OBSERVATION OF LUMINESCENT SPECTRA
IN LOW ENERGY ION-NEUTRAL COLLISIONS

Progress Report
for Period June 1, 1975 - May 31, 1976

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February, 1976

Prepared For

THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. E(11-1)-2718

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ABSTRACT

The experimental investigations reported here have been directed toward obtaining information on the energy partitioning among internal energy states of the product species resulting from collisions between positive ions and neutral molecules at relative kinetic energies below about 500 eV. Two types of inelastic collision processes have been studied: electron exchange and atomic rearrangement. The data, which are obtained by direct observation of emission spectra resulting from the decay of excited collision products, have been used for product identification and for the determination of state distributions and absolute excitation cross sections. The state distributions have been compared to those predicted from theoretical models, and have also been used to elucidate reaction dynamics. The nature of the potential energy curves (and surfaces) for the species involved has been shown to play an important role in determining energetics and excitation cross sections. One class of dissociative charge transfer (electron exchange) process has been found to be an efficient mechanism for creating a population inversion in a discharge laser cavity. The state distributions and excitation cross sections obtained in this work have provided microscopic details of the collisions that occur in the complex environment of a discharge laser cavity.

I. INTRODUCTION

The objective of the research described in this report is to determine the nature and extent of energy transfer in inelastic collisions between positive ions and neutral molecules at relative kinetic energies below about 500 eV. It is well established that at even the lowest relative energies it is possible to store up to several electron volts in internal energy states of the products of these collisions when the reaction energetics is favorable. It is desirable to know how this energy is partitioned among the available states. Such information cannot only elucidate the dynamics of a reaction, but can also provide microscopic details of macroscopic phenomena.

Two types of inelastic collision processes leading to excited products have been investigated: charge transfer and atomic rearrangement. These processes are illustrated by the reactions

where A, B and C can be either atoms or molecules and the asterisk indicates electronic excitation (either or both of the products may be electronically excited). This electronic excitation is detected in our experiments by observing the (collision-produced) emission spectrum resulting from decay of the excited products. A subclass of charge transfer which we have studied extensively during the

last year is an unusual dissociative charge transfer-excitation process:

The unusual feature of Reaction (3) is that the electron "acceptor" molecular ion, He_2^+ , does not have a bound parent molecule, He_2 (in the ground state), so that the charge transfer process is a dissociative one. This type of dissociative charge transfer-excitation process has been shown by us to have unusually high cross sections for selective excitation of product ions,¹ AB^+ ; this selective excitation is the result of the unique nature of the energetics of the electronic recombination of He_2^+ which yields two unbound helium atoms. Since He_2^+ is rapidly formed in high pressure helium discharges, charge-transfer-excitation process such as reaction (3) can be effective laser pumping mechanisms.² The interest shown in our laser related work has prompted extensive study of these pumping mechanisms over the past year.

We have also studied scattering processes such as (1) and (2), and these experiments will also be discussed in this report. The work conducted over the past year can be conveniently discussed by classification according to reactions (1) through (3) above; section III, Results, is therefore subdivided accordingly.

II. EXPERIMENTAL

The apparatus used in these studies is shown schematically in Figure 1. Ions are produced in an electron impact ion source,

FIGURE 1 Schematic diagram of the apparatus

extracted and focused with cylindrical electrostatic lenses before magnetic mass selection. After emerging from the mass selector the ions are focused into the collision chamber at the desired kinetic energy by another set of cylindrical electrostatic lenses; the beam energy is varied by changing the collision chamber potential, and is determined by retardation analysis as shown in the figure. The target gas pressure, usually about one micron, is monitored with a capacitance manometer. Three oil diffusion pumps are employed to obtain the desired differential pumping; base pressure of the entire system is $\sim 10^{-7}$ torr.

Photons exit the collision chamber through a slot (1.5 mm x 2 cm) which is parallel to the ion beam, pass through a quartz window and directly into a Jarrell-Ash model 82-410 scanning monochromator. The entrance slit of the monochromator, which is also oriented parallel to the ion beam, is located approximately 1 cm from the ion beam center. Either of two gratings, blazed at 3000 Å and 5000 Å, is used in the monochromator. Photons are detected with an EMI 9659QAM photomultiplier tube cooled to -75°C. Output pulses from the photomultiplier are counted and stored in a 256 channel multiscaler. Appropriate circuitry controls both the multiscaler and a stepping motor which turns the grating of the monochromator in precise increments. The usual mode of operation is to scan a portion of the spectrum storing the pulses in the multiscaler. Signal averaging may be accomplished by repetitive scans of the same spectral region. A PDP/8E minicomputer is being prepared to replace the multiscaler. When installed this minicomputer will not only accumulate data, but will also be used for data reduction and plotting.

III. RESULTS

A. Dissociative charge transfer [Reaction (3)]

Details of three investigations have been completed and have either appeared in the literature¹ or are currently "in press."^{3,4}

Unusually large cross sections for selective excitation in dissociative charge transfer processes have been observed by us for collisions of He_2^+ with N_2 , CO, O_2 , NO and CO_2 . This selective excitation in many cases results in intense photon emission at specific wavelengths. An example of this selective excitation may be seen in Figure 1 of Reference 1 which shows collision-produced emission spectra for both He_2^+-N_2 and He^+-N_2 collisions. The former spectrum has four distinct peaks corresponding to four different sequences of the $\text{N}_2^+(\text{B} \rightarrow \text{X})$ emission system. The He^+-N_2 spectrum on the other hand exhibits few prominent peaks. The difference in the nature of these two spectra is related to both the nature of the electronic recombination energies (RE) of the electron acceptor species (He^+ or He_2^+) and the difference in their magnitudes. He_2^+ has a variable RE covering the approximate range 18.3-20.3 eV, while the RE of He^+ (in the ground state) is fixed at 24.6 eV. He^+ is thus capable of exciting N_2^+ to higher levels than is He_2^+ , and the resulting He^+-N_2 spectrum contains contributions from many higher lying electronic states; some of these states have not yet been firmly established.⁵ Since He^+ formed in a high pressure helium discharge is rapidly converted to He_2^+ in multibody, He^+-nHe , collisions, reaction (3) can be an effective means of creating a population inversion if low partial pressure of the AB molecules are added to

the helium in the discharge cavity. In fact, strong laser emission at three different wavelengths of the $N_2^+(B \rightarrow X)$ system has been produced in an electron-beam (e-beam) initiated discharge in a mixture of helium and nitrogen.² The dissociative charge transfer-excitation process

is believed to be the pumping mechanism by which the population inversion is created. The work from our laboratory has provided cross sections and vibrational state distributions which have proved to be useful in this field of e-beam laser technology. In addition to the success of the N_2^+ laser, stimulated emission on several lines of CO^+ has been produced.⁶ The pumping mechanism is analogous to reaction (4) in $He_2^+ \cdot CO$ collisions. Our study of this system³ has also provided useful information which is related to the observed stimulated emissions. Reference 4 provides details which are currently being used for guidance in attempts to produce laser action on CO_2^+ emissions in the ultraviolet.

We have attributed the unusually high cross sections for these excitations to the variable RE that results from the unbound He-He ground state.¹ This is illustrated in Figure 2 of Reference 1 where, from the He_2^+ and He-He potential energy curves it is clear that vertical transitions from the He_2^+ ground state to the He-He repulsive state may occur at internuclear separations between about 0.9Å and 1.2Å. Such transitions cause a continuously variable RE

because the repulsive He-He potential does not support bound states. Since RE's in the range 18.3-20.3 eV are sufficient to not only remove an electron from the molecules studied (N_2 , CO, etc.), but in addition to leave the resulting ion in an excited state, these charge transfer-excitation processes can occur at the lowest kinetic energies (they are exothermic or thermoneutral). When the excitation energy of a particular ionic state (above the ground state of the neutral molecule) lies within the RE band of He_2^+ the energy defect of the process can be quite small, a condition favorable for high cross sections. "Resonances" of this kind are illustrated in Figure 1 of Reference 3 where it is seen that radiating states of N_2^+ and CO^+ (as well as O_2^+ and NO^+) lie with the He_2^+ RE band.

We have also obtained vibrational state distributions of the excited ionic species produced in these collisions. These distributions were then compared to distributions obtained in other charge transfer systems such as

and to distributions predicted from the Franck-Condon model of vertical transitions. The results of one such comparison are illustrated in Figure 2 where it is clear that, while the Ar^+-N_2 collisions give a decidedly non-Franck-Condon distribution, the $He_2^+-N_2$ system yields a distribution that closely matches the model. Non-Franck-Condon distributions observed in processes such as (5) above have been attributed to distortion of the target molecule

FIGURE 2 Spectra of the $\Delta v = -1$ sequence of $N_2^+(B \rightarrow X)$ emissions resulting from impact of Ar^+ and He_2^+ on N_2 taken at $4\text{\AA}$ resolution. Also shown in the bar graph are fractional intensities of the indicated bands calculated under the assumption of vertical transitions. The fractional intensity scale was chosen so that the (0,1) bar matched the height of the (0,1) band for $He_2^+ - N_2$.

(N_2 in this case) in the electric field of the slowly moving incoming ion.⁷⁻⁹ This requires vertical transitions from a distorted

N_2 to $N_2^+(B)$ so that overlap integrals would have to be calculated using wave functions appropriate for this stretched molecule. We have attributed the observed agreement with the vertical transition model for $He_2^+ - N_2$ collisions to the large cross section for these processes. Since the cross section for $He_2^+ - N_2$ charge transfer-excitation is roughly one hundred times greater than for the $Ar^+ - N_2$ system, electron transfer to He_2^+ is effected at impact parameters

roughly ten times those for Ar^+ . At large impact parameters the target molecules are essentially unaffected by the electric field of the incoming ion so that negligible distortion takes place and the usual "undistorted" Franck-Condon factors are applicable.

The problems described in this section have proven to be both interesting and practical (laser-related) so that we are continuing to pursue them.

B. Charge transfer [Reaction (1)]

We have studied rotational distributions produced in charge transfer collisions for comparison with rotational distributions produced by atomic rearrangement. Recent studies from our laboratory¹⁰ and Ottinger's laboratory¹¹ in Germany have shown that substantial rotational energy is stored in molecular products of atomic rearrangement so that comparison with charge transfer-produced rotational distributions can provide insight to the collision mechanisms. Our results are still preliminary and have not yet been fully analyzed.

An example of these experiments is a comparison of the rotational distributions of $\text{N}_2^+ [\text{B}^2\Sigma_u^+(v'=0)]$ produced by O^+-N_2 collisions and N^+-N_2 collisions. N_2^+ can only be formed by charge transfer in O^+-N_2 collisions while N_2^+ from N^+-N_2 collisions can be formed by either charge transfer or atomic rearrangement. Our results are shown in Figure 3 which contain high resolution ($4\text{\AA}$) collision produced O^+-N_2 and N^+-N_2 spectra of the $\Delta v=0$ sequence of the N_2^+

FIGURE 3 Spectra of the $\Delta v = 0$ sequence of $N_2^+(B \rightarrow X)$ emissions resulting from impact of O^+ and N^+ on N_2 taken at 4 Å resolution.

first negative system. The $\Delta v=0$ sequence consists primarily of the violet degraded (0,0) band so that the extent of the "tail" of this band may be taken as a measure of the rotational "temperature". Our results show clearly that there is more rotational excitation from the N^+-N_2 system than the O^+-N_2 system. This result may be ascribed to the additional (reactive) channel available to the N^+-N_2 system and is consistent with earlier measurements on other systems.^{10,11} We are continuing to pursue these studies.

C. Reactive scattering [Reaction (2)]

An extensive study of the energy disposal in O^+-H_2 atomic rearrangement collisions was completed during the last year.¹² This

system had several interesting features which made it attractive. The intermediate species, H_2O^+ , has been extensively studied by theorists so that the locations on the energy scale of many of the H_2O^+ excited states are known. This facilitates construction of correlation diagrams (between reactants and products) from which dynamical information about the system may be obtained. Another interesting feature of this system was our observation that two different atomic rearrangement processes occur:

and

From the kinetic energy dependence of the emissions it was determined that both ground state O^+ and metastable excited states of O^+ present in the incident ion beam were responsible for formation of $(\text{OH}^+)^*$, while only excited O^+ participates in the formation of OH^* . Figure 3 in Reference 12 contains collision-produced emission spectra at twelve relative kinetic energies. This figure shows the emergence and disappearance of the OH^+ and OH spectral features as functions of relative kinetic energy. These spectra, in conjunction with our correlation diagram, shown in Figure 7 of that paper, provide information on the evolution of the O^+-H_2 system from reactants to products.

The series of reactive systems, $X^+ - H_2$, where X is one of the first row atoms, C, N, O, or F, have been studied extensively in the past.¹³⁻¹⁵ These earlier studies have provided total cross sections and kinematic details of the processes. We had previously reported chemiluminescence from several excited states of CH^+ formed in $C^+ - H_2$ collisions¹⁰ using our technique. After completion of our $O^+ - H_2$ experiments, we began study of $N^+ - H_2$ reactive collisions. The $N^+ - H_2$ results are incomplete, but we have observed chemiluminescence from the reaction

Figure 4 shows a spectrum from $N^+ - H_2$ collisions at 5 eV relative energy. The locations of pertinent bandheads for NH^+ emission are

FIGURE 4 Spectrum of NH^+ resulting from $N^+ - H_2$ reactive scattering at 5 eV relative kinetic energy. Known bandheads of the indicated emission systems are marked in the figure.

marked in the figure. Although our results are preliminary, it is clear that at least at this kinetic energy, ~ 3 eV (the approximate energy of a 400 nm photon) is stored in the products of N^+-H_2 collisions.

IV. SUMMARY

The research undertaken since the contract was initiated has provided emission spectra from decay of excited products of low energy inelastic collisions. These spectra have been used to identify product species and to obtain internal energy state distributions and absolute cross sections for the processes studied. Two types of processes were investigated, charge transfer and atomic rearrangement. For one type of dissociative charge transfer process unusually high excitation cross sections and anomalous vibrational state distributions were observed. The data relating to these high cross section processes has proven to be valuable in laser technology and our studies have suggested several systems which might be employed to produce population inversions in new high powered devices. Rotational distributions inferred from some charge transfer studies have been compared to similar data taken for systems in which atomic rearrangement was a possible reaction channel. Though the data is preliminary, these comparisons show that, as observed previously, atomic rearrangement ion-molecule collisions result in substantial rotational excitation. Studies of purely reactive systems have yielded data which has elucidated the dynamics and energy partitioning in these processes.

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- *. The work which resulted in these papers was performed under this contract.

VI. PERSONNEL

The following persons are (have been) actively engaged in the research program.

J. J. Leventhal - Principle investigator

H. H. Harris - Faculty associate

G. H. Bearman - Research Associate

F. Ranjbar - Graduate student

R. J. Pieper - Graduate student

J. D. Earl - Undergraduate assistant

During the summer of 1975 the principle investigator devoted 100% of his time to the project. During the academic year 1975-1976 the principle investigator has (will) devote approximately 50% of his time to the project. The time devoted to the project by the principle investigator during the academic year was (is) supported by UMSL.