

CU Proposal No. 0995.08.1221B

NASA-CR-199435

5018

Annual Status Report and
3rd Year Continuation Budget to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
SOLAR SYSTEM EXPLORATION DIVISION
OFFICE OF SPACE SCIENCE
DR. JAY BERGSTRALH, CODE SLC
NASA HEADQUARTERS
WASHINGTON, DC 20546

P-11

LABORATORY STUDIES OF LOW TEMPERATURE RATE COEFFICIENTS: THE
ATMOSPHERIC CHEMISTRY OF THE OUTER PLANETS

Current NASA Grant: NAGW-2438

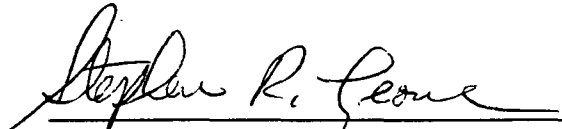
Name and Address of Institution: The Regents of the
University of Colorado
Campus Box 19
Boulder, CO 80309-0019


Research Area: Laboratory Measurements of
Chemical Kinetics, Planetary
Atmospheres Program

Date Submitted: September 30, 1995

Starting Date and Duration: January 1, 1996, 3rd year of grant
for 12 months

Amount:

Principal Investigator: 
Stephen R. Leone, Fellow
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Authorizing Official: 
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Office of Contracts and Grants
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(NASA-CR-199435) LABORATORY
STUDIES OF LOW TEMPERATURE RATE
COEFFICIENTS: THE ATMOSPHERIC
CHEMISTRY OF THE OUTER PLANETS
Annual Report, 1 Jan. - 30 Sep.
1995 (Colorado Univ.) 11 p

N96-10866

Unclas

G3/91 0068084

PROPOSED BUDGET

Institution: The Regents of the
University of Colorado
Campus Box 19
Boulder, CO 80309-0019

Title: Laboratory Studies of Low Temperature
Rate Coefficients: The Atmospheric
Chemistry of the Outer Planets

Principal Investigator: Stephen R. Leone

Duration: 1/1/96 - 12/31/96

01/01/96
12/31/96

Salaries and Wages

Research Associates

To be named - 12.00 Mo. @ \$2333.33/Mo. 28,000

Fringe Benefits

Faculty and Research Associates

Insurance (\$285/Mo.) 3,420

TIAA (9.00%), FICA (6.20%), Medicare (1.45%), 5,330

Wrk. Comp. (1.88%), Unemploy. (0.03%),
and Ann. Ins. (0.47%)

Total Fringe Benefits 8,750

Operating Expenses

Publication Charges 1,200

Supplies and Materials:

Infrared and UV optics 1,100

Sapphire and quartz windows 1,100

Optical mounts 1,100

Liquid nitrogen (\$.40/liq. liter) 1,800

Research compounds 1,600

Excimer laser gases 1,601

Infrared filters 1,100

Instrument Shop Charges @ \$50.00/Hr. 7,000

(Exempt from Indirect Costs)

Total Operating Expenses 17,601

Travel

Domestic Travel 2,126

Total Direct Costs 56,477

Indirect Costs

On Campus: 43.5% of Modified Total Direct Costs, 21,523

predetermined for the period 7/1/94 - 6/30/96.

Per HHS agreement dated 10/20/93.

Total Annual Costs 78,000

Annual Status Report

1 January 1995 - 30 September 1995

The objectives of the research performed under NASA grant NAGW-2438 are to measure low temperature laboratory rate coefficients for key reactions relevant to the atmospheres of Titan and Saturn. These reactions are, for example, $C_2H + H_2$, CH_4 , C_2H_2 , and other hydrocarbons which need to be measured at low temperatures, down to ≈ 150 K. The results of this work are provided to NASA specialists who study modeling of the hydrocarbon chemistry of the outer planets. The apparatus for this work consists of a pulsed laser photolysis system and a tunable F-center probe laser to monitor the disappearance of C_2H . A low temperature cell with a cryogenic circulating fluid in the outer jacket provides the gas handling system for this work. These elements have been described in detail in previous reports.

Several new results are completed and the publications are just being prepared. The reaction of C_2H with C_2H_2 has been measured with an improved apparatus down to 154 K. Figure 1 shows the temperature dependence, which indicates a clear increase in the rate coefficient at the lowest temperatures, most likely because of the long-lived $[C_4H_3]$ intermediate. The fit to all the data in Fig. 1 is $k(T) = 8.6 \times 10^{-16} T^{1.8} \exp[(474 \pm 90)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The capability to achieve the lowest temperatures in this work was made possible by construction of a new cell and addition of a multipass arrangement for the probe laser, as well as improvements to the laser system.

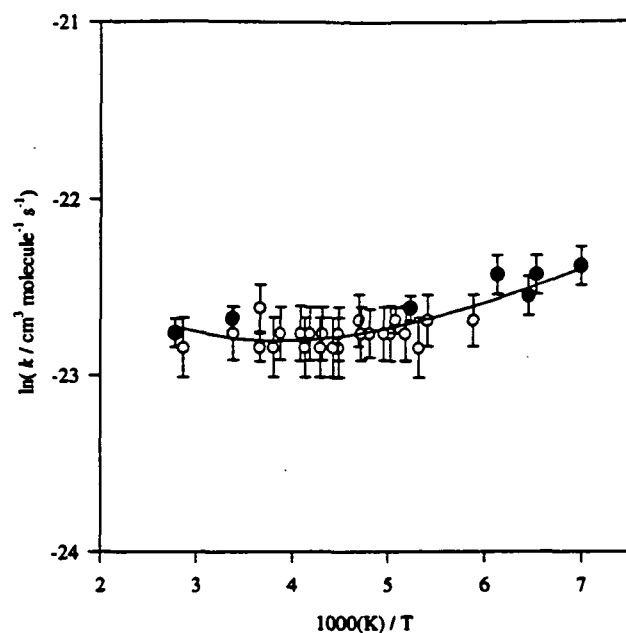


Fig. 1. Arrhenius plot of $C_2H + C_2H_2$. • recent results; o data from Pedersen, Opansky, Leone J. Phys. Chem. 97, 6822 (1993).

The reaction studies of $C_2H + CH_4$ and CD_4 have also been completed. Figure 2 shows an example of the observed rate of removal of C_2H versus $[CH_4]$ and $[CD_4]$ at 359 K, which gives a good idea of the quality of the data.

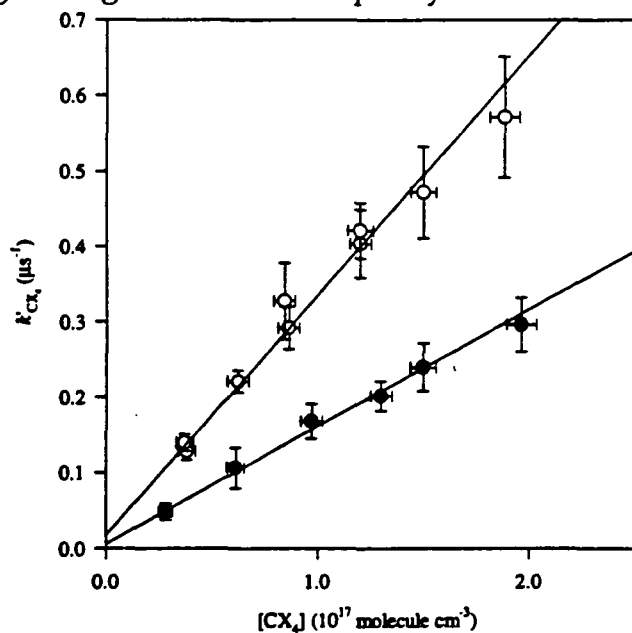


Fig. 2. Plot of observed pseudo first order rate of removal, $k'_{CX} = 1/\tau_{observed}$, for C_2H versus $[CH_4] = o$ and $[CD_4] = \bullet$.

In Fig. 3 is shown an Arrhenius plot for the reactions of C_2H with CH_4 and CD_4 . The best fits are $k(T) = (1.2 \pm 0.1) \times 10^{-11} \exp[(-491 \pm 12)/T]$ for CH_4 and $(8.7 \pm 1.8) \times 10^{-12} \exp[-(650 \pm 61)/T]$, both in $cm^3 \text{ molecule}^{-1} s^{-1}$. The results show a reasonably large activation energy for these reactions and a large isotope effect (2.5 ± 0.2) for CH_4/CD_4 . There is no hint of curvature at the lowest temperatures, most likely because the large activation energy dominates the reaction rate constants.

In a real tour de force experiment, the first low temperature rate coefficients for $C_2H + H_2$ have now been obtained. Figure 4 shows these results along with earlier higher temperature data. There is evidence for some curvature in this plot, which may be indicative of quantum mechanical tunneling.

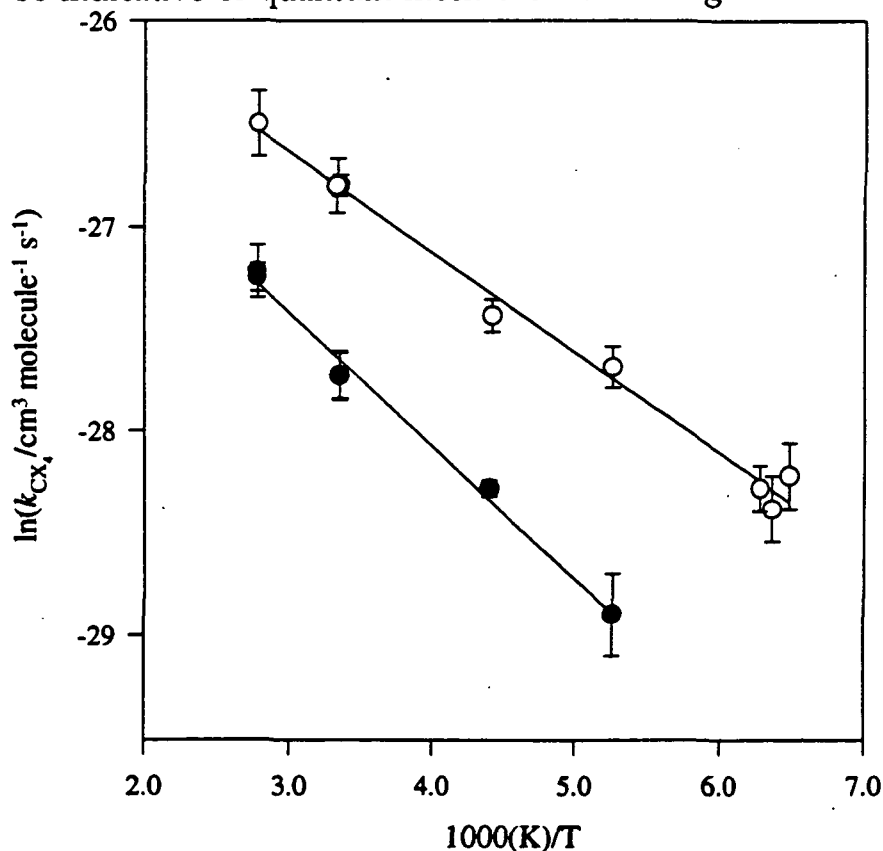


Fig. 3. Arrhenius plot of $C_2H + CH_4 = \circ$ and $CD_4 = \bullet$.

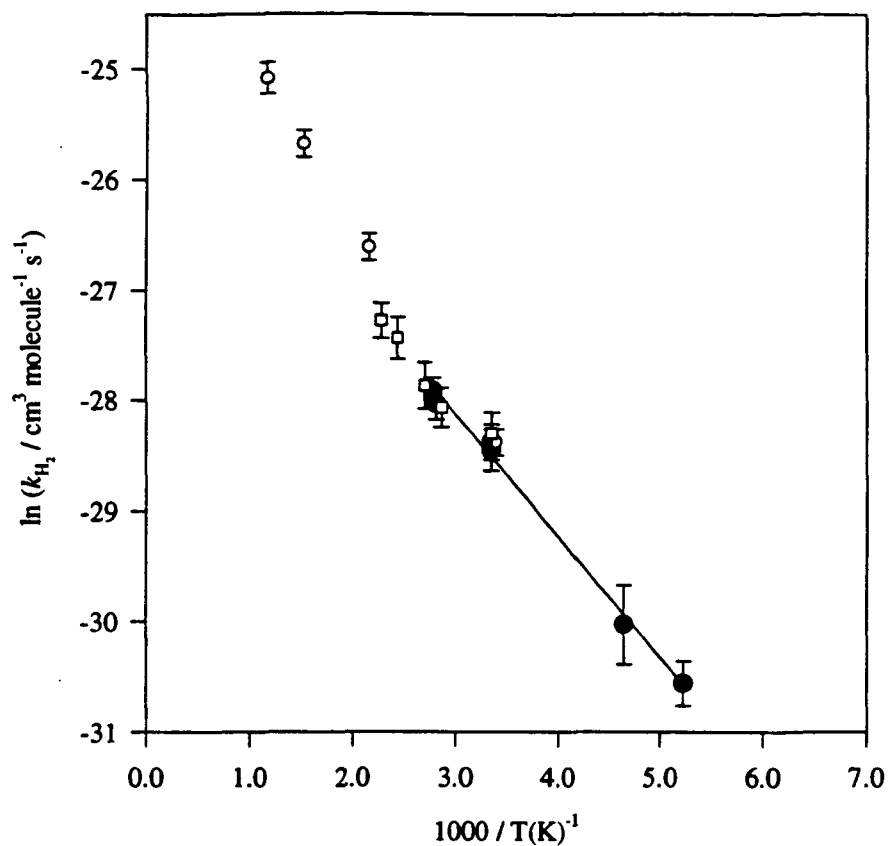


Fig. 4. Arrhenius plot for $C_2H + H_2$. • present results, □ Koshi et al., *J. Phys. Chem.* **96**, 9839 (1992), o Glass et al., *J. Phys. Chem.* **97**, 12789 (1993).

Planned Work

1 January 1996 - 31 December 1996

Immediate work to be pursued will be a study of the reaction rate coefficients of $C_2H +$ ethane, propane, and butane at lower temperatures. The lower vapor pressures of the larger hydrocarbons may limit the lower values of the temperature that can be achieved with the present cell. There is very little work on the reactions

of C_2H with nitrogen containing compounds, such as HCN, CH_3CN , etc. Since the coupling of the carbon chemistry and nitrogen chemistry is an important process in the atmospheres of the outer planets, we intend to direct our studies along these lines in the ear future. This will require a new kind of apparatus, to prevent condensation of the nitrogen compounds on the walls of the flow cell. This work will assess a new jet cooled laval nozzle to achieve even lower temperatures. Such a method will necessitate multiphoton ionization or laser fluorescence schemes of detection as well, and therefore part of our effort will be directed toward this goal.

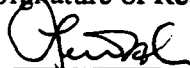
**CERTIFICATION REGARDING DRUG-FREE WORKPLACE REQUIREMENTS
(GRANTS/COOPERATIVE AGREEMENTS)**

- A. The grantee certifies that it will provide a drug-free workplace by:
- (a) Publishing a statement notifying employees that the unlawful manufacture, distribution, dispensing, possession or use of a controlled substance is prohibited in the grantee's workplace and specifying the action that will be taken against employees for violation of such prohibition;
 - (b) Establishing a drug-free awareness program to inform employees about --
 - (1) The dangers of drug abuse in the workplace;
 - (2) The grantee's policy of maintaining a drug-free workplace;
 - (3) Any available drug counseling, rehabilitation, and employee assistance programs; and
 - (4) The penalties that may be imposed upon employees for drug abuse violations occurring in the workplace;
 - (c) Making it a requirement that each employee to be engaged in the performance of the grant be given a copy of the statement required by paragraph (a);
 - (d) Notifying the employee in the statement required by paragraph (a) that, as a condition of employment under the grant, the employee will --
 - (1) Abide by the terms of the statement, and
 - (2) Notify the employer of any criminal drug statute conviction for a violation occurring in the workplace no later than five days after such conviction;
 - (e) Notifying the agency within ten days after receiving notice under subparagraph (d) (2) from an employee or otherwise receiving actual notice of such conviction;
 - (f) Taking one of the following actions, within 30 days of receiving notice under subparagraph (d) (2), with respect to any employee who is so convicted --
 - (1) Taking appropriate personnel action against such an employee up to and including termination; or
 - (2) Requiring such employee to participate satisfactorily in a drug abuse assistance or rehabilitation program approved for such purposes by a Federal, State, or local health, law enforcement, or other appropriate agency;
 - (g) Making a good faith effort to continue to maintain a drug-free workplace through implementation of paragraphs (a), (b), (c), (d), (e), and (f).
- B. The grantee shall insert in the space provided below the site(s) for the performance of work done in connection with the specific grant:

Place of Performance (Street address, city, county, state, zip code):

University of Colorado, Boulder, Colorado, 80309

Signature of Responsible University Official and Date:



9-26-95

Typed Name and Title:

Laurence D. Nelson, Director, Office of Contracts and Grants

Title/Identification of Applicable Research Proposal:

Laboratory Studies of Low Temperature Rate Coefficients: The Atmospheric

Chemistry of the Outer Planets (Continuation of NAGW-2438)


NASA Proposal No.: _____
Laboratory Studies of Low Temperature Rate Coefficients: The Atmospheric
Title: Chemistry of the Outer Planets (Continuation of NAGW-2438)

Principal Investigator(s): Stephen R. Leone

**CERTIFICATION REGARDING DEBARMENT, SUSPENSION AND OTHER
RESPONSIBILITY MATTERS--PRIMARY COVERED TRANSACTIONS**

- (1) The prospective primary participant certifies to the best of its knowledge and belief, that it and its principals:
- (a) Are not presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency;
 - (b) Have not within a three-year period preceding this proposal been convicted of or had a civil judgment rendered against them for commission of fraud or a criminal offence in connection with obtaining, attempting to obtain, or performing a public (Federal, State or local) transaction or contract under a public transaction; violation of Federal or State antitrust statutes or commission of embezzlement, theft, forgery, bribery, falsification or destruction of records, making false statements, or receiving stolen property;
 - (c) Are not presently indicted for or otherwise criminally or civilly charged by a governmental entity (Federal, State or local) with commission of any of the offenses enumerated in paragraph (1) (b) of this certification; and
 - (d) Have not within a three-year period preceding this application/proposal had one or more public transactions (Federal, State or local) terminated for cause or default.
- (2) Where the prospective primary participant is unable to certify to any of the statements in this certification, such prospective participant shall attach an explanation to this proposal.

CERTIFIED BY:

 9-26-95
Signature Date

Laurence D. Nelson
Typed Name

Director, Office of Contracts and Grants
Title

University of Colorado at Boulder
Institution

Section 1352, Title 31, U.S.C. (PL 101-121, Section 319) entitled "Limitation on use of appropriated funds to influence certain Federal contracting and financial transactions."

CERTIFICATION REGARDING LOBBYING

The undersigned certifies, to the best of his or her knowledge and belief, that:

- (1) No Federal appropriated funds have been paid or will be paid by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of an agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Federal contract, the making of any Federal grant, the making of any Federal loan, the entering into of any cooperative agreement, and the extension, continuation, renewal, amendment, or modification of any Federal contract, grant, loan, or cooperative agreement.
- (2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, "Disclosure Form to Report Lobbying," in accordance with its instructions.
- (3) The undersigned shall require that the language of this certification be included in the award documents for all subawards at all tiers (including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements) and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or entering into this transaction imposed by section 1352, title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than \$10,000 and not more than \$100,000 for each such failure.



9-26-95

Signature of the Officer responsible for this transaction, and date

Laurence D. Nelson, Director, Office of Contracts and Grants

Typed name and title of the Officer responsible for this transaction

The Regents of the University of Colorado
Organization

Transaction Number:

Contract/Modification No. _____

Grant/Modification No. _____

ASSURANCE OF COMPLIANCE WITH THE NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION REGULATION UNDER TITLE VI OF THE
CIVIL RIGHTS ACT OF 1964

The institution, corporation, firm or other organization on whose behalf this assurance is signed (hereinafter called "Applicant").

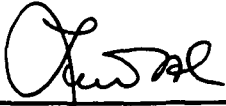
HEREBY AGREES THAT it will comply with Title VI of the Civil Rights Act of 1964 (P.L. 88-352) and all requirements imposed by or pursuant to the Regulation of the National Aeronautics and Space Administration (14 CFR Part 1250) (hereinafter called "NASA") issued pursuant to that title, to the end that in accordance with Title VI of that Act and the Regulation, no person in the United States shall, on the ground of race, color or national origin, be excluded from participation in, be denied the benefits of, or be otherwise subjected to discrimination under any program or activity for which the Applicant receives Federal financial assistance from NASA; and HEREBY GIVES ASSURANCE THAT it will immediately take any measures necessary to effectuate this agreement.

If any real property or structure thereon is provided or improved with the aid of Federal financial assistance extended to the Applicant by NASA, this assurance shall obligate the Applicant, or in the case of any transfer of such property, any transferee, for the period during which the real property or structure is used for a purpose for which the Federal financial assistance is extended or for another purpose involving the provision of similar services or benefits. If any personal property is so provided, this assurance shall obligate the Applicant for the period during which it retains ownership or possession of the property. In all other cases, this assurance shall obligate the Applicant for the period during which the Federal financial assistance is extended to it by NASA.

THIS ASSURANCE is given in consideration of and for the purpose of obtaining any and all Federal grants, loans, contracts, property, discounts or other Federal financial assistance extended after the date hereof to the Applicant by NASA, including installment payments after such date on account of applications for Federal financial assistance which were approved before such date. The Applicant recognizes and agrees that such Federal financial assistance will be extended in reliance on the representations and agreements made in this assurance, and that the United States shall have the right to seek judicial enforcement of this assurance. This assurance is binding on the Applicant, its successors, transferees, and assignees, and the person or persons whose signatures appear below are authorized to sign this assurance on behalf of the Applicant.

Dated 9-26-95

The Regents of the University of Colorado
(Applicant)

By 
(President, Chairman of Board, or
comparable authorized official)

Laurence D. Nelson, Director
Office of Contracts and Grants

Campus Box 19

Boulder, CO 80309-0019
(Applicant's mailing address)