①

AD-A285 151

ON PAGE

Form Approved
OMB No. 0704-0188

Public re
gatheri
collectio
Davis Hi

1 hour per response, including the time for reviewing instructions, searching existing data sources,
ollection of information. Send comments regarding this burden estimate or any other aspect of this
ington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson
agement and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AG

8/9/94

3. REPORT TYPE AND DATES COVERED
Final Report 11/1/90-4/30/94

4. TITLE AND SUBTITLE
Spectroscopy of the Transition State Region in Hydrogen Transfer Reactions

5. FUNDING NUMBERS

6. AUTHOR(S)
Daniel M. Neumark

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California
Sponsered Projects Office
336 Sproul Hall
Berkeley, CA 94720

DTIC
ELECTE
SEP 23 1994
S B D

8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR-TR- 94 0553

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of Scientific Research /NL
Chemistry and Materials Science Research
Bolling Air Force Base, D.C. 20332-6448
Dr. Berman

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-91-0084

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; Distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The research supported by this grant is centered on probing the spectroscopy and dynamics of a variety of transient species using two anion photodetachment techniques: photoelectron spectroscopy and zero electron kinetic energy spectroscopy. Most of the research effort was devoted to the transition state spectroscopy of reactions involving H atom abstraction by fluorine atoms. We have also measured electron affinities of several radicals, and have characterized several of the excited electronic states of O_3 for the first time. Finally, we have begun studying weakly bound clusters in which a halide ion is solvated by a known number of CO_2 molecules

14. SUBJECT TERMS
negative ions, transition state, photoelectron spectroscopy

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UNLIMITED (SAR)

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 3

15 AUG 1994

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

Final Technical Report

The research supported by this grant is centered on probing the spectroscopy and dynamics of a variety of transient species using two anion photodetachment techniques: photoelectron spectroscopy and zero electron kinetic energy spectroscopy. Most of the research effort was devoted to the transition state spectroscopy of reactions involving H atom abstraction by fluorine atoms. We have also measured electron affinities of several radicals, and have characterized several of the excited electronic states of O_3 for the first time. Finally, we have begun studying weakly bound clusters in which a halide ion is solvated by a known number of CO_2 molecules.

A) Experimental Techniques

Two instruments are used in these studies. In both, a beam of cold negative ions is produced by crossing a pulsed molecular beam of the appropriate precursors with the beam from an electron gun. The ions are mass-selected and then photodetached with a pulsed laser. In the photoelectron spectrometer, a fixed-frequency laser is used for photodetachment, and the kinetic energy of the ejected photoelectrons is measured via time-of-flight. The resulting spectrum maps out the electronic and vibrational structure of the neutral species, and the intensity distribution is sensitive to geometry changes between the anion and neutral. The energy resolution of this instrument is 8-10 meV, which is sufficient to resolve at least some vibrational structure in most of the systems we study. In the zero electron kinetic energy (ZEKE) spectrometer, the anions are photodetached with a tunable laser, and only those photoelectrons produced with nearly zero kinetic energy are detected. By plotting this electron signal vs. the laser frequency, we obtain, in principle, the same information as the photoelectron spectrum (PES), but the resolution of the ZEKE spectrometer is much higher, about 0.3-0.4 meV.

Since the photoelectron spectrometer is considerably easier to use, our typical plan of action is to obtain the PES for a many anions of interest, and to look at a subset of these at higher resolution with the ZEKE spectrometer. This combination of techniques is unique to our laboratory and gives us unprecedented flexibility in studying anion photodetachment.

B) Transition State Spectroscopy

In these experiments, the transition state region for the reaction $A + BC \rightarrow AB + C$ is accessed by photodetachment of the stable negative ion ABC^-. Provided that the anion geometry is close to that of the neutral transition state, the anion photoelectron spectrum probes the vibrational spectroscopy and dissociation dynamics of the unstable ABC complex. This provides an invaluable probe of the transition state region for the reaction, arguably the most important part of a reactive potential energy surface.

Our research in this area over the last three years has focused on hydrogen transfer reactions of F atoms. Three of these were "heavy + light-heavy" reactions, in which an H atom is transferred between two much heavier species:

3977

$$F + OH \rightarrow HF + O$$
$$F + CH_3OH \rightarrow HF + CH_3O$$
$$F + C_2H_5OH \rightarrow HF + C_2H_5O$$

The transition states for these reactions are probed by photoelectron spectroscopy of OHF^-, CH_3OHF^-, and $C_2H_5OHF^-$, respectively. Each photoelectron spectrum shows resolved vibrational structure assigned to the "asymmetric stretch", that is, the vibrational mode of the transition state in which the H atom is vibrating between the F and O atoms. There are no high quality potential energy surfaces for these reactions to which we can compare our results, but simulations of the OHF^- photoelectron spectrum on model potential energy surfaces indicated how these surfaces should be modified to better match the experiments.

The other reaction we have studied is the very fundamental reaction:

$$F + H_2 \rightarrow HF + H$$

This reaction has been the subject of innumerable experimental and theoretical investigations since the dawn of reaction dynamics. Nonetheless, there has been considerable uncertainty regarding some very basic features of its potential energy surface, namely the barrier height and the nature of the FHH bend potential. Our photoelectron spectrum of FH_2^- reveals a progression in the FHH bending mode, and since the ion is linear, this means the transition state is bent. While our experimental work was being carried out, a new *ab initio* potential energy surface was calculated for this reaction, and exact quantum mechanical simulations on this new surface show excellent agreement with our spectrum. Hence it appears that this long-standing problem in chemical dynamics has been solved.

C) Studies of Radicals by Anion Photoelectron Spectroscopy

We have also performed several "conventional" photoelectron spectroscopy experiments in which anion photodetachment produces a stable neutral species, typically a free radical. The maximum energy of our photodetachment laser is 5.822 eV, considerably higher than that available from the cw lasers more commonly used in photoelectron spectrometers, so we can study species with high electron affinities as well as excited states of radicals with lower electron affinities. We have obtained the first accurate electron affinities for the CN, NCO, and NCS radicals. Moreover, our photoelectron spectrum of O_3^- yielded the energies of several low-lying states of O_3 that had not been identified previously. This work showed that O_3 has no excited states below the O_2 + O dissociation limit; such states had been postulated in the past to explain some of the atmospheric chemistry of O_3.

D) Solvation of Halide Ions in Size-selected Clusters

Since anions are easily mass-selected, photodetachment of anion clusters offers a powerful means of studying the stepwise solvation of a negative ion. The evolution of the photodetachment spectrum with cluster size enables one, in principle, to track the spectroscopy of an anion from the isolated molecule to condensed phase limits. To this end, we have measured the photoelectron spectrum of the clusters $I^-(CO_2)_{n=1-13}$ and the ZEKE spectrum of I^-CO_2. The "stepwise solvation energies" obtained from the photoelectron spectrum indicate that the first solvation shell occurs for nine CO_2 molecules surrounding the I^- anion. The vibrational structure in these spectra shows that the interaction between the anion and CO_2 is sufficient to distort the CO_2 by several degrees from linearity. The higher resolution ZEKE spectrum reveals the splitting of the I $^2P_{3/2}$ electronic state in the neutral $I \cdot CO_2$ complex, and it also yields vibrational frequencies for the low frequency C-I stretching modes in the anion and neutral. These studies are continuing with other anion chromophores and solvating species.

COMPLETED PROJECT SUMMARY

TITLE: Spectroscopy of the Transition State Region in Hydrogen Transfer Reactions

PRINCIPAL INVESTIGATOR: Daniel M. Neumark

DATES: November 1, 1990 - April 30, 1994

CONTRACT/GRANT NO: AFOSR-91-0084

SENIOR RESEARCH PERSONNEL: none, other than P.I.

JUNIOR RESEARCH PERSONNEL: D. W. Arnold, C. C. Arnold, S. E. Bradforth, E. H. Kim, R. B. Metz, G. Reiser, I. Yourshaw, A. Weaver, C. Xu, Y. Zhao

PUBLICATIONS ACKNOWLEDGING THIS GRANT: See attached

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research program is to use negative ion photodetachment as a means of investigating a variety of transient species which are of fundamental chemical interest and which cannot be studied by other means. The major component of this research is the study of transition states in chemical reactions. Here the transition state for a neutral reaction is accessed by photodetachment of a stable negative ion similar in structure to the neutral transition state. The resulting photoelectron spectrum probes the geometry and dissociation dynamics of the transition state. Our work during the last three years has focused on reactions of the type $F + HB \rightarrow HF + B$ (B=H, OH, CH_3O, C_2H_5O). While all of these studies yielded resolved vibrational structure associated with the neutral transition state, the most successful work was performed on the $F + H_2$ reaction, which was studies by photoelectron spectroscopy of FH_2^-. The spectrum established that the neutral transition state is bent, and a detailed comparison with theory indicates that an accurate potential energy surface for this reaction has finally been developed.

Another component of this research program is to investigate radicals and clusters via the same techniques used to study transition states. To this end, we have measured the electron affinities of CN, NCO, and NCS, and have used photoelectron spectroscopy of O_3^- to make the first experimental identification of several low-lying electronic states of O_3. Finally, we have measured photoelectron spectra and higher resolution zero electron kinetic energy (ZEKE) spectra of I- solvated by known numbers of CO2 molecules in order to examine how stepwise solvation affects the I^- and I chromophores.

LIST OF PUBLICATIONS
AFOSR-91-0084

1. S. E. Bradforth, D. W. Arnold, R. B. Metz, A. Weaver, and D. M. Neumark, "Spectroscopy of the Transition State: Hydrogen Abstraction Reactions of Fluorine," J. Phys. Chem. 95, 8066 (1991).

2. J. Z. H. Zhang, W. H. Miller, A. Weaver, and D. Neumark, "Quantum Reactive Scattering Calculations of Franck-Condon Factors for the Photodetachment of H_2F^- and D_2F^- and Comparisons with Experiment," Chem. Phys. Lett. 182, 283 (1991).

3. D. M. Neumark, "Negative Ion Photodetachment as a Probe of the Transition State Region: The I + HI Reaction," in Advances in Molecular Vibrations and Collision Dynamics, Vol. IA, ed. J. M. Bowman, (JAI Press, Greenwich, 1991) pp. 165-185.

4. A. Weaver and D. M. Neumark, "Negative Ion Photodetachment as a Probe of Bimolecular Transition States: The F + H_2 Reaction," Faraday Discuss. Chem. Soc. 91, 5 (1991).

5. R. B. Metz, S. E. Bradforth, and D. M. Neumark, "Transition State Spectroscopy of Bimolecular Reactions Using Negative Ion Photodetachment," Adv. Chem. Phy. 81, 1 (1992).

6. R. B. Metz and D. M. Neumark, "Adiabatic Three-Dimensional Simulations of the IHI^-, $BrHI^-$ and $BrHBr^-$ Photoelectron Spectra," J. Chem. Phys. 97, 962 (1992).

7. D. M. Neumark, "Transition State Spectroscopy of Bimolecular Chemical Reactions," Ann. Rev. Phys. Chem. 43, 153 (1992).

8. D. W. Arnold, S. E. Bradforth, E. H. Kim, and D. M. Neumark, "Anion Photoelectron Spectroscopy of Iodine-Carbon Dioxide Clusters," J. Chem. Phys. 97, 9468 (1992).

9. D. M. Neumark, "Transition State Spectroscopy via Negative Ion Photodetachment," Accts. Chem. Res. 26, 33 (1993).

10. S. E. Bradforth, E. H. Kim, D. W. Arnold, and D. M. Neumark, "Photoelectron Spectroscopy of CN^-, NCO^-, and NCS^-," J. Chem. Phys. 98, 800 (1993).

11. Y. Zhao, C. C. Arnold, and D. M. Neumark, "Study of the $I{\bullet}CO_2$ van der Waals Complex by Threshold Photodetachment Spectroscopy of I^-CO_2," J. Chem. Soc. Far. Trans. 89, 1449 (1993).

12. S.E. Bradforth, D.W. Arnold, D.M. Neumark, and D.E. Manolopoulos, "Experimental and Theoretical Studies of the F+H_2 Transition State Region via Photoelectron Spectroscopy of FH_2^-," J. Chem. Phys. 99, 6345 (1993).

13. D. E. Manolopoulos, K. Stark, H.-J. Werner, D. W. Arnold, S. E. Bradforth, and D. M. Neumark, "The Transition State of the F+H_2 Reaction," Science 262, 1852 (1993).

14. D. W. Arnold, C. Xu, E. H. Kim, and D. M. Neumark, "Study of Low-Lying Electronic States of Ozone by Anion Photoelectron Spectroscopy of O_3^-," J. Chem. Phys. 101, 912 (1994).