AD-A224 638

DTIC FILE COPY

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1\. AGENCY USE ONLY (Leave blank)

2\. REPORT DATE
May 8, 1985

3\. REPORT TYPE AND DATES COVERED
March 1, 84 - Feb 28, 85

4\. TITLE AND SUBTITLE
Molecular Collision Processes in gases and at surfaces.

5\. FUNDING NUMBERS
F49620-C-84-0038

②

6\. AUTHOR(S)
John B. Fenn

7\. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Yale University/Department of Engineering and Applied
Science.
New Haven, CT 06520

8\. PERFORMING ORGANIZATION REPORT NUMBER
[illegible] 7

9\. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
US Air Force.

10\. SPONSORING/MONITORING AGENCY REPORT NUMBER

11\. SUPPLEMENTARY NOTES

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

12b. DISTRIBUTION CODE

13\. ABSTRACT (Maximum 200 words)

DTIC
ELECTE
JUL 24 1990
S D D

14\. SUBJECT TERMS

15\. NUMBER OF PAGES

16\. PRICE CODE

17\. SECURITY CLASSIFICATION OF REPORT
Unclassified

18\. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19\. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20\. LIMITATION OF ABSTRACT
Unclassified

NSN 7540-01-280-5500

Standard Form 298 (890104 Draft)
[illegible]

[illegible] 30

MOLECULAR COLLISION PROCESSES IN GASES AND AT SURFACES

Interim Scientific Report for Year Ending 2/28/85
Final

AFOSR Grant F49620-C-84-0038

Introduction

Our research centers on the use of Fourier Transform Infrared Spectrometry (FTIS) to determine the distribution of rotational and vibrational energies in molecules. Our particular concern is with the effects of gas-gas and gas-surface collisions on these internal states. By studying the changes in energy and structure that occur during such collisions we aim to elucidate the kinetics and dynamics of the reactive and inelastic scattering events that play leading roles in many important processes of both technological and scientific interest. The collision processes under study are brought about with the aid of supersonic free jets expanding into vacuum from small sonic orifices or nozzles. Three kinds of scenarios are used: (1) Single Free Jets. The jet itself is the stage for collisions that occur while the gas is expanding from stagnation pressure in the source to the background pressure in the vacuum chamber which is always low enough so that the jet gas is in free molecule (collisionless) flow in its terminal state. Because the expansion rates are so rapid the terminal gas state is usually far from equilibrium. Spectroscopic interrogation of jet gas allows us to characterize the nature of the collision processes that lead to the terminal state. (2) Colliding Jets. Two jets intersect at axial distances sufficiently large to insure that each jet is well into the free molecule flow regime so that molecules from one jet undergo single collisions with molecules from the other. The object in this configuration is to study the consequences of gas-gas encounters. In particular, we have been concerned with the cross-sections for translation-vibration (TV) excitation of molecules that radiate in the infrared when they are vibrationally excited. (3) Jet-Surface Combinations. In

A-1

this configuration the jet flux impinges upon a surface in the free molecular regime of the flow field so that the spectrometrically observed changes in molecular internal energy are due to single surface collisions.

These various combinations of free jets, surface and infrared radiometry-spectrometry have made possible a number of important results. Noteworthy among them are: (1) Determination of Translation-Vibration (TV) excitation cross-sections for CO_2 in collisions with H_2, N_2, Ar and O_2 at relative velocities up to 6 km/s. (2) Determinaton of the distribution of rotational energy in TV excited CO_2. (3) Determination of excitation probabilities for rotational and vibrational degrees of freedom during collisions between CO, NO and CO_2 and hot metal surfaces. (4) Elucidation of the distribution of activation energy among the various degrees of freedom in nascent CO_2 molecules formed during the oxidation of CO on platinum surfaces. (5) Determination of the effect of surface coverage on energy distribution in nascent product molecules from the surface catalyzed oxidation of Co by time-resolved FTIS measurements. (6) Elucidation of some mechanistic details of the oxidation of C atoms by O atoms on a platinum surface by FTIS analysis of product CO molecules. (7) Measurements of terminal distributions of internal energy in free jet molecules to determine rotational relaxation rates in CO_2.

Progress During the Grant Year

1. Single Free Jets. We have continued our studies of terminal rotational distributions in both emission and absorption for CO_2, CO and mixtures of these species with N_2, Ar and He. It emerges that diluting with these gases, particular Ar and He, increases the departure from a Boltzmann distribution. It seems possible to explain these observations in terms of a competition between de-Boltzmannizing RT transfers and Boltzmannizing RR transfers. These results are among the very few which show the importance of RR transfers in the rotational

relaxation of polyatomic gases. A paper describing these studies has been published in the Proceedings of the 14th International Symposium on Rarefied Gas Dynamics.

Our ability to determine terminal internal energy distributions in free jet expansions by emission spectrometry stems from the fact that emitting vibrational modes in many molecules do not relax appreciably during free jet expansion because of the limited number of collisions. Clearly, these modes must be excited in the source gas if they are to radiate after the expansion is over. We have depended upon thermal excitation which obviously requires elevated source temperatures. In the hope that we could achieve such excitation at low source temperatures we have recently tried maintaining a DC corona discharge in the source gas. Preliminary experiments with CO_2 and CO, neat or in admixture with N_2 or He, have provided some fascinating spectra rich in a variety of features that invite further exploration and examination. In particular, we have found that much lower terminal rotational temperatures can be achieved because of the lower source temperature. The resulting narrowing of the rotational spread makes it possible to resolve the combination bands involving the bending modes in CO_2. We find that these modes seem to relax during expansion so we can hope to determine their characteristic relaxation rates. Moreover, some new lines appear in the CO_2 spectrum forming what seem to be R and P branches about 70 wave numbers to the red side of the asymmetric stretch $v = 1$ band. We have identified this new band as being due to radiation from the asymmetric stretch mode of $^{13}CO_2$. The intensity is about 15 per cent of that from the $^{12}CO_2$ band although the natural abundance of ^{13}C is only 0.01 that of ^{12}C. Although it is tempting to conclude that we have stumbled upon a remarkable isotope enrichment phenomenon we believe the following explanation is more reasonable. A vibrationally excited $^{12}CO_2$ encounters a ground state $^{13}CO_2$ and transfers a quantum of asymmetric stretch vibrational energy. The excess 70 cm^{-1} is taken up in rotation of both partners. Because the rotational temperature is low, the population of high J levels is so low that the vibrationally excited $^{13}CO_2$ does not encounter a $^{12}CO_2$ in a sufficiently high J level to act as a partner for the reverse reaction. Thus the vibrational energy remains trapped in the $^{13}CO_2$. These results are the basis for a paper in preparation.

2. Colliding Jets. The principal activity has been the development of a gas dynamic method of modulating or chopping the free jet. In our original TV excitation experiments we achieved the necessary sensitivity by measuring total radiation (not spectrally resolved) from collisionally excited species. We took advantage of phase-sensitive detection at imposed frequencies by mechanically chopping one of the jets with a rotating wheel. A major source of noise was due to reflection of photons from the heated nozzle by the chopping wheel. In some recent experiments we have been able to modulate the free jet successfully by using a small auxiliary pulsed jet that intersects the primary jet at right angles to its axis near the nozzle exit. In effect, the primary jet is "blown" out of the collision region and field of view when the auxiliary jet is on. As long as the pulsing gas is transparent to infrared there is no spurious signal to be seen by the detector. The marked reduction in noise has made it possible to obtain useful signals at much lower source temperatures than were possible with the mechanical chopper. Indeed, we have finally obtained clean signals with water vapor jets, an objective that has long eluded us.

3. Jet Surface Studies. We have continued our time resolved studies of surface scattered species, in particular the effect of surface coverage on rotational energy distribution in nascent CO_2 molecules formed by the surface catalyzed oxidation of CO by O_2. It is very difficult to vary surface coverage over an appreciable range in a steady state experiment without a wide variation in surface temperature. With a pulsed nozzle we can achieve very high instantaneous fluxes that flood the surface.

We have also observed an emission continuum from species formed when O atoms react with CO chemisorbed on a Pt surface. A possible explanation attributes this radiation to CO_2 molecules preferentially excited to the v = 9 level. These excited CO_2 molecules apparently can react with O atoms to form excited O_2 and CO excited to the v = 1 level. These observations have been described in a note in Chem. Phys. Lett.

Cumulative Publication List

"Flowfield Calculations in Nonequilibrium Free Jets by the Method of Characteristics," M. Labowsky, S. B. Ryali, J. B. Fenn and D. R. Miller in Rarefied Gas Dynamics (S. S. Fisher, ed.) Prog. in Astro. and Aero. 74, 695 AIAA (1981).

"The Exciting Oxidation of CO on Pt," D. A. Mantell, S. B. Ryali, B. L. Halpern, G. L. Haller and J. B. Fenn, Chem. Phys. Lett. 81, 185 (1981).

"Surface Catalyzed Production of N_2O from the Reaction of N Atoms and O_2 on Platinum," E. J. Murphy, J. B. Fenn and B. L. Halpern, J. Catal. 74, 434 (1981).

"Clusters as a Source of Error in Molecular Beam Scattering Experiments," H. L. Tien, S. B. Ryali, P. J. Gale and J. B. Fenn, Chem. Phys. Lett. 93, 213 (1982).

"Furtner Reflections on the Role of a Mass Flux Gauge in the Calibration of Mass Spectrometers for Dimers," J. B. Fenn and N. Lee, Rev. Sci. Instr. 53, 1494 (1982).

"Research Is Engineering," J. B. Fenn, Chem. Eng. Educ., Fall 1982, 190.

"Collisional Excitation of CO_2 by N_2, O_2, and Ar," S. B. Ryali, J. B. Fenn, C. E. Kolb and J. A. Silver, J. Chem. Phys. 76, 5878 (1982).

"Rotational Energy Distribution in CO_2 Vibrationally Excited by Collision with N_2," S. P. Venkateshan, S. B. Ryali and J. B. Fenn, Chem. Phys. Lett. 92, 606 (1982).

"Terminal Distributions of Rotational Energy in Free Jets of CO_2 by Infrared Emission Spectrometry," S. P. Venkateshan, S. B. Ryali and J. B. Fenn, J. Chem. Phys. 77, 2599 (1982).

"Collision Kinetics in Gas Dynamics," J. B. Fenn in Applied Atomic Collision Physics, Vol. 5 (K. W. McDaniel, ed.) Academic Press (New York) 1982, p. 349.

"Vibrational Energy Distribution of CO in the Oxidation of C on Pt," M. Kori and B. L. Halpern, Chem. Phys. Lett. 98, 32 (1983).

"Distribution of Internal Energy in NO Vibrationally Excited by a Hot Platinum Surface," D. A. Mantell, Y.-F. Maa, G. L. Haller and J. B. Fenn, J. Chem. Phys. 78, 6338 (1983).

"Distribution of Internal Energy in CO and CO_2 Scattered by a Hot Platinum Surface," D. A. Mantell, S. B. Ryali, G. L. Haller and J. B. Fenn, J. Chem. Phys. 78, 4250 (1983).

"On the Time Required to Reach Fully Developed Flow," J. B. Fenn and K. J. Saenger, J. Chem. Phys. 79, 6043 (1983).

"The Dynamics of CO Oxidation on Pt Deduced from Translational, Rotational and Vibrational Excitation in Product CO_2," D. A. Mantell, S. B. Ryali, G. L. Haller and J. B. Fenn, submitted to Surface Science.

"Time Resolved Infrared Emission Studies of CO_2 Formed by CO Oxidation on Pt and Pd," D. A. Mantell, S. B. Ryali and G. L. Haller, Chem. Phys. Lett. 102, 37 (1983).

"Where Are We Going With Molecular Beams," J. B. Fenn, Proc. 13th Rarefied Gas Dynamics Symposium (in press).

"Clustering in Free Jets — Aggregation by Dispersion," S. B. Ryali and J. B. Fenn, Ber. Bunsenges. Phys. Chem. 88, 245 (1984).

"Terminal Rotational Energy Distributions in Free Jets," S. B. Ryali, S. P. Venkateshan and J. B. Fenn, Proc. 14th Rarefied Gas Dynamics Symp. (H. Oguchi, ed.) Vol. II, University of Tokyo Press, 1984, p. 567.

"Vibrationally Excited CO_2 from the Reaction of O Atoms and Adsorbed CO on Platinum," M. Kori and B. L. Halpern, Chem. Phys. Lett. 110, 223 (1984).

Personnel

Principal Investigators: J. B. Fenn and S. B. Ryali
Faculty Associates: G. L. Haller and B. L. Halpern
Postdoctoral Associates: Shi-da Shen and K. Kunimori
Graduate Students: Yih-Fen Maa and Moris Kori

Professor Ryali left in September to accept a position at Aerodyne Research Laboratories, Billerica, MA.