Collision-induced Dissociation Reactions and Pulsed Field Ionization Photoelectron

by

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To my beloved Mother, family, and friends
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GENERAL INTRODUCTION

Dissertation Organization

This dissertation is composed of four papers formatted for journal publication. Each paper contains an abstract, introduction, experiment, results and discussion, and conclusion section. The experimental conditions for each experiment are reported within each separate paper and only pertain to that paper. In addition, references, tables, and figures within each paper also pertain only to that individual paper. Following the last paper is a general conclusion.

Introduction

The first paper contains the collision-induced dissociation (CID) study of the methanethiol cation CH$_3$SH$^+$($^1A^\pi$) with Ar. This experiment was performed on a triple-quadrupole double-octopole photoionization apparatus located at Iowa State University. As an important atmospheric pollutant emitted from combustion, industrial, and oceanic sources, the photochemistry of CH$_3$SH has recently received a great deal of experimental and theoretical attention. Being the simplest alkyl mercaptan cation, the structure, energetics, and dissociation dynamics of CH$_3$SH$^+$ have also been the focus of many theoretical and experimental efforts. The dissociation dynamics of CH$_3$SH$^+$, which addresses the fundamental question of hydrogen scrambling, has been investigated previously by charge exchange, mass spectrometry, and photoelectron-photoion coincidence (PEPICO) techniques. In a similar energy range above the ground state of CH$_3$SH$, the major product ions observed in the charge exchange and photoionization studies are in agreement. The products include CH$_2$SH$^+$ (CH$_3$S$^+$), CH$_3$S$^+$, HCS$^+$, HS$^+$, and CH$_3$. The absolute total cross sections for the product ions CH$_2$SH$^+$ (CH$_3$S$^+$), CH$_3$S$^+$, HCS$^+$, HS$^+$, CH$_3$+, and CH$_2$+ produced by CID were measured. The relative yields for the product ions formed in the CID reaction, which strongly favor the C-S bond scission process leading to the formation of CH$_3$+ + SH, are significantly different from those measured in previous photoionization and charge exchange studies. Since the CH$_3$+ + SH channel is not among the most stable product channels, this observation shows that the collision-induced dissociation of CH$_3$SH$^+$ is non-statistical. The high yield for CH$_3$+ + SH observed in CID is attributed to the more efficient translational to vibrational energy transfer for the C-S stretch than for C-H stretches of CH$_3$SH$, and to weak couplings between the low frequency C-S and high frequency C-H stretching vibrational modes of CH$_3$SH$. The differences in excitation mechanisms for CH$_3$SH$^+$ via collision activation, photoionization, and charge exchange are responsible for the different fragment ion distributions from CH$_3$SH$^+$ observed in these experiments.
The second, third, and fourth papers contain the vacuum ultraviolet pulsed field ionization photoelectron (VUV-PFI-PE) spectroscopy studies of OCS (X'\Sigma^+), \text{H}_2 (X'\Sigma^+_g), and HD (X'\Sigma^+) respectively. These experiments were performed on the Chemical Dynamics Beamline at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.

Recently, we have developed a high resolution monochromatic vacuum ultraviolet undulator synchrotron radiation source associated with the Chemical Dynamics Beamline at the ALS with a tunable energy range from 5 to 27 eV.^{28,29} An experimental scheme for PFI-PE detection using a multibunch synchrotron source has also been implemented.^{30-33} The PFI-PE technique provides a means for spectroscopic and energetic characterization of gaseous ionic species. As demonstrated in recent PFI-PE experiments on Ne, Ar, Kr, and \text{O}_3, the photoelectron energy resolution achieved was 3-6 cm\(^{-1}\) (FWHM). This is comparable to the resolution obtained in VUV laser studies.^{24,25,27} Although VUV laser radiation with useful intensities can in principle be generated up to \approx 17.7 eV, the processes involved remain inefficient for routine experimentation compared with the ease in tuning VUV synchrotron radiation.

Carbonyl sulfide (OCS) is a linear molecule with the dominant ground state electronic configuration\(^{34}\) \(\ldots(6\sigma)^2(7\sigma)^2(8\sigma)^2(9\sigma)^2(2\pi)^4(3\pi)^4\) X'\Sigma^+. Taking into account the spin-orbit interaction, the removal of an electron from the highest occupied 3\pi-orbital (mostly having the sulfur 3p character)\(^{34}\) results in the formation of the OCS' (X^2\Sigma^+) spin-orbit states. The OCS' cation has been investigated previously by many experimental techniques, including dispersed fluorescence,\(^{35-40}\) laser-induced fluorescence,\(^{41}\) photodissociation,\(^{42}\) photoionization,\(^{43,44}\) and \text{HeI} \(^{45-48}\) and threshold photoelectron (TPE) spectroscopy.\(^{44,49}\) High resolution spectroscopic data for the OCS' (X^2\Sigma^+) states have been obtained recently by laser ion photodissociation techniques.\(^{50}\)

The VUV-PFI-PE bands of OCS' (X^2\Sigma) in the energy region of 11.09-11.87 eV were measured using the high-resolution monochromatic synchrotron radiation of the Chemical Dynamics Beamline at the ALS. The ionization energies (IEs) for the formation of the (0,0,0) \(X^2\Pi_{3/2}\) and (0,0,0) \(\bar{\Pi}_{1/2}\) states of OCS' were determined to be 11.1831 \pm 0.0005 eV and 11.2286 \pm 0.0005 eV, respectively, yielding a value of 367 \pm 1.2 cm\(^{-1}\) for the spin-orbit splitting.

C. Destandau, G. Chambaud, and P. Rosmus from the Theoretical Chemistry Group at the Université de Marne-la-Vallée in France used the internally contracted multi-reference configuration interaction approach to generate three-dimensional potential energy functions (PEFs) for the OCS' (X^2\Pi) state which were then used in variational Renner-Teller calculations of the vibronic states. The energies of all
vibronic states \((I=P)\) for \(J = 1/2, 3/2, 5/2,\) and \(7/2\) were computed in the energy range of \(\approx 4000\) cm\(^{-1}\) above the IE[OCS\(^+(X^2\Sigma^+_g)\)] for the assignment of the experimental spectrum.

Being the simplest neutral and cationic molecular system, the potential energy surfaces and spectroscopic constants for \(\text{H}_2\) and \(\text{H}_2^+\) and their isotopes in their ground and excited rovibronic states have been calculated with high accuracy.\(^{51-60}\) Reliable and extensive predictions for the bound rovibronic energies of \(\text{H}_2^+\) and \(\text{HD}^+\) have been obtained at different levels of theory.\(^{52-55}\)

The rotationally resolved PFI-PE spectra of \(\text{H}_2\) and \(\text{HD}\) at a resolution of \(\approx 7\) cm\(^{-1}\) FWHM (full-width-half-maximum) in the photon energy range of 15.30-18.11 eV were obtained. The rotational transitions for the \(\text{H}_2^+(X^2\Sigma^+_g, v^* = 0-18)\) and the \(\text{HD}^+(X^2\Sigma^+_g, v^* = 0-21)\) vibronic bands were assigned and then simulated using the Buckingham-Orr-Sichel (BOS) model. From the experimental data, \(\Delta G(v^*+1/2),\ B_v,\) and \(D_v\) were determined and used to calculate the ionic vibrational and rotational constants (\(\omega_o,\ \omega_x,\ \omega_y,\ \omega_z,\ \omega,\ B_o,\) and \(\alpha_o\)), the internuclear separation \((r_o)\), and the dissociation energy \((D_0)\).

References

9. C. Y. Ng, Advances in Photochemistry, 22, 1 (1997); and references therein.
33. C.-W. Hsu, P. A. Heimann, M. Evans, S. Stimson, and C. Y. Ng, Chem. Phys., accepted.
GENERAL CONCLUSIONS

We have examined the CID reaction of CH$_3$SH$^+$ + Ar in the E$_{c.m.}$ range of 2-36 eV. The fragment ions observed were in general agreement with those observed in previous charge exchange and photoionization studies. The most interesting observation of this CID study was that CH$_3$ + SH was found to be the dominant product channel, which is contrary to the QET prediction and results of previous charge exchange and photoionization measurements. Stemming from the fact that the dissociation energy for the CH$_3$-SH bond is greater than that of the H-CH$_2$SH$^+$ bond, this observation clearly indicates non-statistical behavior in the CID of CH$_3$SH$^+(1^2A'^+$. In effect, this system is an example of bond selective dissociation via collisional activation.

A high resolution PFI-PE spectrum for OCS in the energy range of 11.09-11.87 eV was obtained. In addition to strong photoelectron bands assigned to ($v_1^+$, 0, $v_3^+$) $^2\Pi_{3/2}$ and ($v_1^+$, 0, $v_3^+$) $^2\Pi_{1/2}$ for OCS$^+(X^2\Sigma^+)$, weaker Renner-Teller structures were observed for the first time. Accurate theoretical predictions for the Renner-Teller levels of the OCS$^+(X^2\Pi)$ state were also obtained. The observed transitions in the PFI-PE spectrum were assigned satisfactorily by using the calculated energy positions of the vibronic levels.

In addition, the rotationally resolved PFI-PE spectra of H$_2$$(X^2\Sigma^+_g$, $v^+=0-18$) and HD$^+(X^2\Sigma^+, v^+=0-21)$ were obtained. The analysis of which provided the rovibronic energies, the vibrational constants ($\omega_v$, $\omega_{x_v}$, $\omega_{y_v}$, and $\omega_{z_v}$), the rotational constants (B$_v$, D$_v$, B$_e$, and $\alpha_v$), the internuclear separation (r$_e$), and the dissociation energy, (D$_0$). The simulated photoelectron bands based on the BOS model are in good agreement with the PFI-PE bands of higher $v^+$ states, indicating that the strong perturbation of the relative intensities for rotational transitions occurs mainly at lower $v^+$ (≤6) states.
This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1856 to this thesis.