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INTERMOLECULAR ENERGY EXCHANGE BY INFRARED RADIOMETRY.(U)
JAN 80 J B FENN, S B RYALI, S P VENKATESHAN F49620-79-C

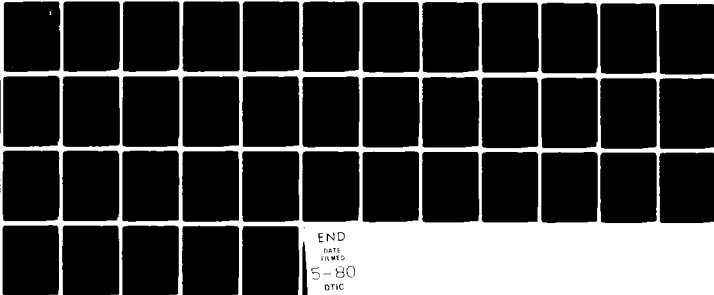
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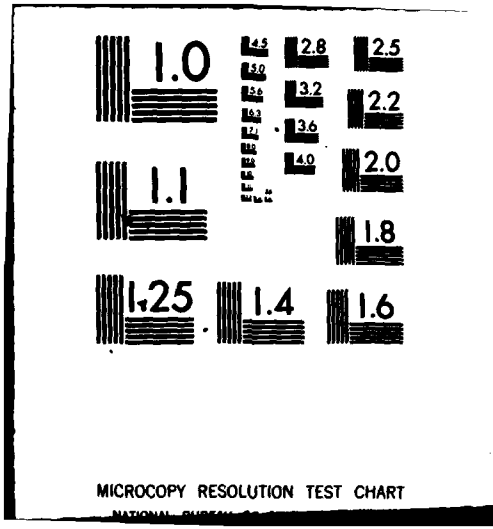
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FINAL REPORT

to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Directorate of Chemical Sciences

for Contract F49620-79-C-0036

on

INTERMOLECULAR ENERGY EXCHANGE BY INFRARED RADIOMETRY

by

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31 January 1980

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Excitation by translational energy of the asymmetric stretch vibrational mode of ground state carbon dioxide molecules in collision with nitrogen, oxygen and argon molecules has been studied, by intersecting two slightly collimated molecular beams in the field of view of an InSb photovoltaic detector which monitored resulting radiation in the 4.3 micrometer band. The excitation cross sections for all three combinations of partners were of similar magnitude and showed a strong dependence upon collision velocity. For nitrogen the measured cross sections ranged from about 0.000 square | | |

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Angstroms at 2 km/s to about 0.5 square Angstroms at 5 km/s. A similar but separate experiment determined an upper limit of 0.1 square Angstroms for the collisional excitation of hydrogen fluoride by krypton at energies up to 1.7 times the threshold requirement. Bulk relaxation rates for molecules in free jet expansion were also investigated. Results obtained from experimental data with the frequently used Sudden Freeze Model have been compared with those obtained by Numerical Integration. Success has been achieved in obtaining Method-of-Characteristics solutions for the free jet expansion with a varying specific heat ratio. This development provides the best description yet of relaxation in free jet expansion for any internal mode which can be characterized by a Boltzmann distribution of energy.

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react the activation energy barriers which must be scaled are vibrational in nature. Consequently, the rate at which vibration can be excited in reactant molecules may play an important role in the rate at which combustion reactions occur. Moreover, it has been found that the energy of exothermic chemical reactions is often released as vibrational excitation of the reaction products. This vibrational energy must be transformed by collisions into the translational kinetic energy by which gaseous molecules are able to perform expansion work. At the low Reynolds numbers associated with air breathing engines at very high altitudes or with the very small rockets sometimes used for stabilizing or orienting satellites, the number of collisions which the average molecule undergoes during expansion in the nozzle can be relatively small. The exchange efficiency per collision may thus become an important design parameter. In air breathing engines for flight at very high Mach numbers, e.g. SCRAMJETS, the margin of thrust over drag is extremely sensitive to the absolute efficiency of the exhaust nozzle expansion. In such cases the efficiency of collisional energy transfer from vibration to translation may become important even in flows at very high Reynolds numbers. It has also been realized for some time that the efficiency of exchange between translation and internal energy is important in determining the transport properties of gases, particularly in heat transfer. Thus, there can be little doubt that with respect to specific fuel consumption, specific power output, and durability, the design and performance of many propulsion systems are intimately concerned with the rate of collisional energy transfer between the various modes of molecular motion.

Other situations arise in which energy exchange during the intimate encounters between molecules can play an important role. Collisions are the mechanism for providing the requisite population inversions in many gas lasers. In some cases they are responsible for pumping energy into the upper state. In others their function is to deplete the lower product states of the radiating species. Some of the radiation characteristics of rocket exhaust plumes have been attributed to the translational excitation of molecules such as H_2O and CO_2 to radiating states. Much more information is needed before the contribution of these processes can be reliably evaluated.

For these reasons we have been pursuing under the subject contract experimental research aimed at determining the rates and mechanisms for some of these energy transfer processes. Two approaches have been used. In one we have been attempting to measure the cross sections for TV excitation of ground-state molecules by bringing about single collision events at appropriate velocities and measuring the radiation from vibrationally excited molecules resulting from those collisions. In the other approach we have taken advantage of the peculiar characteristics of small freely expanding supersonic jets obtained by passing gas from a source at relatively high pressure through a small sonic orifice into an evacuated chamber. In such jets the expansion is so rapid that the internal degrees of freedom do not remain in equilibrium with translation. By determining the extent of the resulting departure from equilibrium it becomes possible to characterize the rate of the exchange process which has lagged behind the rate at which the translational temperature is changing. In what follows we will summarize our results in each of these endeavors.

A. TV Excitation in Single Collision Experiments. In the course of trajectories at high altitudes and flight velocities the relative velocities between rocket exhaust plume gas and the ambient atmosphere range up to 10 km/s. At these velocities there is ample energy in the center of mass for collisions between plume molecules such as CO_2 and H_2 and atmospheric species such as O , O_2 and N_2 to excite the plume molecules to vibrational states which radiate in the infrared. It has long been suggested that such collisions may account for the far field infrared radiation from rocket plumes which has long been observed but not completely understood. Consequently, it has been of interest to determine the cross sections for these excitation processes and in their velocity dependence. Some years ago in cooperation with Aerodyne Research we undertook with Air Force support an attempt to apply molecular beam methods in the measurement of some of these cross sections and the determination of their energy dependence.

The idea of the experiment is to bring about the high energy collisions by opposing two uncollimated beams (free jets in the free molecular flow regime). Each jet is obtained by expanding a dilute "solution" of one of the species of interest in hydrogen or helium. The intersection region of the two jets, where the high energy collisions occur, occupies the field of view of a sensitive infrared detector. Collision energy can be varied by changing the concentration of seed species in the carrier gas. To a more circumscribed extent, the source temperature can also be changed. There are two prerequisites to obtaining observable signals: molecules must become excited and they must radiate before they leave the field of view of the detector. This latter

requirement compounds the problem of an already harassed experimenter because the radiative lifetimes of the expected states are at least several milliseconds. The residence time of an excited molecule in the field of view of the detector is of the order of a few times 10^{-5} seconds. The net result is that we can only hope to see a small fraction of the excited molecules, the impatient ones which radiate early.

In the initial attempt to carry out this experiment in the joint venture with Aerodyne we were unable to obtain any resolvable signal from H_2O or CO_2 molecules bombarded with N_2 at energies up to about $5 eV$ in the center of mass. Taking into account as best we could the sensitivity of the detector (InSb) and other features of the apparatus including the sources of noise, we were able from this negative result to put an upper limit on the cross section of excitation of about $2 \times 10^{-15} \text{ cm}^2$, somewhat smaller than the viscosity cross section. (13) In other words a detectable signal would have required excitation to a radiative state for every collision in which there was a substantial momentum transfer. It seems unlikely that TV cross sections could be that large.

Subsequent to that first attempt we undertook with AFOSR sponsorship in the program on which we here report a substantial refinement of the experiment. By painstaking attention to many small details such as alignment, optical focusing, careful baffling and improved calibration procedures, we have over the past three years succeeded in increasing signal and reducing noise to the point where we are now able to measure cross sections as small as a few times

10^{-20} cm^2 . We have determined the TV cross section for excitation of the asymmetric stretch mode of CO_2 by collisions with N_2 and find that it rises steeply from a value of $3 \times 10^{-20} \text{ cm}^2$ at collision energies just above the threshold value of 0.288 eV to about $5 \times 10^{-17} \text{ cm}^2$ at a collision energy of 2 eV. Most gratifying is the fact that measurements made when the jets intersect at 90 degrees are entirely consonant with those made when the intersection angle is 180 degrees. We have determined cross sections for excitation of the same mode with argon, oxygen and hydrogen as the collision partners. This work has been summarized in a paper which will shortly be submitted to the Journal of Chemical Physics. A preprint of that paper comprises Appendix I of this report and should be referred to for further details.

We have not yet been successful in obtaining corresponding cross sections for the excitation of H_2O molecules but we are continuing our efforts in a subsequent program and hope for early success. Meanwhile, we note that there is also interest in the collisional excitation of HF molecules because they are likely to be present in the exhaust plumes from future propellants. It happened that Professor John Polanyi's group at the University of Toronto had developed methods for measuring cross sections for the TR transfers resulting from collisions between HF and various target molecules. They were in a position to make some attempts to measure the TV excitation cross sections for HF in collision with krypton molecules. Accordingly, we engaged Professor Polanyi in a consultant role to perform these measurements for us. His report comprises Appendix II. He was unable to achieve any collisional excitation of

HF vibration at translational energies in the center of mass up to 1.7 times the threshold value of 0.47 eV for HF ($v=1$) to HF ($v=2$). An analysis of the sensitivity of the detection system led to the conclusion that the cross section for this excitation must be smaller than 10^{-17} cm².

This result strongly suggests that HF molecules are more difficult to excite in TV encounters than is CO₂. One can rationalize this still speculative conclusion by noting that because the H atom is so light a very high velocity collision would be required to achieve any efficiency in giving it enough kinetic energy to result in stretching and therefore exciting the HF bond. Similarly, a very high kinetic energy would have to be transferred to F in order for its velocity relative to the H atom to approach the value achieved during vibration. This rationale would also seem to apply to other hydrogen halides.

The cross sections which we measured for CO₂ excitation and those which we are trying to measure for H₂O excitation are total in the sense that our detector responds to all radiation over its bandwidth. It happens that the InSb detector we have been using can in the case of CO₂ see only the radiation in the band from the asymmetric stretch mode of vibration so we can relate the excitation process to that mode. However, we do not resolve the rotational fine structure of the band. It would be of great interest to determine whether particular rotational levels were favored in the excitation process. Moreover, in the longer view it would be highly desirable in general to be able to resolve collision induced radiation spectrally. As we have noted, it was already some-

thing of a tour de force even to detect the radiation from TV excitation under single collision conditions because it is so weak. To resolve it spectrally would be much more difficult but it did seem to be within the capability of newly developed Fourier Transform Infrared (FTIR) spectrometric methods. AFOSR was kind enough to provide the non trivial amounts of money necessary to purchase an FTIR spectrometer (Nicolet 1180) which we welcomed into the laboratory last summer. After some shakedown problems and a fairly extensive learning process on our part we have developed some reasonable skills in using the instrument.

The major problem which remains to be solved and which is occupying our continuing attention is to provide an efficient and effective means of coupling the spectrometer with the crossed beam experiment. The radiation is produced inside a vacuum system. The spectrometer is housed inside a purged enclosure at a pressure very slightly above that of the ambient atmosphere. We must collect the very weak radiation as efficiently as possible inside the vacuum system and transmit it outside with as few losses as possible. At the same time we must protect it against intrusion from all sources of noise which are ubiquitous because practically all surfaces at room temperature radiate like mad in the 4.3 micron band of the signal from the excited molecules. In attempting to arrive at proper optimum alignment, maximum signal collection and muffling of noise it was convenient to use a single free jet from a heated nozzle as the radiation source. In earlier experiments with velocity analysis of molecular beams extracted from free jets we had found that for some molecules the vibrational relaxation rate is so slow that the vibrational energy content of the molecules is the same after expansion in small free jets as it is at

equilibrium in the source gas before expansion. Indeed, we took advantage of this fact to calibrate the detection system in the TV experiments as discussed in Appendix I. Our first attempts last summer to obtain spectra from free jet radiation were disappointing. Since then we have gradually improved our techniques and apparatus so that at this writing we have achieved beautiful spectra of CO₂ and CO free jets with very clear rotational line distributions from which we can obtain quite precise values of the rotational temperature. We are now encouraged to think that we are on the verge of being able to obtain well defined spectra of molecules excited under the single collision conditions of intersecting molecular beams. Meanwhile, this ability to determine the terminal internal state (e.g. rotational temperature) of jet molecules after expansion opens an exciting prospect for measuring energy exchange relaxation rates. One of the original objectives of the research which we are here reporting was to study relaxation rates by taking advantage of the characteristics of free jet expansions. We did not then anticipate that we might be able to use spectrometry for this purpose but the advent of FTIR to our laboratory has greatly enhanced the prospects for this technique. In the next section we discuss these prospects in connection with what we have been doing in the course of the present contract.

B. Energy Exchange Rates from Observations on Free Jet Expansions. In the small supersonic free jets which are widely used as molecular beam sources, and which we have been using in our TV excitation experiments, expansion is often so rapid that substantial departures from equilibrium occur. Sometimes referred to as "heat capacity lags" these departures manifest themselves in a divergence of translational, rotational and vibrational temperatures in the molecules of

jet gas after the expansion has been completed in the sense that the density is so low that no more collisions occur. In some cases it may happen that a Boltzmann distribution does not obtain in one or more of the possible modes of motion so that it or they cannot be characterized by a temperature. These departures from equilibrium have in the past been observed experimentally in several ways. Among them are: (a) by measurement and analysis of the velocity distribution in molecular beams extracted from the jets; (b) by spectral analysis of fluorescence induced in beam or jet molecules by electron bombardment or laser excitation; (c) by similar analysis of laser induced Raman spectra; (d) by interpretation of fragmentation patterns in mass spectrometric analysis of beam molecules; (e) by state selection of beam molecules using magnetic or electric fields. To this list we can now add: (f) by infrared emission spectroscopy of jet molecules after expansion. As we have already mentioned, we used this last kind of observation to calibrate our detection system. Observations of the magnitude of the divergence and its dependence upon source conditions make possible the determination of the characteristic relaxation rate, i.e., the energy exchange rate for the lagging process.

Our laboratory pioneered the determination of relaxation rates by velocity analysis of molecular beams from these small free jets and were able to show how advantageous free jets are for determining rapid rates. Such a velocity analysis in conjunction with an enthalpy balance provides information on the amount of energy remaining in the internal degrees of freedom of the jet molecules. In some cases this energy content can be related to a particular degree of freedom in the molecule. In many more cases additional information is required before such an assignment can be made. The big advantage of FTIR spectro-

metry of free jets is that it gives direct and unequivocal information on the terminal state of particular degrees of freedom. It also tells immediately whether that degree of freedom has a Boltzmann distribution of energy and is thus amenable to analysis by means of the standard relaxation rate equation. Our newly acquired ability to obtain infrared emission spectra thus opens the way to determining energy exchange rates which cannot readily be obtained by other means.

Relating the experimentally observed terminal state to the relaxation rate is a very important step in the overall procedure. In the course of this contract we have made some substantial progress in the development of appropriate analytical procedures which we will now discuss.

In the original studies we used a Numerical Integration (NI) of the relaxation rate equation through the expansion with characteristic rate as a parameter. A match of experimental results with calculated values of the terminal state allowed us to identify the appropriate characteristic rate. Another approach is based on the so-called Sudden Freeze Model (SFM). It assumes that equilibrium is maintained in the jet until the density decreases to a critical value. At that point the relaxing process suddenly stops, i.e. freezes. The observed terminal value of the relaxing state thus tags the point in the jet at which this freezing occurred. The SFM then further assumes that the actual kinetic rate is just equal to the rate called for by the gas dynamic requirement to maintain equilibrium. This gas dynamic rate is obtained from well-known Method-of-Characteristics solutions of the hydrodynamic equations of motion of the jet gas. Although both the NI and SFM approaches have been

used by several investigators they had never been carefully compared. We undertook such a comparison and were able to show that the results obtained by the two methods could be greatly different, especially for polyatomic molecules. A paper on this comparison was presented at the 11th Symposium on Rarefied Gas Dynamics. It is more precisely identified in Section III where it is the first paper on the list of publications. The results in that paper related to pure gases. We carried out another set of calculations for the important case of a dilute solution of a polyatomic species in a nonatomic carrier gas. It is identified in the publication list as paper number two.

More recently we have made an important advance in the analysis of free jet expansion data. We have succeeded in working out a computer program which obtains Method-of-Characteristics solutions of the hydrodynamic equations when relaxation is occurring. In the past all such solutions have been forced to assume equilibrium. The net result is that we now have a truly accurate way to obtain rate data from measurements of the terminal internal state of molecules in free jet expansion. Thus far we have carried out calculations only for the case of gases with a specific heat ratio of $7/5$ corresponding to linear molecules with two degrees of rotational freedom. The results show that the "true" rates which we obtain from our new method are intermediate between those obtained by the SFM and those obtained by the earlier NI methods. A paper on this new development has been submitted for publication to the 12th Symposium on Rarefied Gas Dynamics which will be held at the University of Virginia in July. The abstract of this paper comprises Appendix III.

C. Some Associated Research. The presence of the FTIR spectrometer in our laboratory has stimulated some ancillary activities. It sometimes happens that the instrument is not in use for our energy exchange experiments because of troubles in the vacuum system, modifications to the apparatus, etc. On those occasions we have encouraged our colleagues to take advantage of its powers. Some interesting results and exciting prospects have emerged from these "bootlegged" activities. Professor Haller, who has long been interested in surface chemistry and catalysis, has been exploring the use of the spectrometer in some internal reflection spectroscopy experiments. In particular he has addressed the problem of characterizing the interaction between catalytic metal particles and the substrate surface, e.g. rhodium on alumina or titania. By means of a diamond internal reflection prism he has been able to "see" the shift in rhodium-carbon bonds due to the presence of oxygen. The experiments are in the preliminary stages but are extremely promising.

In another surface related experiment Professor Bret Halpern has been trying to determine whether nascent molecules formed by exothermic surface processes are vibrationally hotter than the surface which they leave, i.e. whether they retain appreciable fractions of the energy released by reaction in their internal modes. Professor Halpern hoped to form NO molecules by exposing a platinum surface bathed in oxygen molecules to a stream of nitrogen atoms from a microwave discharge and to examine the product NO molecules by FTIR emission spectroscopy to see if they were vibrationally excited. Much to his and our surprise, instead of NO he found that copious quantities of N₂O were formed in the surface reaction. Moreover, the N₂O molecules were vibrationally excited.

Unfortunately, it turned out that the vibrationally excited nitrogen molecules in the stream from the microwave discharge excite the N_2O molecules in gas-gas encounters so that he has not yet been able to determine whether the nascent N_2O molecules are vibrationally excited when they leave the surface.

These are two examples of what we expect will be an increasing impact of the FTIR spectrometer on the research in our department. In any papers resulting from these ancillary efforts, AFOSR will receive appropriate acknowledgements for its most valuable contribution in the form of the FTIR spectrometer.

III Publications

1. "Internal Energy Relaxation Rates from Observations on Free Jets", C. G. M. Quah, J. B. Fenn and D. R. Miller, Rarefied Gas Dynamics 11th Symposium, Vol II 885, (Ed. R. Campargue - Commissariat a L'Energie Atomique, Paris 1979).
2. "Internal Energy Relaxation in Methane and Its Chlorinated Derivatives," R. J. Gallagher and J. B. Fenn," ibid. page 935.
3. "Internal Energy Relaxation Rates from Seeded Supersonic Beams with a Monatomic Host Gas," C. G. M. Quah, Chem.. Phys. Letters 63, 141 (1979).
4. "Collisional Excitation of CO₂ by N₂, O₂ and Ar," S. B. Ryali, J. B. Fenn and C. E. Kolb. To be submitted to Journal of Chemical Physics.
5. "Relaxation of Internal Energy During Free Jet Expansion," M. Labowsky, D. R. Miller, S. B. Ryali and J. B. Fenn. Submitted for presentation at the 12 International Symposium on Rarefied Gas Dynamics to be held at the University of Virginia in July 1980.
6. "Energy Transfer as a Function of Collision Energy IV: State to State Cross Sections for Rotation to Translation Energy Transfer in HF plus NE, Ar and Kr," J. A. Barnes, M. Kiel, R. E. Kutina and J. C. Polanyi. To be submitted to Journal of Chemical Physics.

IV Personnel

A. Participants on Yale Staff.

Fenn, J. B., Principal Investigator, Professor of Engineering and Applied Science.

Haller, G. L. Professor of Engineering and Applied Science.

Labowsky, M., Visiting Assistant in Research - former graduate student.

Mantell, D. A., Graduate Student.

Quah, C. G. M. Graduate Student.

Venkateshan, S. P., Postdoctoral Research Associate.

B. Participants from outside Yale.

Kolb, C. E., Consultant (Research Scientist at Aerodyne Research, Inc.)

Polanyi, J. C., Consultant (Professor of Chemistry, University of Toronto)

Ryali, S. B., Consultant (Professor of Mechanical Engineering, University of Connecticut)

Miller, D. R., Visiting Professor at Yale (Professor of Applied Mechanics and Engineering Science, University of California, San Diego).

V. Interactions

(a) Papers presented. The following papers were read at the international symposia.

1. "Translational Excitation of CO₂ to a Radiating State", S. B. Ryali, J. B. Fenn and C. E. Kolb, presented at the Vith International Symposium on Molecular Beams, Noordwijkerhout, the Netherlands, April 1977.
2. "Internal Energy Relaxation Rates from Observations on Free Jets," C. G. M. Quah, J. B. Fenn and D. R. Miller, presented at the 11th International Symposium on Rarefied Gas Dynamics, Cannes, July 1978.
3. "Internal Energy Relaxation in Methane and its Chlorinated Derivatives", presented at the 11th International Symposium on Rarefied Gas Dynamics, Cannes, July 1978.
4. "Vibrational Excitation of CO₂ by Collisional T-V Exchange" presented at the VIIth International Symposium on Molecular Beams, Riva del Garda, June 1979.

(b) Talks and Seminars: Invited lectures in which the main subject was our research on energy exchange.

1. Indian Institute of Science, Bangalore, India- several lectures during January and February 1979.
2. University of Hyderabad, Hyderabad, India- 8 February 1979
3. Vikram Sarabhai Space Center, Trivandrum, India- 16 February 1979
4. National Chemical Laboratory, Poona, India - 19 February 1979
5. Indian Institute of Technology, Madras, India- 26 February 1979
6. University of Malaya, Kuala Lumpur, Malaysia- 28 February 1979
7. The Chinese University of Hong Kong , 5 March 1979
8. Institute of Space and Aeronautical Sciences, University of Tokyo, Several lectures in March, April and May 1979

9. University of Tsukuba, Institute of Applied Physics, Tsukuba Japan, 7 April 1979
10. Kyoto University, Department of Engineering Physics, Kyoto, 11 April 1979
11. Nagoya University, Department of Aeronautical Engineering, Nagoya, 18 April 1979
12. Toyota Central Research and Development Laboratories, Nagoya, 20 April 1979
13. University of Tokyo, College of General Education, Department of Pure and Applied Science, 23 April 1979
14. Toyama University of Medical and Pharmaceutical Sciences, Toyama, Japan, 19 May 1979
15. Max Planck Institut für Strömungsforschung, Göttingen, West Germany- 20 June 1979
16. University of Bern, Institute for Physical Chemistry, Bern, Switzerland 20 June 1979
17. University of Karlsruhe, Institut für Physikalische Chemie, Karlsruhe, West Germany, 25 June 1979

(c) Participation in Contractors Meetings and Working Groups:

1. AFOSR Contractors Meeting AFGL - October 1976
2. AF-ARPA Plume Group Meeting AFGL August 1977
3. AFOSR/AFRPL Rocket Propulsion Research Meeting March 1979
4. AFGL- Yale Research Meeting New Haven and Hanscomb AFB September 1979
5. AFOSR Molecular Dynamics Conference, Air Force Academy October 1979
6. AF-ARPA Plume Group Meeting, Calspan, November 1979

APPENDIX I

COLLISIONAL EXCITATION OF CO₂ BY N₂, O₂ and Ar

S. B. Ryali and J. B. Fenn

Yale University

and

C. E. Kolb, Aerodyne Research, Inc.

Summary

We have measured cross sections for the T-V excitation of the ν_3 mode of groundstate CO₂ molecules in collision with N₂, O₂ and Ar molecules at relative velocities in the range from 2 to 6 km/s. The exciting collisions were brought about by intersecting two slightly collimated molecular beams in the field of view of an InSb photovoltaic detector which monitored resulting radiation in the 4.3 μm band. The excitation cross sections for all three combinations of partners were of similar magnitude and strongly depended upon collision velocity. In the case of N₂-CO₂, for which we have the most data the measured cross sections range from about $8 \times 10^{-20} \text{ cm}^2$ at 2 km/s to about $5 \times 10^{-17} \text{ cm}^2$ at 5 km/s.

I. Introduction

We became interested in determining cross sections for the vibrational excitation of ground state molecules during collisions at high relative velocity. In particular, we wanted to know the cross section for exciting the asymmetric stretch (ν_3) mode of ground state CO_2 by collision with N_2 , O_2 and Ar at velocities up to several km/s. To achieve these collision velocities by thermal means would require temperatures in the range from say 3000 K to 30,000 K. While temperatures in this range can be achieved by shock tube and arc techniques they would result in such rapid decomposition of CO_2 that to study its T-V excitation at high collision velocities by thermal means would seem almost hopeless. Of course, one could in principle observe the converse process and monitor at somewhat lower temperatures the decay of molecules which had been excited by photons. The advent of tunable lasers has made this method powerful and popular. Unfortunately, it has not yet been possible in such an experiment to determine the relative velocities of the partners after they have engaged in a quenching collision. Therefore, one cannot single out those events which are the true converse of collisional excitation at high velocity. Moreover, in these or any other relaxation experiments there often are many alternate pathways by which energy can and does make its way from or to an observable state. The association of a measured rate with a particular path or sequence of states is in many cases at least difficult and sometimes impossible.

For these reasons there is no body of experimental results in the literature from which the desired cross sections can be extracted. The only relevant previous results are those obtained by Dunn, Skinner and Treanor . (1)

They expanded shock heated nitrogen to high Mach number and low density in a hypersonic wind tunnel. Carbon dioxide was introduced in transverse flow and radiation from excited molecules was monitored by sensors strategically located downstream from the injection point. Unfortunately, the gas densities were high enough so that the possibility of multiple collision paths to excitation could not be ruled out. Moreover, the band pass of their detector was unduly narrow so that their results needed some corroboration.

It occurred to us that a judicious application of molecular beam methods might be able to provide values for T-V excitation cross sections which related unequivocally to single collision transitions from the ground state. Our approach was to oppose molecular beams of each species and to measure radiation from species excited by the resulting collisions. The beams were produced from supersonic free jet sources which permitted aerodynamic acceleration of the colliding species by helium or hydrogen.⁽²⁾ In combination with high source temperature this so-called seeded beam technique could provide collision velocities up to about 6km/s. The jets were only slightly collimated in order to obtain high fluxes and to maximize the total number of exciting collisions. The background pressure was low enough (ca 10^{-5} torr) to insure that the possibility of multiple collisions could be ignored. Radiation from a volume of about one cm^3 of the beam intersection region was focused on the detector which comprised an Indium Antimonide chip cooled to liquid nitrogen temperatures. Its response fell abruptly at wave lengths shorter than 2.5 μm and longer than 5 μm . The only possible radiation from CO_2 within this wavelength range is that due to the ν_3 mode which falls in a

band centered at 4.3 μm . Consequently, all signal could be directly related to the concentration of molecules in which the ν_3 mode was excited. The radiation lifetime of this mode is about 3.5 msec. The excited molecules were travelling at about 10^5 cm/s in the laboratory frame of reference. Therefore, only a very small fraction of the excited molecules could contribute to the detector signal. In addition, the cross sections turned out to be relatively small so that the experiment became an exercise in extracting a whisper of signal from a loud cacophony of noise. The next section will set forth the methods and means which provided some modest success in obtaining useful signals.

II. Apparatus and Procedures

Figure 1 shows schematically the arrangement of essential elements of the apparatus. The nozzles were made from rhenium tubes with an o.d. of 3.18 mm and a wall thickness of 0.25 mm. Several nozzles were used with throat diameters ranging from 0.08 mm to 0.16 mm. The inlet end of each nozzle tube was clamped in a water-cooled block of brass which was electrically grounded. Several turns of tungsten wire wrapped around both exit end of the nozzle tube and a parallel rod insulated from ground and maintained at a desired potential by a high-current power supply external to the vacuum system. The nozzle tube could thus be heated by an electric current to temperatures as high as 2000 K. Two of these assemblies were mounted on base plates equipped with lockable slides so that alignment and distance between the nozzles could be adjusted. The latter could range from 8 to 12cm but was maintained at 9 cm in these experiments. Two configurations were

employed. In one the nozzles were opposed on a common axis so that the beams intersected at 180 degrees, i.e. met head on. In the other the axes intersected at 90 degrees. The 90 degree configuration probably provided somewhat better definition of the collision region but it did sacrifice some collision velocity. A stainless steel shield helped to keep radiation from the hot nozzle away from the detector. A boron nitride retainer disk surrounded each of the nozzle tubes and helped to maintain alignment. A micro-optical pyrometer was used to determine the nozzle tip temperature. Time-of-flight velocity measurements on the beams indicated that the effective source stagnation temperature was very close to the apparent tip temperature.

The infrared detector (Santa Barbara Mod. 9906) comprised a high impedance photovoltaic chip of InSb 2mm in diameter with a quantum efficiency of about 0.32 in the wave length range from 1.5 to 5.0 μm . The efficiency drops off sharply at longer and shorter wavelengths. It was mounted on the bottom end of a stainless steel Dewar assembly which permitted a 60 degree field of view. The entire assembly was inside the vacuum system so that no window was needed between the chip and its surroundings. On the optical axis there was a pair of convex germanium lenses with diameters and focal lengths of 5 cm which focused on to the chip the radiation from a region 1.1 cm in diameter at the intersection of the beams. The lenses had anti-reflective coatings and provided a measured transmission efficiency of 0.21 for 4.3 μm radiation. The effective aperture of this arrangement was allowed a solid angle of radiation which reached the detector from the collision region was .084 steradians. Also along the optical path between the chip and the beam

intersection region as shown were various optical baffles including the trap at the end. The purpose of these baffles, of course, was to shield the detector against stray radiation from the nozzles and other sources in the system. In order to enhance their effectiveness they were all made of aluminum and provided with good conducting paths to the stainless steel U-tube on which they were clamped. This tube was connected to a liquid nitrogen Dewar at the top of the tank. In this way all the surfaces which could be seen by the detector were maintained at temperatures below about 125 K. As a further precaution against stray radiation all the surfaces were coated with non-reflecting paint (Black Velvet Optical Spray from 3M Company). Unfortunately, molecules travel in straight lines just like photons but are not completely absorbed by black surfaces. Therefore, appropriate openings had to be provided to let the beam molecules into and out of the "optically anechoic" region surrounding the detector and the collision region.

The entire detector assembly was suspended between the nozzles in a vacuum chamber 80 cm in diameter exhausted by an oil diffusion pump (NRC H-32-SP) having a nominal pumping speed of 30,000 l/s effectively halved by a freon-cooled baffle. With both beams on the background pressure was typically about 2×10^{-5} torr. Some probing with an ion gauge indicated that in the immediate vicinity of the beam intersection region the background pressure was less than 10 times higher. Even so the mean free path was at least tens of centimeters.

In order to take advantage of ac signal processing techniques the CO₂ jet was chopped with a rotating shutter at 100 hz. The voltage output

from the detector was fed into a two stage amplifier designed for frequencies between 4 and 900 Hz. Even though this arrangement could discriminate against dc background signal any infrared flux above 20 nanowatts was sufficient to overload the preamp circuit. It was for this reason that we had to pay so much attention to optical baffling and shielding. The output from the amplifier went to a signal averager (PAR Waveform Educator Mod.TDH-9) whose output was recorded on a strip chart. Note that it is the cold CO₂ jet which was chopped. We learned after much frustration that any attempt to chop a beam from a hot nozzle always gave a big spurious signal due to the modulation of radiation from the hot nozzle surfaces. In order to obtain a cross section from the experimental observations it is of primary importance to calibrate the detector, i.e. to determine the proportionality factor which relates the signal amplitude on the strip chart to the concentration of excited molecules in the detector field of view.

During the early stages of this study we tried to determine this factor on an absolute basis by measurements of the output when the detector was looking at a black body of known temperature. This approach was awkward and proved to be unsatisfactory for a number of reasons. We then realized that we could take advantage of some experimental results obtained by Gallagher in our laboratory.⁽³⁾ By time-of-flight analysis of beams from CO₂ jets he was able to show that over the range of source Reynolds numbers in which we were operating there was no relaxation of the ν_3 mode during free jet expansion. In other words, the mol fraction of vibrationally excited molecules was the same after expansion as it was back in the source. It is easy to determine this mol fraction from the source temperature. Moreover, because free jet expansion

are well understood we can calculate with confidence the density of gas at any distance from the nozzle exit. Consequently, it became a straightforward exercise to calibrate the detector "in situ". We had simply to measure the chart recorder signal when CO₂ was issuing from its nozzle at a known temperature and pressure. There is one precaution to be observed. The density distribution in the jet is scaled by the flow diameter at the nozzle throat where the Mach number is unity. At low Reynolds numbers, i.e. low source pressures and high source temperatures, the boundary layer thickness at the nozzle throat makes the effective flow diameter smaller than the geometric throat diameter. In order to make sure that the boundary layer thickness is negligible one must measure detector output dependence on pressure at constant temperature. Data for the calibration are taken from that part of the curve over which the signal has reached a plateau and does not depend upon pressure. Figure 2 illustrates the situation for two source temperatures. The ordinate parameter B, which will be described shortly, is essentially the total signal divided by the number of excited molecules calculated to be in the field of view assuming that the flow diameter equals the geometric throat diameter. As the pressure increases along the abscissa the ordinate value of signal per molecule rises until it approaches a steady value which corresponds to the absence of appreciable boundary layer blockage of the throat. There is some scatter in these calibration results but a reasonable asymptotic value could be estimated. Note that this calibration procedure is so simple that it could be performed at the beginning of any run. In this way we overcame problems of long term drift and variations in optical alignment.

III. Data Reduction and Analysis

It is now appropriate to set forth the basis for obtaining the excitation cross section $\sigma(v_3)$ from the observed detector signal. The flux of photons to the detector chip can be represented by:

$$F = N^* \Omega \theta / \tau 4\eta \quad (1)$$

where F is photons/sec arriving at the detector, Ω is the solid acceptance angle in steradians (0.084) for the lens system (i.e. the fraction of all photons emitted in the field of view whose trajectories lead to the chip), θ is the lens transmission factor for 4.3 μm radiation (0.21) and τ is the average radiative life time for the N^* excited molecules in the field of view of the detector. The power P delivered to the detector is the product of the flux and $h\nu_3$ which has the value of 4.67×10^{20} joules/photon. The detector-amplifier combination converts this power into a voltage V so that overall we can write

$$V = A n^* \quad (2)$$

Where A includes all of the constant factors in Eq. (1) including the characteristics of the detector, amplifier and optical system including the effective volume in the field of view by which n^* must be multiplied to give the N^* of Eq (1). We determine A by the calibration procedure which is based on a computation of the density ratio n/n_0 from the method-of-characteristics solutions of the equations for free jet expansion (4), and the assumption that the mol fraction of excited molecules is the same in the field of view as it was in the source gas or:

$$n^* = n \exp(-h\nu_3/kT_0) \quad (3)$$

There remains the problem of relating the excitation cross section $\sigma(v_3)$ to

an n^* resulting from collisions and measured while the two beams are intersecting. We assume that all the excited molecules in the field of view are produced by collisions occurring therein. This assumption is tantamount to assuming that the number of excited molecules drifting into the field of view, having been formed by collisions outside, is equal to the number formed inside and drifting out while still excited. Further, we suppose that the average radiation life time is the same for those drifting in and for those formed. In other words, the field of view is a sample volume of a homogenous region in which excited species are being formed by collisions between the molecules of two intersecting streams in otherwise collisionless flow. This assumption is clearly crucial. As we will note later, it is supported by the reassuring observation that similar values for $\sigma(v_3)$ were obtained whether the beams intersected at 90° or 180° .

The other important factor in determining $\sigma(v_3)$ from observed values of n^* is the average residence time of an excited molecule in the volume comprising the field of view of the detector. This residence time is clearly given by R/\bar{v}_p the ratio of the effective radius of the collision volume to the mean post collision velocity of the excited molecule. Silver and Kolb have carried out an analysis which assumes an isotropic angular distribution of post collision velocities. (5) They arrive at the result:

$$\begin{aligned} (1/\bar{v}_p) &= \pi/2 u; \quad 0 \leq (c/u) \leq 1 & (4) \\ &= \frac{1}{c} + u^3/3c^4; \quad c/u > 1 \end{aligned}$$

where $u = v_2 - c$, v_r being the relative velocity of the colliding partners and c the center-of-mass velocity. We used this result in analyzing our experimental

data. If we combine the above relations we finally obtain:

$$\sigma(v_3) = V_d / B n_1 n_2 v_r (R/\bar{v}_p) \quad (5)$$

where V_d is the detector voltage output, B is the calibration factor determined as described earlier, n_1 and n_2 are the number densities of molecules in the two beams at the intersection region, v_r is their relative velocity when they collide, R is the effective radius of the field of view, 0.503 cm in our experiment.

IV. Results and Discussion

Table 1 contains the results for $N_2 - CO_2$ excitation cross sections $\sigma(v_3)$ obtained from the experiments by the procedures we have described. Figure 3 shows a plot of these cross sections against the relative velocity of the colliding partners. They invite a number of comments and explanations. First to be noted is that the values obtained in the 90° configuration with pure N_2 are about ten times higher than consistency with the other results would dictate. We have puzzled a great deal about this apparent anomaly but have no satisfactory explanation. Among the possibilities we have considered is a V-V transfer. In order to obtain the indicated relative velocities with pure N_2 we had to raise the source temperature as high as 1600 K at which point about 10 per cent of the molecules would be vibrationally excited. The V-V transfer cross section for N_2 to excite the v_3 mode of CO_2 is famously large as the popularity of the CO_2 laser witnesses. It would have to be about 100 times larger than the TV cross sections we have found to account for the observed discrepancy. Moreover, source temperatures were just as high in the 180° configuration for pure N_2 and in some of the seeded N_2 results at higher

relative velocities and cross sections for these cases show no anomaly.

In sum, we are still puzzled.

We would note in passing that the results shown in Table 1 and Fig. 3 were taken from experiments performed over a two year period during which two different detectors and a number of different nozzles were used as well as the two indicated configurations. Except for the open circle points we have been discussing, the overall concordance is both satisfying and reassuring. An appropriate inference from the fact that these measurements required two years is that they are tedious and difficult to perform. Success was achieved only by devoting painstaking and time-consuming attention to the elimination of noise from many sources. It often seemed that as fast as one source of noise was eliminated another would take its place.

We should explain the two arrows on the abscissa. The one at about 1.8 km/s corresponds to the threshold energy required for N_2 to excite the v_3 mode in a ground state CO_2 molecule. The arrow near 4 km/s shows the velocity required for a helium atom to excite the same mode. Helium was the carrier gas in the seeded beam experiments. Consequently, some of the excitation assigned to N_2 at the highest velocities may have been due to He- CO_2 collisions.

Results with O_2 and Ar as collision partners are also in Table 1 and are shown in Fig. 4. They are much less extensive than those with N_2 but are of similar magnitude and velocity dependence. In the case of Ar there can be no question of V-V transfer. Its similarity to N_2 and O_2 strongly supports our contention that what we have been observing is truly T-V excitation. We also

obtained a few results with H_2 . The velocity required for excitation was of course much higher because of its much smaller mass. On a cross section vs. energy plot, however, all four collision partners share a common curve within a factor of about two. This similarity of these quite different species is consistent with the usual presumption that the repulsive part of the potential plays the major role in any T-V exchange.

The only published experimental results with which our data could be reasonably compared are those mentioned earlier which were obtained by Dunn, Skinner and Treanor in a hypersonic tunnel.⁽¹⁾ They report a "partial" cross section of about $1.7 \times 10^{-20} \text{ cm}^2$ at a relative collision velocity of 5.8 km/s, nearly three orders of magnitude smaller than we find at that velocity. They used a filter between the collision region and their detector which only passed radiation between 4.28 and 4.34 μm . It may be that the rotational bandwidth was great enough to put most of the radiation outside of this band pass. It was for this reason that we used the term "partial" in reference to the cross section which they reported. Also to be noted is that in their experiment there was a somewhat greater chance of multiple collisions and convection complications, e.g. quenching after excitation.

More recent and more reassuring are some results obtained by Rahbee, Gibson and Dolan.⁽⁵⁾ In an apparatus similar to ours they have obtained spectra of the 4.3 μm radiation from CO_2 molecules excited by collision with N_2 at relative velocities between 2 and 4 km/s. They have not yet obtained absolute cross sections but the velocity dependence of their relative total cross sections matches ours almost precisely.

Finally, we would remark on the nature of that velocity dependence for the T-V excitation cross section as shown in Fig. 3. Its most noteworthy feature is the sharp rise with velocity above the threshold value which is identified with an arrow on the abscissa. The steepness of this rise might be expected from the predictions of the well known Landau-Teller theory which says that for collisions at kinetic energies substantially above threshold the transition probability should increase exponentially with collision velocity. Levine and Bernstein discuss the probable behavior near threshold and conclude from detailed balancing arguments together with empirical information on the de-excitation process that the excitation cross section should also increase exponentially in the energy regime immediately above threshold. (7)

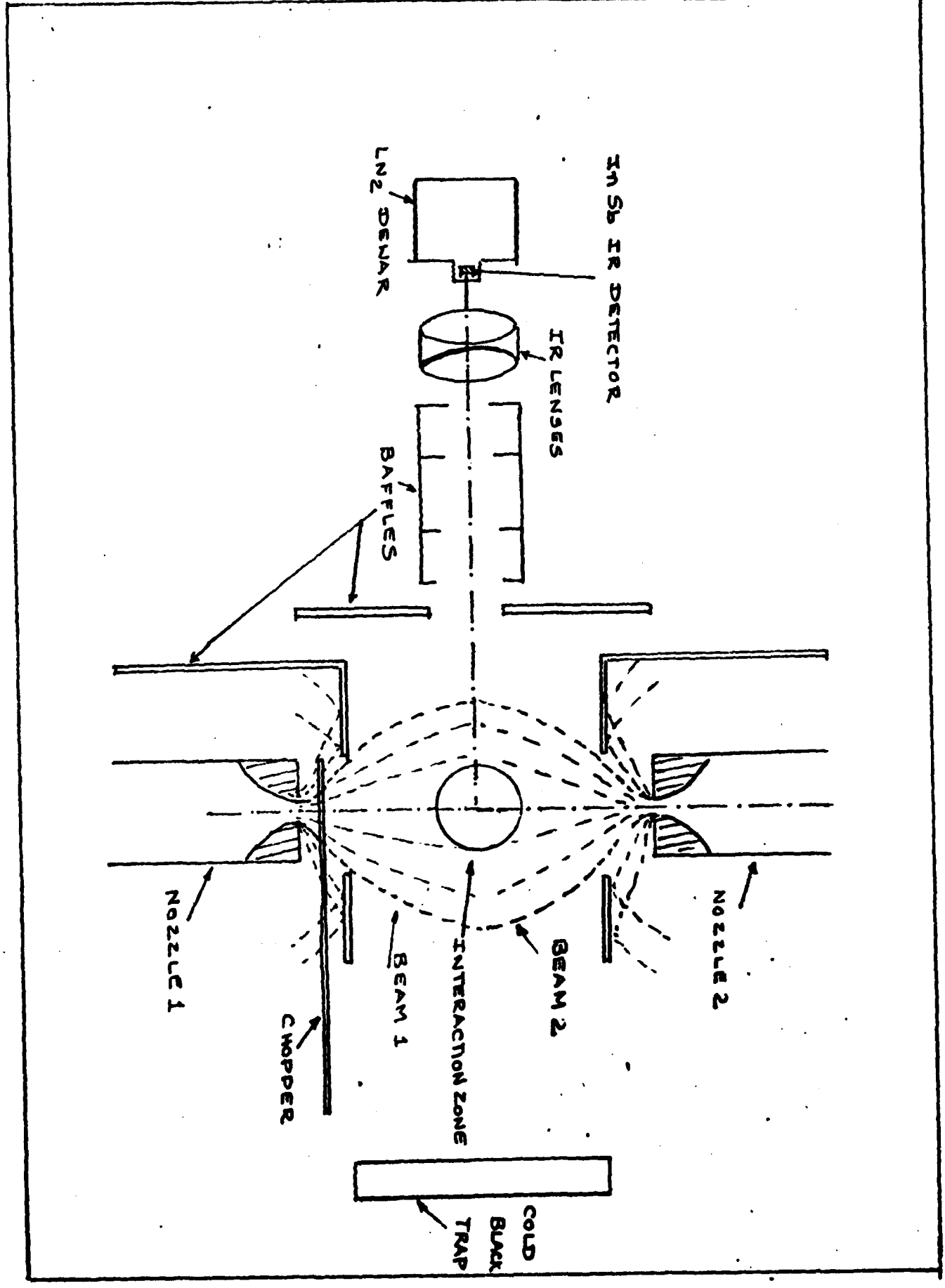
Recently Faist applied information theoretic considerations to the TV excitation process which we have described here. Absolute values cannot readily be obtained but the velocity dependence which comes out of the analysis is in remarkable agreement with our measurements. (8)

Acknowledgement

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CALIBRATION DATA FOR CO₂ (ν₃) RADIATION - JUNE 1978

AL-79-460

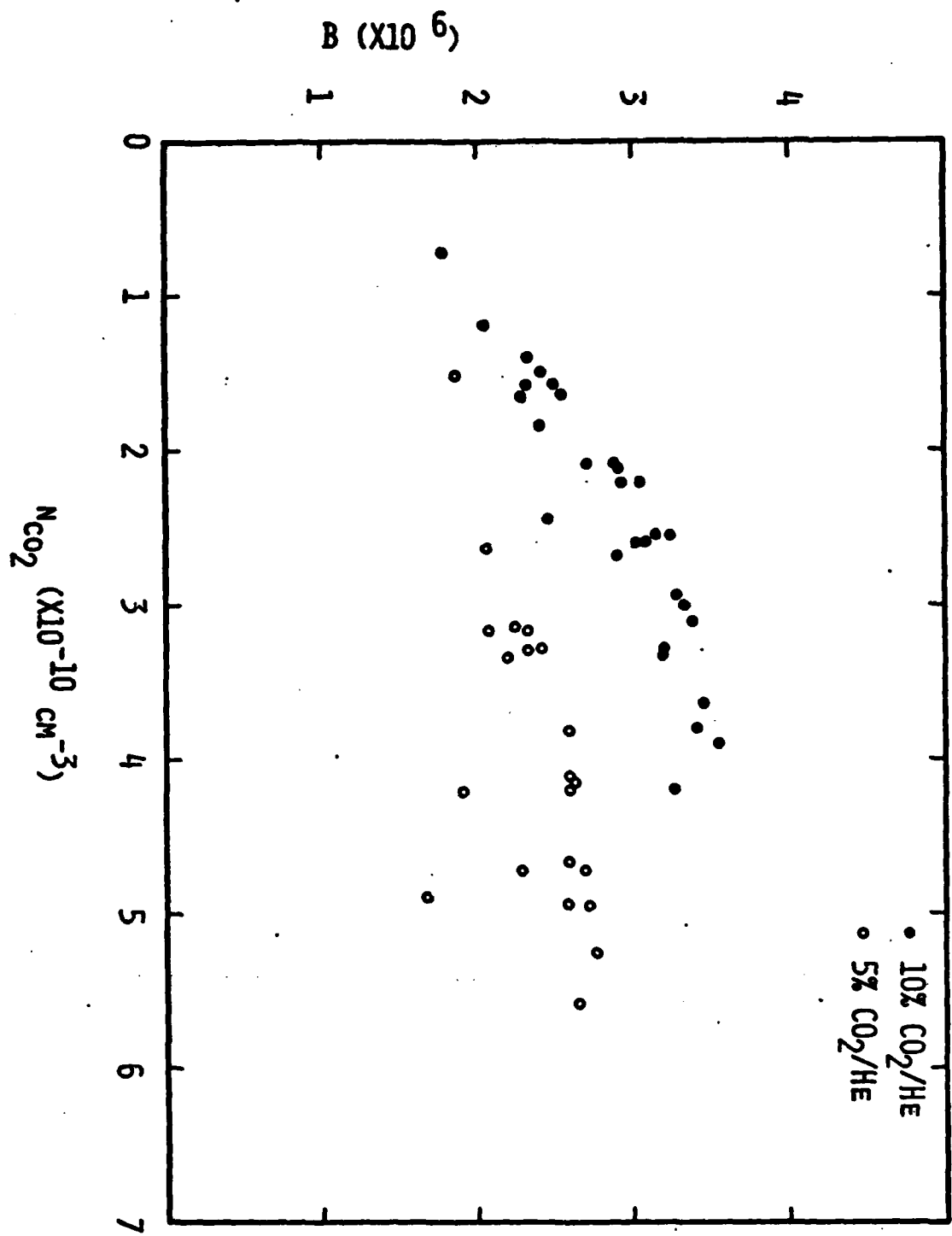
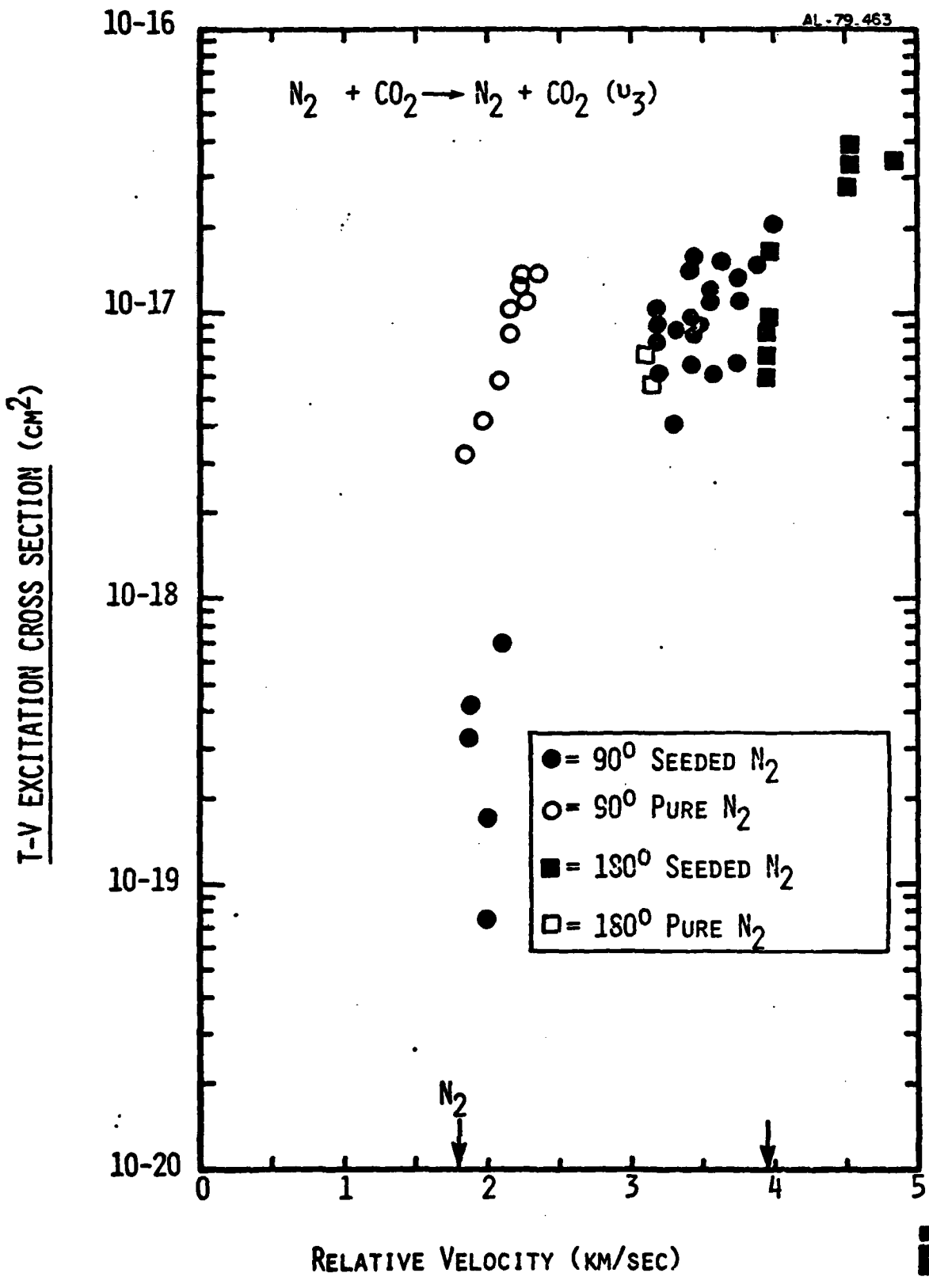
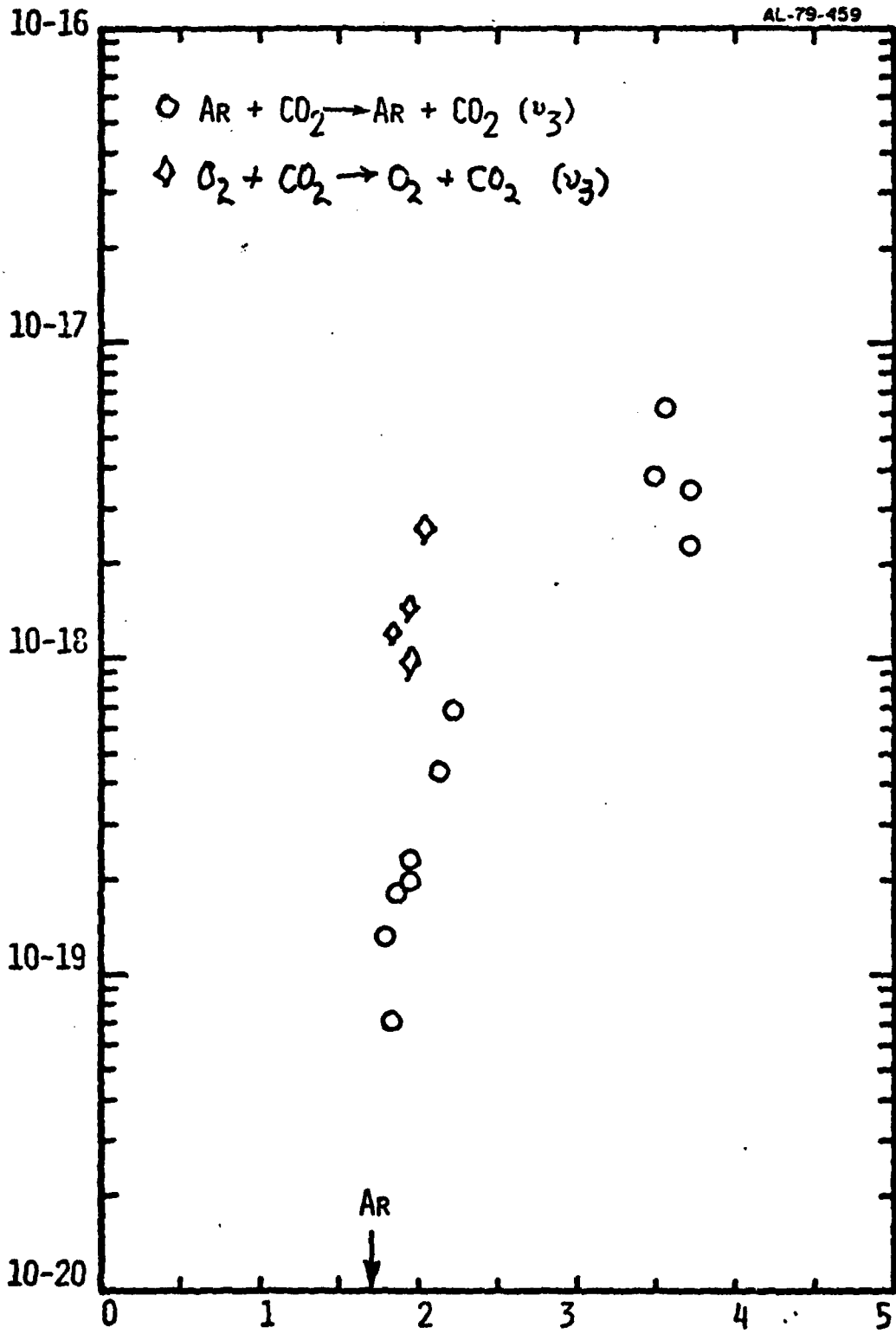


Fig 3



AL-79-459

T-V EXCITATION CROSS SECTION (CM²)



RELATIVE VELOCITY (KM/SEC)



Translation-to-Vibration Energy-Transfer in HF+Kr Collisions

State-to-state supersonic jet experiments ~~carried out under a~~ consultant's agreement with Prof. J.B. Fenn's research program by Prof. J.C. Polanyi's research group at the University of Toronto. The experiments were performed by Mr. Jack Barnes, Mr. Ray Kutina and Dr. Mark Keil, at the University of Toronto.

1. Introduction

The apparatus used for this exploratory work at the University of Toronto resembles the infrared emission apparatus used successfully in studies of vibrational excitation of CO₂ at Yale. The differences are that in Toronto a) the supersonic jet emanates from a separately pumped chamber, b) the initial state of the HX (hydrogen halide) molecule is selected by excitation using a cw infrared laser, c) the final state of the HX is monitored by grating spectroscopy and d) the range of collision energies achievable in the Toronto apparatus is less since only one collision partner is accelerated by supersonic expansion.

2. Apparatus

The Toronto apparatus is described in outline below.

a) Primary beam source: HF

A mixture of 90% H₂ and 10% HF at a total pressure of 800 torr expanded from a 0.4mm diameter orifice in a resistively-heated graphite oven at 1800°K. The primary beam chamber was pumped to 10^{-2} torr (pressure measured with gases flowing) by means of a 16" ring-jet booster pump rated at 4300 l/sec, backed by an 85 l/sec mechanical pump. The nozzle-skimmer distance was 4mm., and the

skimmer orifice diameter was 1.33 mm.

The HF beam emerged from the skimmer into the main scattering chamber which was maintained at 10^{-5} - 10^{-4} torr, with the HF beam on. Pumping in the main chamber took place by way of a 32" diam. 32,000 l/sec diffusion pump, and by concurrent liquid-nitrogen cryopumping.

b) Secondary source: Kr

The source of secondary gas, i.e. the collision partner, was a copper ring placed around the primary beam axis, with 22 holes drilled around a 4.6 cm circumference. The holes were 0.3 mm diameter, and were drilled so as to angle the 22 jets inward at 30° to the primary beam axis. The pressure ahead of the 0.3 mm orifices was approx. 5 torr, hence the gas emerged initially as a jet (the mean-free-path at 5 torr is $\sim 10^{-3}$ mm, i.e. less than the orifice diameter).

3. Experiment

The initial vibrotational state, $v_i=1$, $J_i=3$, was selected by laser excitation from $v=0$, $J=4$ using a single line of approx. 400 mW power from a cw infrared chemical laser operating on the reaction $F+H_2 \rightarrow HF+H$. The laser emission was reflected ~ 30 times across the molecular beam with a resultant population ratio $N(v=1, J=3)/N(v=0, J=4) \approx 0.3$.

The collision of the vibrationally excited HF with Kr took place 4 cm within the (13 cm diameter) 'Welsh cell'; a multiple pass cell designed to collect isotropic emission. The infrared fluorescence emerging from the Welsh cell was focussed on the slits of a Perkin Elmer single-pass grating spectrometer (slit width 0.75 mm). The infrared radiation coming from the spectrometer was focussed by an off-axis ellipsoid

onto a liquid-nitrogen-cooled PbS detector.

The infrared laser radiation was chopped mechanically en route to the reaction vessel. The chopping frequency was monitored, and the infrared fluorescence signal was amplified by a phase-sensitive amplifier locked to this frequency.

4. Results

Fluorescence from the laser-excited vibrotational level, $v_i=1$, $J_i=3$, gave rise to a signal of 216 μ V from the PbS detector. When the HF($v_i=1$, $J_i=3$) molecules were crossed with the Kr at a centre-of-mass collision energy of $E_{rel}=18.5$ kcal mole⁻¹, and the spectrometer was tuned successively to adjacent rotational states $J_f=1-4$ of $v_f=2$, no signal was detectable. Since translation-to-rotation, $T \rightarrow R$, with $v=1$ could be observed with a signal-to-noise of ~ 100 at inelastic cross-sections of $S_{T,R} \sim 10 \text{ \AA}^2$, we estimate that the inelastic cross section for $T \rightarrow V$ is $< 0.1 \text{ \AA}^2$ to yield a particular J_f state of $v_f=2$. This is despite the fact that E_{rel} exceeds the threshold energy for $T \rightarrow V$ by a factor of $E_{rel}/[E(v=1)-E(v=0)]=1.7$.

Our limiting value for the $T \rightarrow V$ inelastic cross-section in HF($v=1$)+Kr collisions is subject to the possible criticism that some HF($v=2$) is formed in low-impact parameter collisions that scatter HF outside the field of view of the Welsh cell. We have considered this possibility and adjudge it to be of minor importance. For our (fast) HF colliding with (heavy) Kr the laboratory scattering angles and centre-of-mass scattering angles are virtually equivalent. HF($v=2$) if scattered forward or backward will be carried through the normal viewing region in the Welsh cell. If scattered sideways at

90° out of the plane of the Welsh cell it will be less efficiently viewed than normal, but if scattered sideways into the plane of the Welsh cell it will be more efficiently viewed. To summarize; by locating the collision region within the White cell we have achieved a sufficiently broad viewing region for HF($v=2$) that we can depend on our (order-of-magnitude) upper limit for T→V inelastic cross-section; viz $S_{T,V} < 0.1 \text{ \AA}^2$ to yield a particular J_f state of $v_f=2$ in collisions of HF($v_i=1, J_i=3$)+Kr at $E_{rel}=18.5 \text{ kcal mole}^{-1}$.

APPENDIX III

RELAXATION OF INTERNAL ENERGY DURING FREE JET EXPANSION

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Abstract

In the small supersonic jets widely used as molecular beam sources the rapidity of the expansion can lead to substantial departures from equilibrium. The extent of these departures is reflected in the distribution of internal energy states of the jet molecules after the density reaches such low values that the state of the gas becomes frozen. For any particular degree of molecular freedom the extent of departure is determined by its characteristic relaxation rate in conjunction with the density-temperature history of the gas during expansion. A quantitative description of the relation between relaxation rate, source conditions and final gas state would be very useful (a) for estimating the terminal state of jet molecules when the characteristic relaxation rate is known and (b) for determining the characteristic rate from experimental observations of that terminal state.

There have been two approaches most commonly used in attempts to relate characteristic rates to final states. One which was first proposed by Bray and which has been applied by Knuth and others to free jet expansions invokes the "Sudden Freeze Model" or SFM.^(1,2,3) It assumes that equilibrium obtains in the expansion until the gas density drops to some critical value at which a particular degree of freedom instantly stops changing and remains frozen throughout the remainder of the expansion. SFM further assumes that the kinetic rate for the change of this degree of freedom, as determined by the characteristic rate and the density and temperature in the jet, can be identified with the minimum kinetic rate which the gas dynamic expansion rate requires to maintain equilibrium at the freezing point. The other approach

is based on a Numerical Integration (NI) of characteristic relaxation rate throughout the expansion assuming that the temperature and density at all times are determined by the equilibrium solution of the equations of motion obtained numerically by the method of characteristics.^(4,5)

In a paper at the last symposium results obtained by the SFM and NI were compared.⁽⁶⁾ Substantial differences were found especially in expansions involving low values of γ , the specific heat ratio. It was suggested but not shown that the NI results were probably more to be believed than those obtained with the SFM.

We have continued an investigation of this problem and have gone through two stages of refinement. In an Energy Balance Modification of the Numerical Integration (EBNI) we have taken account of the energy sequestered in the freezing mode by subtracting it from the equilibrium state of the gas as the expansion proceeds. In previous use of NI it has been assumed that the temperature and density of the gas were the same as in an equilibrium expansion. Recently, in a more ambitious refinement we have undertaken to write a computer program for the method of characteristics solution of the equations of motion with γ varying in accordance with a prescribed relaxation rate. In principle, this "None Equilibrium Method of Characteristics" (NEMOC) approach should be the ultimate solution to the problem, at least for any case in which the distribution of states is Boltzmann and only one mode is relaxing incompletely, all other modes being completely frozen or in equilibrium.

Thus far preliminary calculations have been completed for the case in which there is one internal degree of freedom which is freezing, i.e. rotation in a diatomic gas for which $\gamma = 1.4$. Results in terms of the parameter B, which is proportional to the product of source Reynolds number and characteristic rate, are shown in Figure 1. They indicate that the SFM tends to overestimate the rotational relaxation rate while the NI model underestimates it. The EBNI is a bit closer to the NEMOC result. We hope to have more complete results by the time of the symposium.

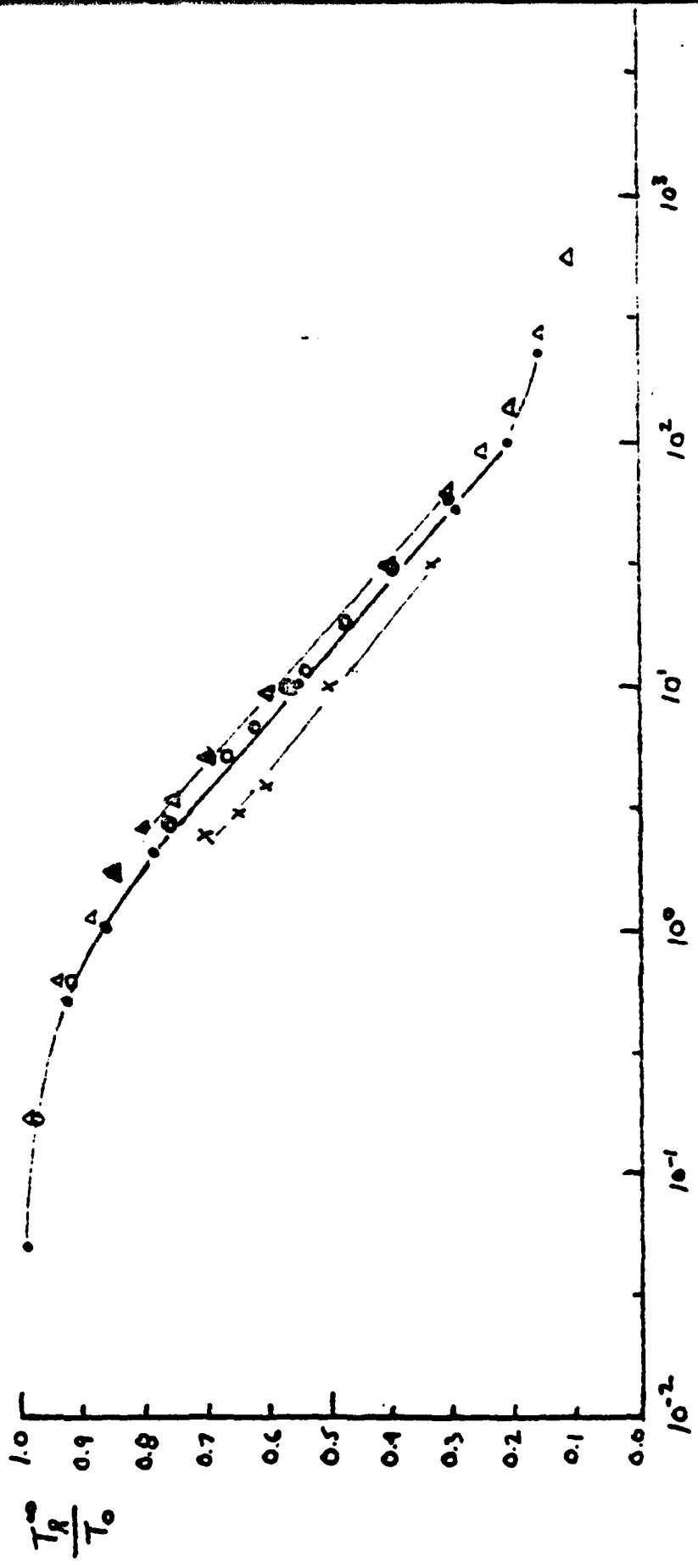
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ROTATIONAL RELAXATION
 COMPARISON OF MODELS

$\gamma_{eq} = 1.1$

- NEMOC
- EBN1
- △ NI
- × SFM



B_{QUAN}