State of California
AIR RESOURCES BOARD

Resolution 02-11

March 21, 2002

Agenda Item No.: 02-2-2

WHEREAS, the Air Resources Board has been directed to carry out an effective research program in conjunction with its efforts to combat air pollution, pursuant to Health and Safety Code sections 39700 through 39705;

WHEREAS, a research proposal, number 2515-224, entitled "Gas-Phase Formation Rates of Nitric Acid and its Isomers under Urban Conditions," has been submitted by NASA/Jet Propulsion Laboratory/California Institute of Technology;

WHEREAS, the Research Division staff has reviewed and recommended this proposal for approval; and

WHEREAS, the Research Screening Committee has reviewed and recommends for funding:

> Proposal Number 2515-224 entitled "Gas-Phase Formation Rates of Nitric Acid and its Isomers under Urban Conditions," submitted by NASA/Jet Propulsion Laboratory/California Institute of Technology, for a total amount not to exceed $180,000.

NOW, THEREFORE BE IT RESOLVED, that the Air Resources Board, pursuant to the authority granted by Health and Safety Code section 39703, hereby accepts the recommendation of the Research Screening Committee and approves the following:

> Proposal Number 2515-224 entitled Gas-Phase Formation Rates of Nitric Acid and its Isomers under Urban Conditions," submitted by NASA/Jet Propulsion Laboratory/California Institute of Technology, for a total amount not to exceed $180,000.

BE IT FURTHER RESOLVED, that the Executive Officer is hereby authorized to initiate administrative procedures and execute all necessary documents and contracts for the research effort proposed herein, and as described in Attachment A, in an amount not to exceed $180,000.

I hereby certify that the above is a true and correct copy of Resolution 02-11, as adopted by the Air Resources Board.

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Marie Kavan, Clerk of the Board

ATTACHMENT A

"Gas-Phase Formation Rates of Nitric Acid and its Isomers under Urban Conditions"

Background
Urban airshed models are indispensable tools in the assessment of control strategies for NO_X and VOCs. The controlling processes for ozone formation in such models are fast free-radical reactions. These reactions involve the generation of free radicals (primarily through photolysis reactions), conversion and regeneration of radicals, and removal of radicals through termination reactions. An important process in this latter category is the formation of nitric acid from the hydroxyl radical OH and nitrogen dioxide NO_2: $OH + NO_2 + M = HNO_3 + M$, where M is an inert bath gas, such as N_2. This reaction removes two short-lived reactive intermediates, OH and NO_2, and produces a relatively long-lived product, HNO_3. The significance of the termination step to urban airshed models is reflected in the high sensitivities of the spatial and temporal distributions of ozone from models to the value of the rate constant. For example, propagation of the uncertainty in the $OH+NO_2$ rate constant (~25 percent) in an urban airshed model produces an uncertainty of 35 ppbv in the calculated ozone concentration at a site downwind (i.e., ~25-50 percent uncertainty in the total ozone concentration). Also, this overall reaction is comprised of two reaction channels in which nitric acid HNO_3 and peroxynitrous acid HOONO are produced; complications arising from these channels introduce an additional uncertainty of 10-20 percent in the rate constant.

Objective
This primary objectives of this research are: 1) determine kinetic data for the radical termination reaction $OH + NO_2 + M \rightarrow$ products, and 2) measure the branching ratio for the formation of the isomers, HNO_3 and HOONO, which are produced by this reaction.

Methods
A new laser photolysis/laser-induced fluorescence apparatus will be used to obtain kinetic data for the reaction $OH + NO_2$. The reaction will be studied over the temperature range 250-310 K and the pressure range 500-800 Torr. The Chemical Kinetics and Photochemistry Group will carry out this work at NASA Jet Propulsion Laboratories. The targeted uncertainty in the rate constant is 15 percent or less. The branching ratios for the formation of the products HNO_3 and HOONO will also be measured. The groups of Prof. M. Okumura and Prof. P. Wennberg at the California Institute of Technology will carry out these studies using the techniques of infrared cavity ringdown spectroscopy and near-infrared photofragment (action) spectroscopy.

Expected Results
This project will determine kinetic and mechanistic information about a key radical termination process under urban conditions. This information is essential to improve the predictive capabilities of urban airshed models with respect to oxidant formation.

Significance to the Board
This project will improve our understanding of an important termination pathway for both OH and NO_X. The kinetic information obtained about this process will further the predictive capabilities of urban airshed models, which in turn will help determine the relative effectiveness of NO_X and VOC controls on oxidant formation in urban areas. In

addition, since this termination step is the primary pathway for the production of gas-phase nitric acid, this project may also have implications for the control of particulate matter.

Contractor:
NASA/Jet Propulsion Laboratory/California Institute of Technology

Contract Period:
24 Months

Principal Investigator (PI):
Dr. Stanley Sander

Contract Amount:
$180,000

Basis for Indirect Cost Rate:
The Jet Propulsion Laboratory is using a federally approved rate.

Past Experience with this Principal Investigator:
Dr. S. Sander is team leader of the Chemical Kinetics and Photochemistry Group at NASA JPL. This group is a recognized leader in research concerning elementary reaction kinetics and photochemical processes relevant to the earth. Dr. S. Sander is also the chairman of the NASA Panel for the Evaluation of Chemical Kinetic and Photochemical Data for Atmospheric Modeling, which provides a critical tabulation of the most recent kinetic and photochemical data for use by modelers in computer simulations of atmospheric chemistry.

Prior Research Division Funding to NASA/Jet Propulsion Laboratory/California Institute of Technology:

Year	2001	2000	1999
Funding	$0	$0	$0

B U D G E T   S U M M A R Y

NASA/Jet Propulsion Laboratory/California Institute of Technology

"Gas-Phase Formation Rates of Nitric Acid and its Isomers under Urban Conditions"

DIRECT COSTS AND BENEFITS			
1.	Labor and Employee Fringe Benefits	$44,700	
2.	Subcontractors	$60,000[1]	
3.	Equipment	$ 7,000	
4.	Travel and Subsistence	$ 700	
5.	Electronic Data Processing	$ - 0 -	
6.	Reproduction/Publication	$ - 0 -	
7.	Mail and Phone	$ - 0 -	
8.	Supplies	$ 4,000	
9.	Analyses	$ - 0 -	
10.	Miscellaneous	$14,000	
	Total Direct Costs		$130,400
INDIRECT COSTS			
1.	Overhead	$29,100	
2.	General and Administrative Expenses	$10,300	
3.	Other Indirect Costs	$10,200	
4.	Fee or Profit	$ -0-	
	Total Indirect Costs		$49,600
TOTAL PROJECT COSTS			**$180,000**

(notes)

[1] CalTech subcontractor

Labor	$34,600
Tuition	4,640
Indirect Cost	$20,760
	$60,000

Attachment (##)

S U B C O N T R A C T O R S' B U D G E T S U M M A R Y

Subcontractor: Caltech Work Order (Postdoctoral Scholar and Graduate Research Assistant)

Description of subcontractor's responsibility: Carry out IR-CRDS and Near-IR Photofragment studies, analyze data, and prepare the results for publication.

DIRECT COSTS AND BENEFITS			
1.	Labor and Employee Fringe Benefits	$42,430	
2.	Subcontractors	$ - 0 -	
3.	Equipment	$ - 0 -	
4.	Travel and Subsistence	$ - 0 -	
5.	Electronic Data Processing	$ - 0 -	
6.	Reproduction/Publication	$ - 0 -	
7.	Mail and Phone	$ - 0 -	
8.	Supplies	$ - 0 -	
9.	Analyses	$ - 0 -	
10.	Miscellaneous	$ - 0 -	
	Total Direct Costs		$42,430
INDIRECT COSTS			
1.	Overhead	$17,440	
2.	General and Administrative Expenses	$ - 0 -	
3.	Other Indirect Costs	$ - 0 -	
4.	Fee or Profit	$ - 0 -	
	Total Indirect Costs		$17,400
TOTAL PROJECT COSTS			**$60,000**

(notes)