. Project Title: Determination of Accurate Energetic and Spectroscopic Database for Combustion Radicals and Molecules by High-Resolution Photoion-Photoelectron Methods

1.2. Refereed journal publications acknowledged to DOE support (2011-2014)

The DOE support was acknowledged in 22 refereed articles, including seven *Communications* to the *J. Chem. Phys.*, and one invited review in the *Annu. Rev. Phys. Chem*. Four of the *Communications* are among the most read of the months or year. This grant contributed in a major way to Publications 1, 3-8, 10, 12, 16, 19, 21 and 22, and less so to Publications 1, 9, 11, 13-15, 17, 18, and 20.

1. C.-S. Lam, Hailing Wang, Yuntao Xu, K. C. Lau, and C. Y. Ng, "A Vacuum-Ultraviolet Laser Pulsed Field Ionization-Photoelectron Study of Sulfur Monoxide (SO) and its Cation (SO^+)", *J. Chem. Phys*. **134**, 144304 (2011).
2. Yih Chung Chang, Hong Xu, Yuntao Xu, Zhou Lu, Yu-Hui Chiu, Dale J. Levandier and C. Y. Ng. "*Communcation*: Rovibrationally selected study of the $N_2^+(X; v^+ = 1, N^+ = 0\text{-}8)$ + Ar charge transfer reaction using the vacuum ultraviolet laser pulsed field ionization-photoion method", *J. Chem. Phys*. **134**, 201105 (2011).
3. Yan Pan, Hong Gao, Lei Yang, Jingang Zhou, C. Y. Ng, and W. M. Jackson, "*Communication*: VUV laser photodissociation studies of small molecules by the VUV laser photoionization time-sliced velocity-mapped ion imaging method", *J. Chem. Phys.* **135**, 071101 (2011). Top 20 most accessed JCP articles in Aug., 2011.
4. Hong Gao, Lei Yang, Yan Pan, Jingang Zhou, C. Y. Ng, and W. M. Jackson, "Time-sliced velocity-map imaging studies of the predissociation of single ro-vibronic energy levels of N_2 in the extreme ultraviolet region using VUV photoionization", *J. Chem. Phys.* **135**, 134319 (2011).
5. Hong Gao, Yuntao Xu, Lei Yang, Chow-Shing Lam, Hailing Wang, Jingang Zhou, and C. Y. Ng, "High-resolution threshold photoelectron study of the propargyl radical by the vacuum ultraviolet laser velocity-map imaging method", *J. Chem. Phys.* **135**, 224304 (2011).
6. Hong Gao, Yu Song, Lei Yang, Xiaoyu Shi, Qingzhu Yin, C. Y. Ng, and W. M. Jackson, "*Communication*: Branching ratio measurement in the predissociation of $^{12}C^{16}O$ by time-slice velocity-map ion imaging in the vacuum ultraviolet region", *J. Chem. Phys*. **135**, 221101 (2011). Top 20 most accessed JCP articles in Aug., 2011.
7. Kai-Chung Lau and C. Y. Ng, "Accurate *ab initio* predictions of ionization energies of propargyl radical: revisited", *J. Chem. Phys.* **135**, 246101 (2011).
8. Hong Gao, Yang Pan, Lei Yang, Jingang Zhou, C. Y. Ng, and W. M. Jackson, "Time-sliced velocity-map ion imaging studies of the photodissociation of NO in the extreme vacuum ultraviolet (EUV) region", *J. Chem. Phys.* **136**, 134302 (2012).
9. Xiaoyu Shi, Huang Huang, Brian Jacobson, Yih-Chung Chang, Qing-Zhu Yin, and C. Y. Ng, "A high-resolution photoionization and photoelectron study of ^{58}Ni using a vacuum ultraviolet laser", *Astrophys. J.* **747**, 20 (2012).
10. Hong Gao, Yu Song, Lei Yang, Xiaoyu Shi, Qing-Zhu Yin, Cheuk-Yiu Ng, and William M. Jackson, "Branching ratio measurements of the predissociation of $^{12}C^{16}O$ by time-slice velocity imaging in the energy region from 108,000 to 110,500 cm^{-1}", *J. Chem. Phys*. **137**, 034305 (2012).
11. Yih-Chung Chang, Yuntao Xu, Zhou Lu, Hong Xu, and C. Y. Ng, "Rovibrationally selected ion-molecule collision study using the molecular beam vacuum ultraviolet laser pulsed field ionization-photoion method: charge transfer reaction of $N_2^+(X; v^+ = 0\text{-}2, N^+ = 0\text{-}9)$ + Ar, *J. Chem. Phys.* **137**, 104202 (2012).

12. Hong Gao, Zhou Lu, Lei Yang, Jingang Zhou, and C. Y. Ng, "*Communication*: A vibrational study of propargyl cation using the vacuum ultraviolet laser velocity-map imaging photoelectron method", *J. Chem. Phys.* **137**, 161101 (2012).
13. Yuntao Xu, Bo Xiong, Yih Chung Chang, and C. Y. Ng, "*Communication*: Rovibrationally selected absolute total cross sections for the reaction $H_2O^+(X^2B_1; v_1^+v_2^+v_3^+ = 000; N^+_{Ka+Kc+}) + D_2$: Observation of the rotational enhancement effect", *J. Chem. Phys*.**137**, 241101 (2012). Top 15 most accessed JCP communications of 2013.
14. Yih-Chung Chang, Huang Huang, Zhihong Luo, and C. Y. Ng, "*Communication*: A vibrational study of titanium dioxide cation using the vacuum ultraviolet laser pulsed field ionization-photoelectron method", *J. Chem. Phys.* **138**, 041101 (2013).
15. Huang Huang, Yih Chung Chang, Zhihong Luo, Xiaoyu Shi, Chow-Shing Lam, Kai-Chung Lau, and C. Y. Ng, "Rovibronically selected and resolved two-color laser photoionization and photoelectron study of cobalt carbide cation", *J. Chem. Phys*., **138**, 094301 (2013).
16. Hong Gao, Yu Song, Yih-Chung Chang, Xiaoyu Shi, Qing-Zhu Yin, Roger C. Wiens, William M. Jackson, and C. Y. Ng, "Branching ratio measurements of the photodissociation of $^{12}C^{16}O$ by time-slice velocity-map imaging photoion method in the vacuum ultraviolet region from 102,500 to 106,300 cm^{-1}", *J. Phys. Chem. A* (invited), (published March 20, 2013, online ASAP article).
17. Yuntao Xu, Yih Chung Chang, Zhou Lu, and C. Y. Ng, "Absolute total cross sections and product branching ratios for the vibrationally selected ion-molecule reactions: $N_2^+(X^2\Sigma_g^+; v^+ = 0$-$2) + CH_4$", *Astrophys. J.* **72**, 769 (2013).
18. Huang Huang, Zhihong Luo, Yih Chung Chang, Kai-Chung Lau, and C. Y. Ng, "Rovibronically selected and resolved two-color laser photoionization and photoelectron study of titanium monoxide cation", *J. Chem. Phys.* **138**, 174309 (2013).
19. Hong Gao, Yu Song, William M. Jackson, and C. Y. Ng, "*Communication*: State-to-state photodissociation study of $^{12}C^{16}O$ by the VUV-VUV pump-probe Time-Slice Velocity-Map Imaging Photoion Method", *J. Chem. Phys.* **138**, 191102 (2013). Top 20 most accessed JCP communications in May, 2013.
20. Yuntao Xu, Bo Xiong, Yih Chung Chang, and C. Y. Ng, "Translational, rotational, and vibrational energy effects on the chemical reactivity of water cation $H_2O^+(X\ ^2B_1)$ in the collision with deuterium molecule D_2", *J. Chem. Phys.* **139**, 024203 (2013).
21. Hong Gao, Yuntao Xu, Lei Yang, Chow-Shing Lam, Hailing Wang, Jingang Zhou, and C. Y. Ng, "Erratum: High-resolution threshold photoelectron study of the propargyl radical by the vacuum ultraviolet laser velocity-map imaging method [*J. Chem. Phys.* 135, 224304 (2011)], J. Chem. Phys. **139**, 079902 (2013).
22. Cheuk-Yiu Ng, "State-to-state spectroscopy and dynamics of ions and neutrals by photoionization and photoelectron methods", Annual Review Physical Chemistry, **65**, 197-224 (2014).

This DOE support was also acknowledged in 23 invited lectures given by members of my group at research institutes, universities, and national and international conferences and workshops in the period of 2011-2014.

2. Highlights of selected scientific results and technical developments

Selected results obtained during this funding period are highlighted below.

1. **Publication 1:** Vacuum ultraviolet (VUV) laser pulsed field ionization-photoelectron (PFI-PE) spectroscopy has been applied to the study of the sulfur monoxide radical (SO) prepared by using

a supersonically cooled radical beam source based on the 193 nm photodissociation of SO_2. The vibronic VUV-PFI-PE bands for the photoionization transitions $SO^+(X\ ^2\Pi_{1/2};\ v^+ = 0) \leftarrow SO(X\ ^3\Sigma^-;\ v = 0)$ and $SO^+(^2\Pi_{3/2};\ v^+ = 0) \leftarrow SO(X^3\Sigma^-;\ v = 0)$ have been recorded. The simulation of rotational branch contours observed in these PFI-PE bands has yielded highly precise ionization energies (IEs) of 83 034.2 ± 1.7 cm^{-1} (10.2949 ± 0.0002 eV) and 83 400.4 ± 1.7 cm^{-1} (10.3403 ± 0.0002 eV) for the formation of $SO^+(X^2\Pi_{1/2};\ v^+=0)$ and $SO^+(^2\Pi_{3/2};\ v^+=0)$, respectively. This VUV-PFI-PE study also allows the direct determination of the spin-orbit coupling constant (A_0) for $SO^+(X^2\Pi_{1/2,3/2})$ to be 365.36 ± 0.12 cm^{-1}. High-level *ab initio* quantum chemical calculations at the CCSDTQ(Full)/CBS approach, which involves the approximation to the complete basis set (CBS) limit at the coupled cluster level up to full quadruple excitations, along with the zero-point vibrational energy correction, the core-valence electronic correction, the spin-orbit coupling, and the high-level correction, have also been performed for comparison with the experimental results. The IE[$SO^+(X^{22}\Pi_{1/2,3/2})$] and A_0 predictions thus calculated are found to be in remarkable agreement with the experimental determinations.

2. **Publications 2 and 11:** We have developed an ion-molecule reaction apparatus for state-selected absolute total cross section measurements by implementing a high-resolution molecular beam VUV laser PFI-photoion (PFI-PI) ion source to a double-quadrupole double-octopole (DQDO) ion guide mass spectrometer. Using the total cross section measurement of the state-selected $N_2^+(v^+, N^+)$ + Ar charge transfer (CT) reaction as an example, we describe in detail the design of the VUV laser PFI-PI ion source used, which has made possible the preparation of reactant $N_2^+(v^+ = 0\text{-}2, N^+ = 0\text{-}9)$ PFI-PIs with high quantum state purity, high intensity, and high kinetic energy resolution. The PFI-PIs and prompt ions produced in the ion source are shown to have different potential energies, allowing the clean rejection of prompt ions from the PFI-PI beam by applying a retarding potential barrier upstream of the PFI-PI source. By employing a novel pulsing electric field scheme to the VUV-PFI-PI source, we show that the reactant N_2^+ PFI-PI beam can be formed with a laboratory kinetic energy resolution of ΔE_{lab} = ± 50 meV. As a result, the total cross section measurement can be conducted at center-of-mass kinetic energies (E_{cm}'s) down to thermal energies. An important feature of the present experiment is that a VUV monochromator was not used, and thus the diffraction loss of the VUV laser intensity was avoided, resulting in a higher intensity for PFI-PIs. Absolute total rovibrationally selected cross sections $\sigma(v^+ = 0\text{-}2, N^+ = 0\text{-}9)$ for the $N_2^+(X\ ^2\Sigma_g^+;\ v^+ = 0\text{-}2, N^+ = 0\text{-}9)$ + Ar CT reaction have been measured in the E_{cm} range of 0.04-10.0 eV, revealing strong vibrational enhancements and E_{cm}-dependencies of $\sigma(v^+ = 0\text{-}2, N^+ = 0\text{-}9)$. The

thermochemical threshold at E_{cm} = 0.179 eV for the formation of Ar^+ from $N_2^+(X; v^+ = 0, N^+)$ + Ar was confirmed by the measured $\sigma(v^+ = 0)$, confirming the narrow ΔE_{cm} spread and the purity of the rovibrational state achieved in the present study. The $\sigma(v^+ = 0\text{-}2; N^+)$ values obtained here are compared with previous experimental and theoretical results. The theoretical predictions calculated based on the Landau-Zener-Stückelberg formulism are found to be in fair agreement with the present measured $\sigma(v^+ = 1 \text{ or } 2; N^+)$. Taking into account of the experimental uncertainties, the measured $\sigma(v^+ = 1 \text{ or } 2, N^+)$ for N^+ = 0-9 at E_{cm} = 0.04-10.0 eV are found to be independent of N^+.

3. **Publication 3:** We report on a novel experimental method for the study of VUV photodissociation dynamics of small molecules based on time-slice VUV-velocity-map-imaging photoion (VUV-VMI-PI) detection. In this method, the two VUV lasers required for state-selected photodissociation and state-selected photoionization sampling in the respective energy ranges of 9.6-10.3 and 13.0-13.7 eV were generated simultaneously by four-wave difference and sum-frequency mixings, respectively, using a Kr jet as the nonlinear medium. Preliminary experimental results on VUV state-selected photodissociation of N_2 and CO_2 are presented, where atomic photofragments O and N states were detected by the VUV laser VMI-PI method. These results indicate that the VUV laser photodissociation with the VUV-VMI-PI detection is a attractive method for studying the tunable single-photon VUV laser photodissociation from the ground state of simple molecular species.
4. **Publication 4:** The predissociation of N_2 from the rotational levels in the $o^1\Pi_u$ (v'=2) and $b'^1\Sigma_u$ (v'=8) bands in the VUV range of 109,350-109,580 cm^{-1} (13.5577-13.5862 eV) has been studied by the time-slice VUV laser VMI-PI technique with VUV photoionization detection of photoproduct N atoms. These levels were excited from the ground state of N_2 ($X^1\Sigma_g^+$, v'' = 0) levels using an unfocused VUV laser via a one-photon process. The same VUV laser is used to ionize the metastable $N(^2D^o)$ photoproducts; and the time-sliced VMI-PI technique is used to determine their velocity and angular distributions. Two different theoretical methods developed previously were used to calculate the anisotropic parameters for the predissociation to the channel $N(^4S^o)$ + $N(^2D^o)$ to compare with the observed value for each of the rotational levels. Good agreement between experimental and calculated results was observed for both methods. Possible predissociation mechanisms were suggested based on this study.
5. **Publications 5 and 21:** In Publication 5, we introduced a new high-resolution VUV laser threshold photoelectron (TPE) detection scheme based on VUV laser VMI-photoelectron (VMI-PE) scheme to discriminate energetic photoelectrons. Using this approach, we have measured the VUV-VMI-TPE spectrum of propargyl radical $[C_3H_3(X^2B_1)]$ near its ionization threshold,

achieving a photoelectron energy resolution of 2 cm^{-1} (FWHM). The comparison of the VUV laser VMI-TPE and PFI-PE spectra obtained for $C_6H_5Cl^+$ indicates that the energy resolution achieved in the VUV laser VMI-TPE and PFI-PE measurements are comparable. The simulation of the VUV laser VMI-TPE spectrum for C_3H_3 thus obtained, along with the Stark shift correction, has provided the IE(C_3H_3) = 70,156 ± 4 cm^{-1}, where the Stark shift correction is determined by comparing the VUV-VMI-TPE and the VUV-PFI-PE spectra for the origin band of $C_6H_5Cl^+$. Recently, Prof. Frederic Merkt pointed out to us that an incorrect nuclear-spin statistical weights of even K_a'' : odd K_a'' = 1 : 3 was used in our original simulation of the VMI-TPE spectra of C_3H_3. This leads to K_a'' = 1 as the most populated level and the assignment of the strongest peak observed in the VUV-VMI-TPE spectrum to be the K_a^+ =2 ← K_a'' = 1 transition. By using the correct nuclear-spin statistical weights (even K_a'' : odd K_a'' = 3 : 1), K_a'' = 0 becomes the most populated level and the strongest peak is assigned to be the K_a^+ = 1 ← K_a'' = 0 transition. As a result, the IE(C_3H_3) obtained by the previous simulation is lower by 19 cm^{-1}. Publication 21 is the Erratum that reports on the revised simulation of the VUV-VMI-TPE spectrum for the origin band of $C_3H_3^+(X)$, providing the IE(C_3H_3) = 70175 ± 2 cm^{-1} (8.7006 ±0.0005 eV), which is identical to the value of 70174.5 ± 2.0 cm^{-1} (8.7005 ±0.0005 eV) obtained by the VUV laser PFI-PE measurement. The best simulation spectrum is obtained by using a Gaussian line-width of 2 cm^{-1} (FWHM) and a rotational temperature of ≈ 40 K for the C_3H_3 sample.

6. **Publication 7:** We have reexamined the CCSDTQ/CBS IE calculations for propargyl (C_3H_3) and allyl (C_3H_5) radicals by including the high-order correction term, which was not taken into account in previous calculations. Both CCSDTQ/CBS IE predictions thus calculated, IE(C_3H_3) = 8.706 eV and IE(C_3H_5) = 8.144 eV, are found to agree favorably with the most recent experimental IE values of 8.7006±0.0005 eV for C_3H_3 and 8.1314 ± 0.0003 and 8.1309 ± 0.0003 eV for C_3H_5 determined by rotationally resolved photoelectron measurements. The discrepancies of 6-13 meV are within the accuracy of the CCSDTQ/CBS IE calculations established in previous comparison between experimental and theoretical results.
7. **Publication 12:** By employing the VUV laser VMI-PE method, we have obtained a vibrationally resolved photoelectron spectrum of $C_3H_3(X)$ at the energy range of 0-4,600 cm^{-1} above its IE. Here, the cold C_3H_3 sample was produced from a supersonically cooled radical beam source based on 193 nm photodissciation (PD) of C_3H_3Cl. The VUV laser VMI-PE spectrum of C_3H_3 thus obtained reveals a Franck-Condon factor (FCF) pattern with a strongly dominated origin band along with weak vibrational progressions associated with the excitation of the symmetric C–C $\nu_5^+(a_1)$ and C≡C $\nu_3^+(a_1)$ stretching modes and the CCH $\nu_7^+(b_1)$ out-of-plane

bending mode of $C_3H_3^+(X^1A_1)$. The $\nu_5^+(a_1)$ vibrational frequency of 1120 cm^{-1} determined in the present study is lower than the value deduced from the recent Ar-tagged IRPD study by 102 cm^{-1}, confirming vibrational frequency predictions obtained by the recent state-of-the-art *ab initio* quantum calculations. The observation of the FCF disallowed $\nu_7^+(b_1)$ mode may be attributed to vibronic interactions.

8. **Publication 6:** The first direct branching ratio measurement of the three lowest energy dissociation channels of CO that produce $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$, and $C(^3P) + O(^1D)$ is reported. Rotational resolved C^+ ion yield spectra for two Π bands ($W(3s\sigma)^1\Pi$ (v'=3) at 108,012.6 cm^{-1} and $^1\Pi$(v'=2) at 109,017 cm^{-1}) and two Σ bands (($4s\sigma)^1\Sigma^+$(v'=4) at 109,452 cm^{-1} and $(4p\sigma)^1\Sigma^+$(v'=3) at 109,485 cm^{-1}) of CO were obtained. Our measurements show that the branching ratio in this energy region is strongly dependent on the electronic and vibrational states, but is independent or just weakly dependent on the parity and rotational energy levels. To our knowledge, this is the first time that the triplet channel producing $O(^1D)$ has been experimentally observed and this is also the first time that a direct measurement of the branching ratio for the different channels in the predissociation of CO in this energy region has been made.
9. **Publication 10:** Direct branching ratio measurements of the three lowest dissociation channels of $^{12}C^{16}O$ that produce $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ are reported in the VUV region from 108,000 to 110,500 cm^{-1} using the combination of time-slice VMI-PI and nonlinear resonant four-wave mixing techniques. Rotationally resolved carbon ion yield spectra for both $^1\Sigma^+$ and $^1\Pi$ bands of CO in this region have been obtained. Our measurements show that the branching ratio in this energy region, especially the relative percentages of the two spin-forbidden channels, is strongly dependent on the electronic and vibrational energy levels of CO. Predissociation of CO into the two spin-forbidden channels is observed for almost all of the $^1\Pi$ bands in this region but only for some of the $^1\Sigma^+$ bands. The $^1\Sigma^+$ bands have all been assigned as Rydberg states but only the $(4s\sigma)^1\Sigma^+$(v'=4), $(4p\sigma)^1\Sigma^+$(v'=3) and $W(7p\sigma)^1\Sigma^+$(v'=0) bands appear to be strongly coupled to repulsive triplet states.
10. **Publication 16:** The branching ratios for the spin-forbidden photodissociation channels of $^{12}C^{16}O$ in the VUV photon energy region from 102,500 cm^{-1} (12.709 eV) to 106,300 cm^{-1} (13.180 eV) have been investigated using the time-slice VUV laser VMI-PI technique. The excitations to three $^1\Sigma^+$ and six $^1\Pi$ Rydberg-like states, including the progression of $W(3s\sigma)$ $^1\Pi$(v′ = 0, 1, and 2) vibrational bands of CO, have been identified and investigated. The branching ratios for the product channels $C(^3P) + O(^3P)$, $C(^1D) + O(^3P)$ and $C(^3P) + O(^1D)$ of these predissociative states are found to depend on the electronic, vibrational, and rotational states of CO being excited.

Rotation and parity dependences of the branching ratios into the spin-forbidden channels have been confirmed for several of the $^1\Pi$ states, which can be explained using the heterogeneous interaction with the repulsive $D'^1\Sigma^+$ state. The percentage of the photodissociation into the spin-forbidden channels is found to increase with increasing the rotational quantum number for the $K(4p\sigma)$ $^1\Sigma^+$ ($v'=0$) state. This has been rationalized using a $^1\Sigma^+$ to $^1\Pi$ to $^3\Pi$ coupling scheme, where the final $^3\Pi$ state is a repulsive valence state correlating to the spin-forbidden channel.

11. **Publication 19:** We demonstrate that combining two independently tunable VUV lasers and the time-slice VMI-PI method allows the rovibronically state-selected photodissociation study of CO in the VUV region along with the state-selective detection of product $C(^3P_{0,1,2})$ using the VUV-UV (1+1′) resonance-enhanced photoionization and the VUV Rydberg autoionization methods. Both tunable VUV lasers are generated based on resonance-enhanced four-wave mixing schemes in rare gases. The observed fine-structure distributions of product $C(^3P_J)$, J = 0, 1, and 2, are found to depend on the CO rovibronic state populated by VUV photoexcitation. The branching ratios for $C(^3P_0) + O(^3P_J) : C(^3P_0) + O(^1D_2)$, $C(^3P_1) + O(^3P_J) : C(^3P_1) + O(^1D_2)$, and $C(^3P_2) + O(^3P_J) : C(^3P_2) + O(^1D_2)$, which were determined based on the time-slice VMI-PI measurements of C^+ ions formed by J-state selective photoionization sampling of $C(^3P_{0,1,2})$, also reveal strong dependences on the spin-orbit states of $C(^3P_{0,1,2})$. By combining the measured branching ratios and fine-structure distributions of $C(^3P_{0,1,2})$, we have determined the correlated distributions of $C(^3P_{0,1,2})$ accompanying the formation of $O(^1D_2)$ and $O(^3P_J)$ produced in the VUV photodissociation of CO. The success of this demonstration experiment shows that the VUV photodissociation pump-VUV photoionization probe approach is promising for state-to-state photodissociation studies of many small molecules, which are relevant to planetary atmospheres as well as fundamental understanding of photodissociation dynamics.
12. **Publication 8:** The time-slice VMI-PI and the resonance-enhanced four-wave mixing techniques are combined to study the photodissociation of NO in the VUV region of around 13.5 eV. The neutral atoms, $N(^2D^o)$, $O(^3P_2)$, $O(^3P_1)$, $O(^3P_0)$, $O(^1D_2)$, are probed by exciting to an autoionization line of $O(^1D_2)$ or $N(^2D^o)$, or an intermediate Rydberg-like state of $O(^3P_{0,1,2})$. Old and new autoionization lines of $O(^1D_2)$ and $N(^2D^o)$ near this region have been measured and the frequencies of new autoionization lines are given for them. The photodissociation channels producing $N(^2D^o) + O(^3P)$, $N(^2D^o) + O(^1D_2)$, $N(^2D^o) + O(^1S_0)$ and $N(^2P^o) + O(^3P)$ have all been identified. This is the first time that a single VUV photon has been used to study the photodissociation of NO in this energy region. Our measurements of the angular distributions show that the recoil anisotropy parameters (β) for all the dissociation channels except for the

$N(^2D^o) + O(^1S_0)$ channel are minus at each of the wavelengths used in the present study. Thus direct excitation of NO by a single VUV photon in this energy region leads to excitation of states with Σ or Δ symmetry ($\Delta\Omega = \pm 1$), explaining the observed perpendicular transition.

13. **Publication 9:** Absolute vibrationally selected integral cross sections (σ_{v+}'s) for the ion-molecule reaction $N_2^+(X^2\Sigma_g^+; v^+ = 0\text{-}2) + CH_4$ have been measured by using the newly developed VUV laser PFI-PI double-quadrupole-double-octopole ion guide apparatus. By employing a novel electric field pulsing scheme to the VUV laser PFI-PI ion source, we have been able to prepare reactant N_2^+ ions in single rovibrational quantum states with not only high intensity and high purity, but also high kinetic energy resolution, allowing integral cross section measurements to be conducted in the center-of-mass kinetic energies (E_{cm}'s) from 0.05 to 10.00 eV. Three primary product channels corresponding to the formations of CH_3^+, CH_2^+ and N_2H^+ were identified. We have also determined the σ_{v+} values of the formation of these primary product ions, $\sigma_{v+}(CH_3^+)$, $\sigma_{v+}(CH_2^+)$, and $\sigma_{v+}(N_2H^+)$, and their branching ratios, $[\sigma_{v+}(CH_3^+) : \sigma_{v+}(CH_2^+) : \sigma_{v+}(N_2H^+)]/\sigma_{v+}(CH_3^+ + CH_2^+ + N_2H^+)$, $v^+ = 0\text{-}2$, in the E_{cm} range of 0.05-10.0 eV, where $\sigma_{v+}(CH_3^+ + CH_2^+ + N_2H^+) = \sigma_{v+}(CH_3^+) + \sigma_{v+}(CH_2^+) + \sigma_{v+}(N_2H^+)$. The branching ratios are found to be nearly independent of the v^+ state and E_{cm}. Complex v^+-state and E_{cm} dependences for $\sigma_{v+}(CH_3^+)$, $\sigma_{v+}(CH_2^+)$, and $\sigma_{v+}(N_2H^+)$, along with vibrational inhibition for the formation of these product ions are observed. The vibrational effects on the σ_{v+} values are sufficiently large to warrant the inclusion of the vibrationally excited reactions $N_2^+(X^2\Sigma_g^+; v^+ \geq 1) + CH_4$ for a more realistic modeling of the ion and neutral densities observed in the atmosphere of Titan. The cross sectional data obtained in the present study are also useful for benchmarking theoretical calculations on ion-neutral collision dynamics.

14. **Publications 13 and 20:**

By employing the newly established VUV laser PFI-PI double quadrupole-double octopole ion guide apparatus, we have examined the translational, rotational, and vibrational energy effects on the chemical reactivity of water cation $H_2O^+(X^2B_1)$ in the collision with deuterium molecule D_2. The application of a novel electric-field pulsing scheme to the VUV laser PFI-PI ion source has enabled the preparation of a rovibrationally selected $H_2O^+(X^2B_1; v_1^+v_2^+v_3^+; N^+_{Ka+Kc+})$ ion beam with not only high internal-state selectivity and high intensity, but also high translation energy resolution. Despite the unfavorable FCFs, we are able to prepare the excited vibrational states

($v_1^+v_2^+v_3^+$) = (100) and (020) along with the (000) ground vibrational state, for collisional studies, where v_1^+, v_2^+, and v_3^+ represent the symmetric stretching, bending, and asymmetric stretching modes of $H_2O^+(X^2B_1)$. We show that a range of rotational levels from $N^+_{Ka+Kc+} = 0_{00}$ to 3_{22}, covering a rotational energy range of 0-200 cm^{-1} of these vibrational states, can also be generated for absolute integral cross section (σ) measurements at center-of-mass collision energies (E_{cm}'s) from thermal energies to 10.00 eV. The E_{cm} dependences of the σ values are consistent with the prediction of the orbiting model, indicating that translational energy significantly hinders the chemical reactivity of $H_2O^+(X^2B_1)$. Rotational enhancements are observed at $E_{cm} < 0.30$ eV for all the three vibratioal states, (000), (100) and (020). While the σ values for (100) are found to be only slightly below those for (000), the σ values for (020) are lower than those for (000) and (100) by up to 20% at $E_{cm} \leq 0.20$ eV, indicative of vibrational inhibition at low E_{cm} by excitation of the (020) mode. Rationalizations are proposed for the observed rotational enhancements and the bending vibrational inhibition. Rigorous theoretical calculations are needed to interpret the wealth of rovibrationally selected cross sections obtained in the present study.