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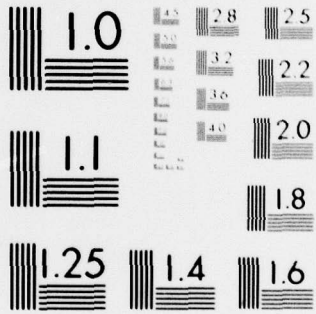
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This is the final report for Grant AFOSR 75-2770. Advances in chemical dynamics are not usually achieved by a single experiment but rather by a blend of informations using a variety of techniques. As a consequence, the results of this research project may be classified in three separate categories: a) preparation of and experiments with electronically excited atoms and molecules; b) measurements of kinetic energy thresholds for ion-pair production from molecular collisions, with subsequent derivation of molecular binding energies and electron affinities; and c) thermal energy chemi-ionization processes.

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In experiments of type a) electronically excited sodium was used to promote the chemi-ionization reaction with O_2 and SO_2 . Two photon ionization of Na_2 and Li_2 was also studied in order to investigate laser selectivity. Isotope fractionation is observed in the case of Li_2 using a single mode Ar^+ ion laser. Category b) type measurements have been performed on HNO_3 , PCl_3 , PBr_3 , PCl_2Br , PBr_2Cl , CO_2 , SO_2 , SO_3 , Cl_2 , Br_2 , I_2 and CF_3I . Thermal energy chemi-ionization reactions of many of the alkali dimers with the halogens and interhalogens as well as UF_6 , MoF_6 and WF_6 were observed.

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AFOSR-TR- 79 - 0942

STUDIES OF IONIZATION PROCESSES

May, 1979

FINAL REPORT

AFOSR-75-2770

August 1, 1975 to September 30, 1978

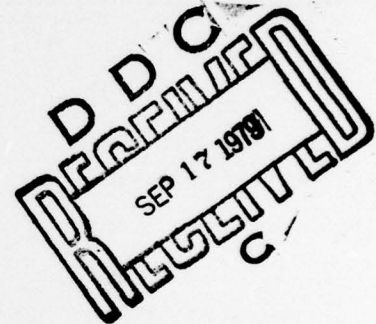
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**Erhard W. Rothe
Principal Investigator**

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Prepared by the

**Research Institute for Engineering Sciences
College of Engineering
Wayne State University
Detroit, Michigan 48202**

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ABSTRACT

This is the final report for Grant AFOSR 75-2770. Advances in chemical dynamics are not usually achieved by a single experiment but rather by a blend of informations using a variety of techniques. As a consequence, the results of this research project may be classified in three separate categories: a) preparation of and experiments with electronically excited atoms and molecules; b) measurements of kinetic energy thresholds for ion-pair production from molecular collisions, with subsequent derivation of molecular binding energies and electron affinities; and c) thermal energy chemi-ionization processes.

In experiments of type a) electronically excited sodium was used to promote the chemi-ionization reaction with O_2 and SO_2 . Two photon ionization of Na_2 and Li_2 was also studied in order to investigate laser selectivity. Isotope fractionation is observed in the case of Li_2 using a single mode Ar^+ ion laser. Category b) type measurements have been performed on HNO_3 , PCl_3 , PBr_3 , PCl_2Br , PBr_2Cl , CO_2 , O_3 , SO_2 , SO_3 , Cl_2 , Br_2 , I_2 and CF_3I . Thermal energy chemi-ionization reactions of many of the alkali dimers with the halogens and interhalogens as well as UF_6 , MoF_6 and WF_6 were observed.

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A. INTRODUCTION

This is the final report for AFOSR Grant 75-2770. This program was jointly supported by AFOSR and ARO. In doing this work, we attempted to maintain a balance between a) research that might be classified as essentially pure (in scientific areas, however, which are related to DoD missions) and b) similar problems which involve atomic and molecular species that are directly involved in systems of DoD interest. As an example of the former, the entire field of ionization processes is of DoD interest, primarily because the charge balance in the atmosphere (both normal and disturbed) determines the ability of electromagnetic signals of various frequencies to propagate through it. We have done a variety of ionization studies which contribute to further understanding of these properties. An example of more directly relevant research are our measurements of the electron affinities and other negative ion properties of such species as O_2 , O_3 , NO_2 , OH , NO_3 , HNO_3 , etc.

The experiments supported under this grant were all performed via various combinations of molecular beam and laser techniques in order to more fully exploit the advantages of each.

The three main categories of experiment were:

1. Lasers were used to produce and characterize atoms in specific electronic states or molecules in specific electronic vibrational and/or rotational states. We performed two photon ionization experiments on alkali dimers and observed ionization from specific vibrational and rotational states. We also prepared $Na(3p)$ and used it to promote the collisional ionization of O_2 and SO_2 . In both these experiments, energy for ionization was produced wholly or partially from photons. It is expected

that two photon ionization may be used to characterize the products of chemical reactions while electronically excited atomic states will be useful in further understanding chemical reactivity.

2. In addition, we continued our well-established program for determining the electron affinities and bond strengths for negative molecular ions. This was done with a variety of molecules including a number of important atmospheric species. Molecular beams in the electron-volt kinetic energy region were used. In this case translational motion supplied the energy for the chemi-ionization process.
3. Several examples of chemi-ionization at thermal energies, where the energy for ion productions comes from the energy released in new bond formation, were also found. These occur in the reactions of the alkali dimers with the halogens, IBr, ICl, MoF₆, WF₆ and UF₆.

All of the techniques used and systems studied have focused on the role of energy in chemical reactivity. We have examined the effect of translational, electronic and vibrational-rotational energy on the ionization as this is the simplest type of chemical change. The stability and accessibility of product states is also important for understanding chemical reactivity. Our results for electron affinities and bond strength for a variety of systems are summarized in Table 1.

B. DISCUSSION AND RESULTS

In order that one may more fully understand the goals and scope of our program we will briefly discuss and summarize the published work. We will also attempt to provide the motivation for it and the relationship between the various areas.

1. Preparation of excited atoms or molecules in specific quantum states.

One of the most important goals in reaction dynamics is the theoretical prediction of probabilities of chemical reactions or other physical processes. Although macroscopic rate constants are usually determined by bulk experiments and tabulated for most practical applications, they are very difficult to compare with theory.

The job of obtaining a sufficient number of relevant rate constants and their temperature dependence so as to be useful in predicting practical situations is usually difficult. The value of microscopic rate constants has been recognized for many years. These more detailed building blocks are very useful in gaining an understanding of a variety of collision processes. However, their use is usually limited to situations where the internal states of both reagents and products can be characterized by a temperature. Even then, in order to compare such theories with experiment, it is usually necessary to compute a large number of constituent processes to obtain a rate constant. This is so because the microscopic rate constant is an average value resulting from many collisions which have a large range of initial quantum states, kinetic energies, impact parameters and mutual orientation of the molecules. It is unsatisfactory to undergo this calculational labor to obtain only two parameters, perhaps a rate constant and its temperature dependence, since it is difficult to attribute deviations to one of the specific factors and thus makes the exercise less meaningful.

Molecular beam studies have contributed to unraveling this situation, since the initial and final relative kinetic energies have been controlled and measured, respectively. Some information about the initial impact parameters has also been deduced from the angular distributions of reactive and non-reactive collisions.

Such studies have shown that, frequently, products of single collisions cannot be described by temperatures, even within a particular degree of freedom. Accordingly, it becomes appropriate to study the individual cross sections for passing from specified initial to final quantum states.

With the advent of laser technology, it is now possible, in addition to the advances mentioned above, to start reactions with molecules which have definite electronic, vibrational or rotational states, or with atoms in a definite electronic state. Likewise, the internal energy distributions of the product states may be deduced with lasers. With polarized light, inferences may be made about the relative orientation of the two species.

We have been engaged in molecular beam research for many years and in the past two years we have started to use lasers as tools for use with the beam techniques, as have others. This provides a slightly different point of view from laser workers who have found molecular beams a useful tool. The latter normally are not interested in subsequent collision studies. With either point of view, however, in addition to the virtues of molecular beams cited above, there are two additional advantages: a) if a molecular beam crosses a laser beam at right angles, the Doppler shift of frequencies becomes vanishingly small. This means that a very narrow laser frequency width can be used for excitation, so that a de-

sired frequency can be saturated; and b) there is no collisional relaxation to disturb the newly formed excited molecules.

Our initial studies on chemi-ionization induced by electronic excitation has been with Na atoms as the D states are easily reached with existing laser technology as described in the paper below:

Volume 51, number 1

CHEMICAL PHYSICS LETTERS

1 October 1977

NEAR-THRESHOLD IONIZATION OF EXCITED Na(3^2P) BY COLLISIONS WITH O₂ AND SO₂ [†]

Erhard W. ROTHE, B.P. MATHUR

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and

Gene P. RECK

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Received 20 June 1977

Positive ions are produced in crossed beams of eV-range sodium atoms and thermal O₂ or SO₂. Resonant laser light is used to excite a small fraction of the sodium to Na*($3^2P_{1/2}$ or $3^2P_{3/2}$). Product ions are observed at lower reagent kinetic energies with Na⁺ than with Na.

The major result of these studies was that electronic excitation could be used to promote the chemi-ionization processes.

Two photon ionization of alkali molecules may also be easily studied because a) these molecules have sufficiently low-lying electronic states that they can be excited with a single photon in the convenient range of visible ϵ -light obtainable from argon-ion lasers, b) their vibrational and rotational spacings are such that they can be excited exclusively to single upper state v, J levels, c) the specific transitions excited by the argon-ion laser lines for the molecules Li₂ and Na₂ have been identified so that this

upper state level is known, d) the number of argon-ion laser lines is sufficient that the molecules may be prepared with a wide range of vibrational and rotational energies and, consequently, the dissociation energy may be varied from maximum to almost zero, and finally, e) the same laser frequency that excites the molecules can also be used to ionize the excited state, so that the excited state population can be monitored by two-photon ionization.

We have already excited, and ionized, a few such states in Li_2 and Na_2 and accounts of these experiments are described in the four papers below:

2518 J. Chem. Phys. 68(5), 1 Mar. 1978

0021-9606/78/6805-2518\$01.00

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Two-photon ionization of Na_2 by an Ar^+ laser^{a)}

B. P. Mathur and Erhard W. Rothe

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 13 September 1977)

Volume 53, number 1

CHEMICAL PHYSICS LETTERS

1 January 1978

ISOTOPE FRACTIONATION IN TWO-STEP PHOTOIONIZATION OF Li_2 [☆]

Erhard W. ROTHE, B.P. MATHUR

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202, USA

and

Gene P. RECK

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Received 12 September 1977

A cw argon-ion laser beam intersects a thermal-energy lithium-beam. Sequential two-photon ionization of Li_2 is observed. Li_2^+ ions are formed by most of the available laser lines. Large isotope fractionations result from this process.

TWO-PHOTON IONIZATION OF Li_2 :
ISOTOPIC SEPARATION AND DETERMINATION OF $I_P(\text{Li}_2)$ AND $D_e(\text{Li}_2^+)^*$

B. P. MATHUR, Erhard W. ROTHE

*Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University,
Detroit, Michigan 48202, USA*

Gene P. RECK

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

and

Allan J. LIGHTMAN

*Department of Electrical and Computer Engineering, Wayne State University,
Detroit, Michigan 48202, USA*

Received 13 February 1978

Complete isotope separation is achieved by two-photon ionization of Li_2 by a single mode Ar^+ laser. With the use of two Ar^+ lasers, the ionization potential of Li_2 is found to be 5.174 ± 0.013 eV, and the dissociation energy $D_e(\text{Li}_2^+)$ to be 1.274 ± 0.019 eV.

2262

J. Chem. Phys. 69(5), 1 Sept. 1978

0021-9606/78/6905-2262\$01.00

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Calculated transitions in Li_2 isotopes at argon laser frequencies

Allan J. Lightman

*Department of Electrical and Computer Engineering and Research Institute for Engineering Sciences,
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B. P. Mathur

*Research Institute for Engineering Sciences, Wayne State University, Detroit, Michigan 48202
(Received 29 March 1978)*

These studies demonstrate the selectivity of laser excitations particularly for the isotopes of Li. In the future we hope to use this selectivity to probe the internal state distributions of product molecules using two-photon ionization techniques as developed and demonstrated here.

2. Electron affinities.

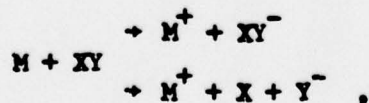
An understanding of complex chemical systems in which energy deposition and flow are important, such as in plasma, atmospheric chemistry, combustion,

flames and lasers, involves the knowledge of the energetics of ionic species as well as their reactions with neutral species. In many cases, trace impurities may in fact be a major determinant of performance.

Gaseous negative ions have received considerably less attention than have positive ions. Nevertheless, an understanding of the role negative ions play in various chemical processes is of fundamental importance a) in the formation of ions and electrons in the ionosphere (which, in turn, is intimately connected with propagation of electromagnetic radiation at communication frequencies), b) in the production of ions in flames and shocks, c) in fundamental chemical structure problems and in energetics, d) in radiation phenomena, and e) in the use of negative ions in mass spectrometry.

The electron affinities of a wide range of species are needed in order to estimate anion stabilities and map out the energy flow in these complicated systems. Theoretical calculations of the electron affinities of atoms is still considered difficult since electron correlation must be included. The electron affinity of molecular species is even more difficult to calculate exactly and only rather general empirical rules exist as a guide. For the immediate future, direct measurement of the electron affinity is the only course.

In 1969, two papers were published, almost simultaneously, which presented experimental results on processes of the type



where M is an alkali atom and XY may be diatomic or polyatomic. One of these measurements was performed at the FOM Laboratory in Amsterdam,

the other was done by E. W. Rothe in collaboration with Dr. R. K. B. Helbing. These two groups have continued with similar work, and other laboratories have now entered this field. In these experiments, interest is generally focused upon the XY molecules rather than upon the alkali atom. The appeal of these reactions lies in at least two areas, both of which were studied here, and which we plan to continued to study.

The first area is the determination of molecular properties. These reactions have energy-thresholds which lie where the molecular energies predict; i.e., the products do not contain excess kinetic or internal energy, in contrast to behavior frequently observed with photon or electron impact. Accordingly, this approach may be used to measure such molecular parameters as bond energies in neutrals or in negative ions, and to measure electron affinities in atoms, molecules and radicals. This laboratory has been active in developing the relatively complex experiments and computer codes that are required to obtain very precise energies. The particular methods are described in the reports and publications:

The Journal of Chemical Physics, Vol. 62, No. 1, 1 January 1975

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Ionizing collisions of cesium with Cl_2 , Br_2 , and I_2 *

S. Y. Tang, C. B. Leffert, and Erhard W. Rothe

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 9 September 1974)

A crossed molecular beam apparatus is used to study ionizing collisions of energetic cesium atoms with Cl_2 , Br_2 , and I_2 . The cross sections for formation of Cs^+ are reported in the near-threshold region. The experiment combines an energy resolution better than 0.1 eV (FWHM) with a deconvolution procedure. An electron affinity of 2.50 eV is deduced for all three halogens, in good agreement with previous work. In a separate experiment, with cesium energies from threshold to 350 eV, and with much poorer energy resolution, the intensity ratios X^-/X_2^- are obtained. The results can be reasonably explained with an electron jump model. At energies below 30 eV, the observed ratios are in agreement with two other investigators, but between 150-350 eV they are drastically different from work reported from a third. Complementary data recently reported by a fourth group are difficult to reconcile with the present results.

Measurement of electron affinities of O_3 , SO_2 , and SO_3 by collisional ionization

Erhard W. Rothe and S. Y. Tang

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Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 29 November 1974)

The Journal of Chemical Physics, Vol. 64, No. 3, 1 February 1976

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Negative gaseous ions from nitric acid*

B. P. Mathur, Erhard W. Rothe, S. Y. Tang,[†] and Kanwal Mahajan

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 17 October 1975)

The Journal of Chemical Physics, Vol. 65, No. 2, 15 July 1976

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Negative ions from phosphorus halides due to cesium charge exchange*

B. P. Mathur, Erhard W. Rothe, and S. Y. Tang[†]

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 2 March 1976)

An experiment has been conducted in which cesium atoms in the kinetic energy range 2–350 eV collide with phosphorus halides. Parent anions and fragments are formed. Molecular energies are obtained from threshold measurements. The electron affinities for PCl_3 , $POCl_3$, PBr_3 , PCl_2Br , PBr_2Cl , and $POCl_2$ are found to be 0.8, 1.4, 1.6, 1.5, 1.6, and 3.8 eV, respectively. The P–X bond energies for PCl_3 , $POCl_3$, and PBr_3 are 3.3, 3.5, and 2.6 eV, respectively.

Another application of these techniques is to a study of the detailed dynamics of a particular process. An analysis of the chemi-ionization of the freons by Cs using simple surprisal theory reveals that the process is direct rather than statistical as described below:

The Journal of Chemical Physics, Vol. 64, No. 4, 15 February 1976

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Negative ion formation in halocarbons by charge exchange with cesium

S. Y. Tang, B. P. Mathur, and Erhard W. Rothe

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

Gene P. Reck

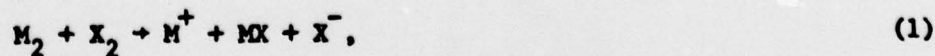
Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 22 September 1975)

A crossed molecular beam apparatus is used to study the formation of anions by charge exchange of fast cesium atoms with a variety of halocarbons. The branching ratios are determined from threshold to 350 eV. Comparison of the spectator stripping and information theoretical models to the data leads to the conclusion that this class of reactions is an example of an ultradirect impulsive mechanism. In the most favorable case, that of CF_3I , we have determined the near threshold relative cross sections for the anions CF_3I^- , I^- , CF_2^- , and IF^- . From these we determine the electron affinity of CF_3I^- to be 1.4 ± 0.2 eV and the bond dissociation energy of CF_3I^- as 0.38 ± 0.1 eV, which disagrees with values obtained in a previous experiment.

3. Chemi-ionization

In addition to the work described above in which ion pairs were formed via the collision of molecules with several electron volts of initial kinetic energy, we also performed measurements in which all the ionization energy was produced by chemical change.

The prototype reaction was that of an alkali dimer with a halogen. A crossed beam apparatus was used to characterize ionic products of thermal energy collisions of alkali dimers M_2 with homonuclear halogens X_2 and with IBr and ICl . All possible alkali-halogen combinations were studied, except Rb_2 with ICl and IBr . The predominant reaction path leading to ions was found to be



when these reactions are exoergic. Reaction via the alternative paths



and



was observed when (1) is endoergic.

For Li_2 and Na_2 , path (1) is energetically forbidden (except with F_2), but paths (2) and (3) are allowed and were found to occur. Some experiments were done with the scientifically interesting UF_6 (electron affinity=6eV) to establish the technologically interesting reaction $Cs + UF_6 \rightarrow Cs^+ + UF_6^-$. These results are described in the papers below:

The Journal of Chemical Physics, Vol. 65, No. 7, 1 October 1976

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Chemi-ionization in thermal energy collisions of K_2 and Cs_2 with halogen molecules*

Erhard W. Rothe and B. P. Mathur

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 24 May 1976)

The Journal of Chemical Physics, Vol. 66, No. 9, 1 May 1977

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3847

Chemi-ionization reactions of alkali dimers with halogen molecules*

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

B. P. Mathur and Erhard W. Rothe

Research Institute for Engineering Sciences and Department of Chemical Engineering, Wayne State University, Detroit, Michigan 48202
(Received 13 October 1976)

A crossed beam apparatus is used to characterize ionic products of thermal energy collisions of alkali dimers M_2 with homonuclear halogens X_2 and with IBr and ICl . All possible alkali-halogen combinations were studied, except Rb_2 with ICl and IBr . When energetically possible the ionic products are mainly M^+ and X^- . When this path is closed two alternative paths are observed. These yield M_2X^+ and X^- , or M^+ and MX_2^- . The results are discussed in the framework of a mechanism proposed by Lin, Whitehead, and Grice. The binding energy of the triatomic ions is computed with the use of an ionic model.

Ionization reactions of metal hexafluorides with alkali atoms and dimers^{a)}

B. P. Mathur and Erhard W. Rothe

Research Institute for Engineering Sciences and Department of Chemical Engineering Wayne State University, Detroit, Michigan 48202

Gene P. Reck

Department of Chemistry, Wayne State University, Detroit, Michigan 48202
(Received 8 February 1977)

Ionization reactions are observed in crossed beams, usually of thermal energy, of alkalis and MoF_6 , WF_6 , and UF_6 . Previous studies have indicated large electron affinities for these hexafluorides, and this is confirmed here. Ionization at thermal energies proceeds with the alkali dimers A_2 for the three hexafluorides, but with alkali atoms A only for UF_6 . Several ionization paths are observed, allowing the deduction of molecular energies. A few experiments are done with eV-range beams. Lower limits for the electron affinities are 4.5, 3.3, 4.9, 4.3, and 1.9 eV for MoF_6 , MoF_5 , WF_6 , UF_6 , and UF_5 , respectively. Possible mechanisms are discussed.

The results of the measurements performed by alkali atom impact and chemi-ionization with alkali dimers are summarized in Table 1. In many cases these measurements provide new information on these systems.

Table 1. Summary of molecular energetics determined by alkali atom impact and dimer reactions:

Molecule	E.A. (eV)	Dissociation Energy (eV)
MoF ₆	>4.5	
MoF ₅	>3.3	
WF ₆	>4.9	D(WF ₅ -F) <5.0
UF ₆	>4.3	
UF ₅	>1.9	
HNO ₃	0.57	D(NO ₃ ⁻ -H) 1.28 D(NO ₂ ⁻ -OH) 0.4
PCl ₃	0.8	D(PCl ₂ -Cl) 3.3
POCl ₃	1.4	D(POCl ₂ -Cl) 3.5
PBr ₃	1.6	D(PBr ₂ -Br) 2.6
PCl ₂ Br	1.5	
PBr ₂ Cl	1.6	
POCl ₂	3.8	
CO ₂	-1.1 > >-2.1	
O ₃	2.14	
SO ₂	1.14	
SO ₃	≥1.70	
Cl ₂	2.5	
Br ₂	2.5	
I ₂	2.5	
CF ₃ I	1.4	D(CF ₃ -I) 2.05 D(CF ₃ -I ⁻) 0.38

C. PERSONNEL SUPPORTED BY GRANT

1) Summer Support for Faculty

The principal investigator, E.W. Rothe, Professor of Engineering and G.P. Reck, Professor of Chemistry have received summer support from this grant. P.K. Rol, Professor of Engineering also worked on this project for a short time in the summer.

2) Post-Doctoral Research Associate

During the entire period of this grant, the research associate was Dr. B.P. Mathur who was supported primarily from this grant. He carried through the difficult portions of the experimental program. He moved to the Georgia Institute of Technology in September, 1978.

3) Graduate Students

Two Ph.D students have been supported by this grant, Mr. Dhruva Sinha and Dr. Gregory Wells. Dr. Wells was granted his degree in June, 1978. The title of his dissertation was "A Molecular Beam Study of Alkali-Halogen Chemi-ionization Reaction Dynamics." Mr. Sinha is now carrying on in the apparatus vacated by Dr. Wells. Mr. Sinha is working toward a degree in Chemical Engineering while Dr. Wells obtained a degree in Chemistry. Wells is now at the University of Utah.

Mr. Kanwal Mahajan worked on this project, primarily doing data analysis of our experiments. He obtained a Masters degree in Chemical Engineering and is now in industry.

Mr. Yoram Hirsch was employed on the project. He is in Electrical Engineering and initially worked for a BS and than as a Masters candidate. His primary contributions were improvement of instrumentation and data handling.

4) Undergraduate Students

In addition to the graduate students, the following undergraduates participated in varied capacities: S. McIntyre, P. Bodner, C. Messner and F. Bean.

D. PUBLICATIONS AND CONFERENCE PRESENTATIONS

Publications in refereed journals credited to AFOSR75-2770, from August 1, 1974 to September 30, 1978.

"Ionizing Collisions of Cesium with Cl_2 , Br_2 and I_2 ," S.Y. Tang, C.B. Leffert, E.W. Rothe and G.P. Reck; *J. Chem. Phys.*, 62, 134 (1975).

"Measurement of Electron Affinities of O_3 and SO_2 and SO_3 by Collisional Ionization," S.Y. Tang, E.W. Rothe and G.P. Reck; *J. Chem. Phys.*, 62, 3829 (1975).

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