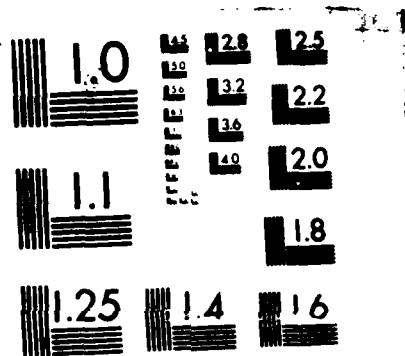


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AD-A179 949

Vibrational Deactivation at Solid Surfaces

FINAL REPORT

Paul L. Houston and Robert P. Merrill

January 1, 1984 through December 31, 1986

U. S. Army Research Office

Grant Number: DAAG29-84-K-0016

Cornell University
Ithaca, New York 14853

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 20919.5-CH	
6a. NAME OF PERFORMING ORGANIZATION Cornell University	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code) Ithaca, New York 14853-1301		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAG29-84-K-0016	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Vibrational Deactivation at Solid Surfaces			
12. PERSONAL AUTHOR(S) Paul L. Houston and Robert P. Merrill			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1/1/84 TO 12/31/86	14. DATE OF REPORT (Year, Month, Day) 1987, March 12	15. PAGE COUNT 8
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Surface Chemistry, Energy Transfer, Vibrations, molecules	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The loss of vibrational energy was monitored by observing the decay of infrared fluorescence following pulsed excitation with a tunable infrared laser of molecules contained within a metallic or non-metallic cylindrical cell. The probability of collisional deactivation was obtained by measuring the decay time for the infrared fluorescence and dividing by the number of collisions per unit time calculated from gas-kinetic theory. The exchange of translational and rotational energy was studied by scattering molecules from a well characterized single-crystal surface. A molecular beam was used to prepare the initial species in its lowest vibrational and rotational levels, while the scattered species were detected either in a state-selected measurement using laser-induced multiphoton ionization or in a total-flux measurement using electron impact mass spectrometry. (Keywords)			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

FINAL REPORT

Vibrational Deactivation at Solid Surfaces

January 1, 1984 through December 31, 1986

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ARO Proposal Number: 20919-CH

Grant Number: DAAG29-84-K-0016

A. Statement of Problem Studied

This investigation focused on the exchange of translational, rotational and vibrational energy which takes place when a gas-phase molecule collides with a solid surface. Such processes are important to heterogeneous catalysis, corrosion, air filtration and pollution control.

The loss of vibrational energy was monitored by observing the decay of infrared fluorescence following pulsed excitation with a tunable infrared laser of molecules contained within a metallic or non-metallic cylindrical cell. The

	
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probability of collisional deactivation was obtained by measuring the decay time for the infrared fluorescence and dividing by the number of collisions per unit time calculated from gas-kinetic theory.

The exchange of translational and rotational energy was studied by scattering molecules from a well characterized single-crystal surface. A molecular beam was used to prepare the initial species in its lowest vibrational and rotational levels, while the scattered species were detected either in a state-selected measurement using laser-induced multiphoton ionization or in a total-flux measurement using electron impact mass spectrometry. The angular intensity, rotational, vibrational, and velocity distributions of the scattered molecules could be determined as a function of crystal temperature.

B. Summary of Results

Surface Scattering: An experimental system capable of measuring the rotational, vibrational, and translational state distributions of molecules scattered from surfaces was designed, constructed, and applied to the particular case of NO scattered from Ir(111). Rotational and vibrational state distributions were determined using multiphoton ionization spectroscopy (MPI). Translational state distributions were measured using time of flight (TOF) mass spectrometry, and angular intensity distributions were measured both selectively (using MPI) and non-selectively (using mass spectrometry). A computer-controlled pulse counting system was implemented to allow measurements to be made at extremely low molecular densities. Attempts were made to produce a beam containing vibrationally excited NO; a single mode F-center laser was used to excite NO ($v=2, J=3/2$) \leftarrow NO ($v=0, J=1/2$) in a molecular beam with simultaneous

detection of the vibrationally excited NO via MPI. The theory and mathematical formalism of polarization spectroscopy was treated in detail.

Results from our laboratory on the interaction of NO($v=0, J$) with Ir(111) have been published in a brief report; a more extensive report is in preparation. Briefly, the angular, velocity, and rotational energy distributions were measured. It was found that NO interacts strongly with the Ir(111) surface. In particular, for surface temperatures less than 300 K, where Ir(111) is covered by an overlayer of NO, a mixture of trapping-desorption and direct-inelastic scattering was observed. Our recent experiments have been directed toward elucidating the details of the NO/Ir(111) interaction that results in this mixture of scattering mechanisms. The velocity distributions have been investigated in more detail by varying beam energy, angle of incidence, and surface composition. For example, we have observed the expected shift of intensity in the trapping-desorption and direct-inelastic modes as the angle from the surface normal is increased or decreased from the angle of 48.5° used previously. As the angle of incidence increases, we observe a decrease in the fraction of translational energy lost to the surface. The velocity distributions were found to be insensitive to variations in surface coverage, including saturation of the surface with oxygen or N and O atoms. More recent efforts have been directed toward a more detailed understanding of the NO/Ir(111) surface chemistry. Sticking probabilities for NO as a function of surface temperature and beam energy have been measured in conjunction with temperature programmed desorption (TPD) profiles as a function of surface dosing temperature.

Vibrational Deactivation: The probability for deactivation for deactivation of $\text{CO}(v=2)$ and $\text{CO}_2(101)$ on collision with polycrystalline silver surfaces has been measured. The deactivation probability for $\text{CO}(v=2)$ was found to decrease from 0.33 at 300 K to 0.20 at 440 K, while the deactivation probability for $\text{CO}_2(101)$ was found to decrease from 0.72 at 300 K to 0.37 at 440 K. Since no population was observed in the $\text{CO}(v=1)$ and $\text{CO}_2(001)$ intermediate levels, it appears that each deactivation proceeds completely to produce the vibrational ground level. The magnitudes for the deactivation probabilities and the temperature dependencies indicate that a dominant mechanism for relaxation involves trapping and subsequent deactivation by one or more of several mechanisms, including electron-hole pair formation, vibration-to-rotation energy transfer, or perhaps even transfer of energy to the surface phonons. The experiments were performed in a UHV chamber by using a tunable infrared laser source to excite gas-phase molecules vibrationally before their collision with the surface and by measuring the population of vibrationally excited molecules through their time-resolved infrared fluorescence.

While this previous work in our laboratory has studied the vibrational deactivation of gas molecules at solid metallic surfaces, in an effort to learn more about the mechanism of vibrational deactivation, we have been extending our studies to non-metallic surfaces -- in particular, aluminum oxide and LiF .

Preliminary experiments on the deactivation of $\text{CO}_2(101)$ at aluminum and aluminum oxide have been started. Aluminum is evaporated from a tungsten filament onto a cylindrical sample cell, in the same manner that silver surfaces were prepared in previous experiments. Aluminum oxide has been prepared by exposing the aluminum surface to 0.5 atm of pure oxygen for several

hours at about 200 °C. There are some difficulties associated with this experiment. One problem is that the sticking coefficient of CO₂ on alumina is not known. Infrared absorption studies¹ of CO₂ adsorbed on aluminum oxide indicate that the sticking coefficient is probably high, a result which will complicate the interpretation of any measurements we obtain. Another problem occurs with the difficulty in evaporating the aluminum. Although tungsten is typically the filament used in aluminum evaporations, it forms an alloy with aluminum, causing premature filament breakage. In order to make repeated measurements at various temperatures and pressures on freshly deposited aluminum surfaces, the filament must be replaced after only one or two evaporations, and the vacuum system must be baked after each replacement. This problem will lengthen considerably the time required to complete these experiments. Preliminary results on this system indicate that the vibrational deactivation probability is high for both aluminum and the oxide (about 0.6-0.7), but the results have not yet been reproduced enough to make comparisons between the two systems.

The experimental apparatus to be used for studying LiF is currently being designed. A rectangular, open-ended box has been constructed from four cleaved pieces of LiF single crystal, each approximately three inches long. The box will be placed inside a stainless steel block which will be used to heat the LiF evenly so that it can be cleaned. The block will be supported inside a specially built cell equipped with feed-throughs to be used for heating the block and for measuring the temperature. This cell will be put on the existing UHV chamber in place of the cylindrical cell that is being used for the

aluminum oxide experiments. LiF was chosen not only because it is a non-metal, but also because it can be cleaned and kept clean relatively easily.

C. List of Publications and Technical Reports

1. J. Misewich, P. L. Houston, and R. P. Merrill, "Vibrational Relaxation of Carbon Dioxide (101) and Carbon Monoxide ($v=2$) During Gas-Surface Collisions," J. Chem. Phys. **82**, 1577-1584 (1985).
2. V. A. Apkarian, R. Hamers, P. L. Houston, J. Misewich, and R. P. Merrill, "Laser Studies of Vibrational Energy Exchange in Gas-Solid Collisions," Proceedings of the Seventeenth Jerusalem Symposium, Dynamics at Surfaces, 1984, D. Reidel, Dordrecht, Holland.
3. R. J. Hamers, P. L. Houston, and R. P. Merrill, "Direct-Inelastic and Trapping-Desorption Scattering of $\text{NO}(v=0, J)$ from $\text{Ir}(111)$: Angular, Velocity and Rotational Energy Distributions," J. Chem. Phys. **83**, 6045-6 (1985).
4. P. L. Houston and R. P. Merrill, "Vibrational Energy Exchange in Gas-Surface Interactions," Chem. Rev., submitted.
5. R. J. Hamers, P. L. Houston, and R. P. Merrill, "Competition between Direct-Inelastic and Trapping-Desorption in the Scattering of $\text{NO}(v=0, J)$ from $\text{Ir}(111)$," prepared for submission to J. Chem. Phys.
6. R. J. Hamers, "Rotationally and translationally inelastic scattering of Nitric Oxide from Iridium(111), Ph.D. Thesis, Cornell University, 1986
7. J. A. Misewich, "Vibrational Deactivation during Gas-Surface Collisions," Ph.D. Thesis, Cornell University, 1984.

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