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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 $\text{CH}_3\text{SH}^+(1^2\text{A}'')$ 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,¹⁻⁸ the photochemistry of CH_3SH has recently received a great deal of experimental and theoretical attention.⁹ Being the simplest alkyl mercapton cation, the structure, energetics, and dissociation dynamics of CH_3SH^+ have also been the focus of many theoretical¹⁰⁻¹² and experimental¹³⁻²⁴ efforts. The dissociation dynamics of CH_3SH^+ , which addresses the fundamental question of hydrogen scrambling, has been investigated previously by charge exchange,²¹ mass spectrometry,^{13,17,19,20} and photoelectron-photoion coincidence (PEPICO)²² techniques. In a similar energy range above the ground state of CH_3SH^+ , the major product ions observed in the charge exchange and photoionization studies are in agreement. The products include CH_2SH^+ (CH_3S^+), CH_2S^+ , HCS^+ , HS^+ , and CH_3^+ .¹⁹⁻²²

In this study the absolute total cross sections for the product ions $\text{CH}_2\text{SH}^+(\text{CH}_3\text{S}^+)$, CH_2S^+ , 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 $\text{CH}_3^+ + \text{SH}$, are significantly different from those measured in previous photoionization and charge exchange studies. Since the $\text{CH}_3^+ + \text{SH}$ channel is not among the most stable product channels, this observation shows that the collision-induced dissociation of CH_3SH^+ is non-statistical. The high yield for $\text{CH}_3^+ + \text{SH}$ 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_3SH^+ , and to weak couplings between the low frequency C-S and high frequency C-H stretching vibrational modes of CH_3SH^+ . The differences in excitation mechanisms for CH_3SH^+ via collision activation, photoionization, and charge exchange are responsible for the different fragment ion distributions from CH_3SH^+ 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 ($X^1\Sigma^+$), H_2 ($X^1\Sigma_g^+$), and HD ($X^1\Sigma^+$) 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 experiments³¹⁻³³ on Ne, Ar, Kr, and O_2 , 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 ≈ 17.7 eV, the processes involved remain inefficient for routine experimentation²⁴⁻²⁷ compared with the ease in tuning VUV synchrotron radiation.

Carbonyl sulfide (OCS) is a linear molecule with the dominant ground state electronic configuration³⁴ $...(6\sigma)^2 (7\sigma)^2 (8\sigma)^2 (9\sigma)^2 (2\pi)^4 (3\pi)^4 X^1\Sigma^+$. Taking into account the spin-orbit interaction, the removal of an electron from the highest occupied 3π -orbital (mostly having the sulfur 3p character)³⁴ results in the formation of the $OCS^+(X^2\Pi_{3/2,1/2})$ 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 HeI^{45-48} and threshold photoelectron (TPE) spectroscopy.^{44,49} High resolution spectroscopic data for the $OCS^+(X^2\Pi_{3/2,1/2})$ states have been obtained recently by laser ion photodissociation techniques.⁵⁰

The VUV-PFI-PE bands of $OCS^+(X^2\Pi)$ 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) $^2\Pi_{1/2}$ states of OCS^+ were determined to be 11.1831 ± 0.0005 eV and 11.2286 ± 0.0005 eV, respectively, yielding a value of 367 ± 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 ($J=P$) for $J = 1/2, 3/2, 5/2$, and $7/2$ were computed in the energy range of $\approx 4000 \text{ cm}^{-1}$ above the $\text{IE}[\text{OCS}^+(\text{X}^2\Pi_{3/2})]$ for the assignment of the experimental spectrum.

Being the simplest neutral and cationic molecular system, the potential energy surfaces and spectroscopic constants for H_2 and 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 H_2^+ and HD^+ have been obtained at different levels of theory.⁵²⁻⁵⁵

The rotationally resolved PFI-PE spectra of H_2 and HD at a resolution of $\approx 7 \text{ cm}^{-1}$ FWHM (full-width-half-maximum) in the photon energy range of 15.30-18.11 eV were obtained. The rotational transitions for the $\text{H}_2^+(\text{X}^2\Sigma_g^+, v^+=0-18)$ and the $\text{HD}^+(\text{X}^2\Sigma^+, v^+=0-21)$ 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 (ω_e , $\omega_e x_e$, $\omega_e y_e$, $\omega_e z_e$, B_e , and α_e), the internuclear separation (r_e), and the dissociation energy (D_0).

References

1. S. W. Benson, *Chem. Rev.* **78**, 23 (1978).
2. A. Levy, E. L. Merryman, W. T. Reid, *Environ. Sci. Technol.* **4**, 653 (1970).
3. C. F. Cullis, M. F. R. Mulcahy, *Combust. Flame* **18**, 225 (1975).
4. S. Hatakeyama, H. Akimoto, *J. Phys. Chem.* **87**, 2387 (1983).
5. A. A. Turnipseed, S. B. Barone, A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).
6. T. S. Bates, B. K. Lamb, A. Guenther, J. Dignon, and R. E. Stroiber, *J. Atmos. Chem.* **14**, 315 (1992).
7. P. A. Spiro, D. J. Jacob, and J. A. Logan, *J. Geophys. Res.* **97**, 6023 (1992).
8. R. J. Charlson and T. M. L. Wigley, *Sci. Am.* **270**, No. 2, 48 (1994).
9. C. Y. Ng, *Advances in Photochemistry*, **22**, 1 (1997); and references therein.
10. S.-W. Chiu, W.-K. Li, W.-B. Tzeng, and C. Y. Ng, *J. Chem. Phys.* **97**, 6557 (1992).
11. R. H. Nobes, W. J. Bouma, L. Radom, *J. Am. Chem. Soc.* **106**, 2774 (1984).
12. L. A. Curtiss, R. H. Nobes, J. A. Pople, and L. Radom, *J. Chem. Phys.* **97**, 6766 (1992).
13. D. Amos, R. G. Gills, J. L. Occolowitz, and J. F. Pisani, *Org. Mass Spectr.* **2**, 209 (1969).
14. B. G. Keyes and A. G. Harrison, *J. Am. Chem. Soc.* **90**, 5671 (1968); A. G. Harrison, *J. Am. Chem. Soc.* **100**, 4911 (1978).
15. D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Phys. Chem.* **76**, 1030 (1972).
16. S. Cradock and P. A. Whiteford, *J. Chem. Soc. Faraday II*, **68**, 281 (1972).

17. J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *J. Am. Chem. Soc.* **104**, 2931 (1982); J. K. Terlouw, W. Heerma, G. Dijkstra, J. L. Holmes, and P. C. Burgers, *Int. J. Mass Spectrom. Ion Phys.* **47**, 147 (1983); J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burges, *Can. J. Chem.* **61**, 2305 (1983).
18. "Handbook of Helium I Photoelectron Spectra of Fundamental Organic Molecules", edited by K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata (Halsted, New York, 1981).
19. M. E. Akopyan, Y. L. Serhiev, and F. I. Vilesov, *Klim. Vys. Energy* **4**, 305 (1970).
20. R. E. Kutina, A. K. Edwards, J. Berkowitz, *J. Chem. Phys.* **77**, 5508 (1982).
21. B.-Ö. Jonsson and J. Lind, *J. Chem. Soc. Faraday Trans. II* **70**, 1399 (1974).
22. S. Nourbakhsh, K. Norwood, H.-M. Yin, C.-L. Liao, and C. Y. Ng, *J. Chem. Phys.* **95**, 945 (1991).
23. Y.-S. Cheung, C.-W. Hsu, J.-C. Huang, W.-K. Li, and S.-W. Chiu, *Int. J. Mass. Spectrom. Ion Proc.* **159**, 13 (1996).
24. C. Y. Ng, in "The Structure, Energetics, and Dynamics of Organic Ions", edited by T. Baer, C. Y. Ng, and I. Powis, Wiley Series in Ion Chemistry and Physics (Wiley, Chichester, 1996), Chap. 2, p. 35; and references therein.
25. F. Merkt and T. P. Softley, in "High Resolution Laser Photoionization and Photoelectron Studies", edited by I. Powis, T. Baer, and C. Y. Ng, *Wiley Series in Ion Chem. and Phys.* (Wiley, Chichester, 1995), p. 119.
26. J. W. Hepburn, in "Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters", edited by C. Y. Ng (World Scientific, Singapore, 1991), p. 435.
27. J. W. Hepburn, in "Laser Techniques in Chemistry", edited by A. Meyers and T. R. Rizzo (Wiley, New York, 1994).
28. C.-W. Hsu, M. Evans, P. Heimann, K. T. Lu, and C. Y. Ng, *J. Chem. Phys.* **105**, 3950 (1996).
29. P. Heimann, M. Koike, C.-W. Hsu, M. Evans, K. T. Lu, C. Y. Ng, A. Suits, and Y. T. Lee, *Rev. Sci. Instrum.*, **68**, 1945 (1997).
30. M. Evans, C. Y. Ng, C.-W. Hsu, and P. Heimann, *J. Chem. Phys.* **106**, 978 (1997).
31. C.-W. Hsu, M. Evans, P. A. Heimann, and C. Y. Ng, *Rev. Sci. Instrum.*, **68**, 1694 (1997).
32. C.-W. Hsu, P. A. Heimann, M. Evans, S. Stimson, T. Fenn, and C. Y. Ng, *J. Chem. Phys.* **106**, 8931 (1997).
33. C.-W. Hsu, P. A. Heimann, M. Evans, S. Stimson, and C. Y. Ng, *Chem. Phys.*, accepted.
34. M.-J. Hubin-Franskin, J. Delwiche, P.-M. Guyon, M. Richard-Viard, M. Lavollée, O. Dutuit, J.-M. Robbe, and J.-P. Flament, *Chem. Phys.* **209**, 143 (1996).

35. M. Horani, S. Leach, and J. Rostas, *J. Chim. Phys.* **63**, 1015 (1966).
36. J. P. Maier and F. Thommen, *Chem. Phys.* **51**, 319 (1980).
37. D. L. Judge and M. Ogawa, *J. Chem. Phys.* **51**, 2035 (1969).
38. D. L. Judge and L. C. Lee, *Int. J. Mass Spectrom. Ion Proc.* **17**, 329 (1975).
39. C. Y. R. Wu, T. S. Yih, and D. L. Judge, *Int. J. Mass Spectrom. Ion Proc.* **68**, 303 (1986).
40. M. Tsuji and J. P. Maier, *Chem. Phys. Lett.* **137**, 421 (1987).
41. M. Ochsner, M. Tsuji, and J. P. Maier, *Chem. Phys. Lett.* **115**, 373 (1985).
42. R. Kakoschke, U. Boesl, J. Herman, and E. W. Schlag, *Chem. Phys. Lett.* **119**, 467 (1985).
43. Y. Ono, E. A. Osuch and C. Y. Ng, *J. Chem. Phys.* **74**, 1645 (1981).
44. J. Delwiche, M. J. Hubin-Franskin, G. Caprace, P. Natalis, and D. Roy, *J. Electron Spectrosc. Relat. Phenom.* **21**, 205 (1980).
45. C. R. Brundle and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.* **2**, 195 (1969).
46. A. W. Potts and G. H. Fattahallah, *J. Phys.* **B13**, 2545 (1980).
47. B. Kovac, *J. Chem. Phys.* **78**, 1684 (1983).
48. L.-S. Wang, J. E. Reutt, Y. T. Lee, and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.* **47**, 167 (1988).
49. R. Frey, B. Gotchev, W. B. Peatman, H. Pollak, and E. W. Schlag, *Int. J. Mass Spectrom. Ion Phys.* **26**, 137 (1978).
50. R. Weinhauf and U. Boesl, *J. Chem. Phys.* **101**, 8482 (1994).
51. K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules" (Van Nostrand, New York, 1979).
52. G. Hunter, A. W. Yau, and H. O. Pritchard, *At. Data Nucl. Data Tables* **14**, 11 (1974).
53. C. L. Beckel, B. D. Hansen, and J. M. Peek, *J. Chem. Phys.* **53**, 3681 (1970).
54. G. Hunter and H. O. Pritchard, *J. Chem. Phys.* **46**, 2153 (1967).
55. L. Wolniewicz and J. D. Poll, *Mol. Phys.*, **59**, 953-964, (1986).
56. D. M. Bishop and L. M. Cheung, *Phys. Rev. A* **16**, 640 (1977).
57. D. M. Bishop, *Mol. Phys.* **28**, 1397 (1974).
58. D. M. Bishop and L. M. Cheung, *J. Chem. Phys.* **75**, 3155 (1981).
59. P. M. Dehmer and W. A. Chupka, *J. Chem. Phys.* **65**, 2243 (1976).
60. P. M. Dehmer and W. A. Chupka, *J. Chem. Phys.* **79**, 1569 (1983).

GENERAL CONCLUSIONS

We have examined the CID reaction of $\text{CH}_3\text{SH}^+ + \text{Ar}$ in the $E_{\text{c.m.}}$ 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 $\text{CH}_3^+ + \text{SH}$ 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 $\text{H}-\text{CH}_2\text{SH}^+$ bond, this observation clearly indicates non-statistical behavior in the CID of $\text{CH}_3\text{SH}^+(1^2\text{A}'')$. 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 $\text{OCS}^+(\text{X}^2\Pi)$, weaker Renner-Teller structures were observed for the first time. Accurate theoretical predictions for the Renner-Teller levels of the $\text{OCS}^+(\text{X}^2\Pi)$ 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 $\text{H}_2^+(\text{X}^2\Sigma_g^+, v^+=0-18)$ and $\text{HD}^+(\text{X}^2\Sigma^+, v^+=0-21)$ were obtained. The analysis of which provided the rovibronic energies, the vibrational constants (ω_e , $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$), the rotational constants (B_{v^+} , D_{v^+} , B_e , and α_e), 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.

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