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MASTER

OBSERVATION OF LUMINESCENT SPECTRA
IN LOW ENERGY ION-NEUTRAL COLLISIONS

Progress Report
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Contents

I. Introduction.....	1
II. Experimental.....	4
III. Results.....	7
IV. Summary.....	28
V. References.....	30
VI. Personnel.....	32

ABSTRACT

The experiments reported here provide detailed information on the fundamental nature of energy transfer processes in ion-molecule or atom-molecule collisions. By combining ion beam techniques with emission spectroscopy, data are obtained which directly lead to internal energy state distributions of atomic and molecular products of these collisions. Data are in the form of emission spectra from nascent energetically excited species formed in the energy transfer process. Changes in the collision-produced spectra as a function of beam kinetic energy yield information on the extent of energy conversion (kinetic $\leftrightarrow$ internal) in the collision process. Some of the specific energy transfer processes studied are applicable to the problem of achieving inverted energy level populations in high pressure gas lasers. Also discussed are experiments designed to test theoretical models which predict product energy partitioning in molecular collisions. Because our experimentally determined energy state distributions deviate substantially from the predicted distributions it is concluded that additional theoretical work is needed. We have developed a simple model which qualitatively reproduces the important features of the data. This model, which is considerably more general than those previously available is outlined and briefly discussed.

I. INTRODUCTION

The work described in this report is directed toward obtaining detailed information about energy conversion (kinetic $\leftrightarrow$ internal) mechanisms in atomic and molecular interactions. Since collisions between atoms and molecules can redistribute energy among the accessible product final states it is desirable to have information on the partitioning of energy among these possible final states. The data needed to determine this energy distribution are obtained in these experiments by spectral analysis of the radiation resulting from the decay of nascent excited species formed in ion-molecule or atom-molecule collisions at relative kinetic energies 1 - 1000eV.

Since the last progress report was submitted (Report No. COO-2708-4, February, 1976) several types of processes leading to energetically excited product species have been studied. Our investigation of possible population inversion mechanisms in charge transfer lasers¹ was continued. In particular, our work on charge transfer reactions of the type

where R_2^+ is He_2^+ or Ne_2^+ and $(X^+)^*$ is a radiating atomic or molecular ion, was continued and some interesting and potentially technologically useful results obtained. Because of recent interest in energy disposal in reactions

involving multiply charged ions², a study of charge transfer to doubly charged ions was undertaken. Some interesting results were obtained for collisions of the type

as well as information on the potential energy curves of the CO^{++} molecular ion.

The problem of predicting final state distributions in atomic and molecular energy transfer processes in this kinetic energy range is one which is not yet solved. The fundamental limitation on predictions of such state distributions is the lack of accurate potential energy surfaces for the systems involved. Since the final molecular states in this work include electronic states as well as vibrational and rotational states of the product species, two or more potential energy surfaces are required. In an effort to circumvent the necessity for accurate potential energy surfaces models to describe the collision process have been developed. We have performed a series of experiments designed to test the validity of these models. Our results showed that the premise upon which the most popular of these models was based could not be justified. Therefore, we have performed additional experiments, and have developed a theoretical model which reproduces the qualitative features of the observed internal energy state distributions.

The work to be described in this report can be conveniently classified as:

- A. Laser pumping mechanisms; reaction (1)
- B. Doubly charged reactions; reaction (2)
- C. Model calculations and experiments

Section III of this report (Results) is subdivided accordingly, and each phase of the work briefly described.

Additional details may be found in the publications resulting from these studies.

II. EXPERIMENTAL

Since submission of the last progress report several significant apparatus modifications have been made as well as modifications of the data acquisition system. The basic apparatus is shown in Figure 1. Ions are produced in an electron impact source and subjected to magnetic mass selection before being accelerated (or decelerated) to the desired collision kinetic energy and focused into the collision cell. After emerging from the collision cell the ions are collected with a Faraday cup. The collision cell containing neutral target molecules at ~ 1 mtorr pressure has a slot oriented parallel to the ion beam trajectory from which photons emerge and pass through a quartz window and into a scanning monochromator. Photon detection is accomplished by counting output pulses from a photomultiplier tube the spectral range of which is 1800-8500 Å.

Figure 1. Schematic diagram of the apparatus.

The entire apparatus function is controlled by a PDP/8E laboratory computer. This computer, which was installed in late 1976, permits more efficient use of available data acquisition time than the more cumbersome multichannel scalar used previously. Data are acquired by stepping the monochromator through the spectral region of interest. The dwell time per channel, spectral range, wavelength increment, and other relevant experimental parameters are entered in the computer prior to the commencement of a run. Photon pulses are counted by the computer during the dwell time at each wavelength setting, and the collision-produced emission spectrum thus assembled. Repetitive scans (also preprogrammed) are employed for signal averaging. After a run the data are stored on a floppy disk system while the spectrum is plotted on a CRT terminal; a hard copy of the spectrum may then be filed for easy access to the data in graphical form. The computer also corrects the data for the spectral response of the optical system which has been determined using standard lamps.

An additional modification has been made to the apparatus to permit investigation of atom-molecule or molecule-molecule collision systems. Most of the work has been conducted with incident neutral ground state hydrogen atoms impinging on neutral molecules. The H atom beam is formed by charge transfer to a mass selected H^+ beam prior to the collision cell as shown in Figure 2. The ion deflecting

elements sweep out unneutralized H^+ ions and also serve to Stark quench any metastable $H(2s)$ atoms formed in the charge transfer process, thus assuring a ground state H atom beam. Detection of the neutral beam is accomplished by secondary electron emission from a Ta grid as shown in Figure 2. As will be discussed later in this report our studies of energy transfer processes in neutral-neutral collisions using this technique have added to our understanding of fundamental energy conversion processes at the molecular level.

Figure 2. Schematic diagram of the apparatus used for neutral beam experiments.

III. RESULTS

A. Laser pumping mechanisms

Since our observation in 1975¹ that charge transfer-excitation (CTE) reactions involving He_2^+ primary ions can have exceptionally large cross sections for selective excitation we have studied a number of such systems. Some of our earlier work has been discussed in the last progress report, but some new investigations have provided additional insight as well as some potentially useful data. The recent trend toward gas lasers operating at very high He partial pressure³ ($\sim$ atmospheres) with a much lower partial pressure of some other molecule has made reactions involving the rare gas dimer ions important. This importance is due to the rapid conversion rate of He^+ ions formed in the discharge to He_2^+ ions in multibody He^+ -He collisions⁴ so that He_2^+ is the dominant ionic species in the discharge. Reactions between these He_2^+ ions and the minor constituent atoms or molecules may then efficiently create a population inversion. The prototype example of such a system is the N_2^+ laser where the upper laser level, $\text{N}_2^+[\text{B}^2\Sigma_u^+(\nu=0)]$, is efficiently produced in He: N_2 discharge (partial pressures $\sim$ 3 atm:100 torr). The population inversion mechanism in this laser is the reaction

Laser oscillation has been achieved on the (0,0), (0,1) and (0,2) bands of the N_2^+ first negative band system, $\text{N}_2^+(\text{B} \rightarrow \text{X})$,

at wavelengths $3914\overset{\text{O}}{\text{\AA}}$, $4278\overset{\text{O}}{\text{\AA}}$ and $4708\overset{\text{O}}{\text{\AA}}$ respectively. The success of this laser and the close correlation between our data for single collision He_2^+-N_2 encounters has led us to examine other He_2^+ -neutral molecule systems as well as He_2^+ -neutral molecule systems.

The high cross sections for selective excitation have been attributed to the unbound nature of the final state of the two helium atoms. Since the He-He potential is essentially repulsive (except for the small long range van der Waals attraction) and supports no bound states, the electronic recombination energy of the He_2^+ is continuously variable. This is illustrated in Figure 3 which shows the bound state potential energy curve for He_2^+ (Morse curve) and the He-He repulsive curve. Vertical acceptance of the electron (no change in internuclear separation) can occur over a continuously variable range of internuclear separation with a continuously variable electronic recombination energy ($\sim 19.3 \pm 1\text{eV}$) which is available to ionize the "electron donor" (the N_2 reactant in equation (3) for example). For most species 19eV is sufficient to not only ionize the neutral reactant, but to also excite the product ion without the necessity of converting kinetic energy to internal energy. The continuously variable nature of the electronic recombination energy permits the reaction to proceed in a resonant fashion ($Q=0$); resonant reactions typically have high cross sections at low collision energies. Unlike processes having only two body final states,

any excess energy can be disposed of as kinetic energy of the product helium atoms. This may be visualized by imagining the system represented by the two product helium atoms as sliding down the repulsive curve in Figure 3 from the point the system occupies when the electron is transferred.

Figure 3. Morse potential for $\text{He}_2^+(X^2\Sigma_u^+)$ and the repulsive He-He potential. The cross hatched region represents neutralization of He_2^+ resulting in two unbound He atoms.

One interesting system which was studied by us is the $\text{He}_2^+-\text{CO}_2$ system.⁵ Since the two radiating states of CO_2^+ , the $\tilde{\text{B}}$ and $\tilde{\text{A}}$ states, are favorably located with respect to the continuously variable He_2^+ recombination energy, it was anticipated that strong emissions originating in either or both of these systems might result, and indeed this was the case. These emissions occurred in the wavelength range 2900-3500Å, and the results suggested that if laser action were achieved in a discharge tube, proper choice of mirrors might make oscillation possible at more than one wavelength. Since CO_2 is both inexpensive and innocuous this system is attractive from the standpoint of laser development.

Since high pressure lasers of the type described above are frequently operated with electron beam initiated discharges (rather than discharges between appropriately shaped electrodes) it has been suggested that substituting neon for helium might result in more efficient use of the electron beam. This is predicated on the higher stopping power of neon to electrons⁶ (neon has higher Z). Since Ne_2^+ is formed at high pressures in multibody collisions analagous to those responsible for the formation of He_2^+ , an investigation of Ne_2^+ CTE was undertaken.⁷ Although the ionization potential on atomic neon is about 3eV lower than that of atomic helium examination of the relevant potential energy curves⁸ for Ne_2^+ and Ne-Ne shows that the range of Ne_2^+ electronic recombination energy is roughly the same as that of He_2^+ . This is in part due to the relatively shallow but broad Ne_2^+ potential well; this last results in a great many more vibrational energy

levels for Ne_2^+ than for He_2^+ . Our results for Ne_2^+ CTE showed:

1. Absolute excitation cross sections that were comparably high to the He_2^+ cross sections with gases such as N_2 , CO , CO_2 and O_2 .
2. Cross sections that depended strongly on the conditions under which the Ne_2^+ ions were formed in the source.
3. Strong dependence of the amount of Ne_2^+ produced in the ion source on the conditions under which it was produced.

Both of these last two effects were found to be enhanced by the addition of helium gas to the ion source. That is, "seeding" the ion source with helium increases the Ne_2^+ ion current as measured at the collision cell (number 3 above), but photon emission from the Ne_2^+ CTE processes increases faster than the Ne_2^+ current (number 2 above). Since the reactant beam (Ne_2^+ in this case) is mass selected, these effects cannot be related to "contamination" of the beam by helium-containing species. We have suggested that these effects are related to the efficiency of production of Ne_2^+ and the vibrational state distribution of the Ne_2^+ that occurs in the presence of He atoms. For example Ne_2^+ formation in multibody collisions may be enhanced by the availability of the

light helium atoms to carry off excess energy as kinetic energy in the ion source. Similarly, Ne_2^+ may be vibrationally cooler when formed in the presence of helium atoms. Our data then suggest that the vibrationally cooler Ne_2^+ ions are more reactive in these CTE processes. Since it is presumed that the vibrationally cooler ions are more efficient it was suggested that the addition of helium gas to a neon-containing laser cavity might facilitate laser oscillation.

B. Doubly charged reactions

The mechanisms of energy disposal in molecular interactions involving multiply charged species has been the subject of recent experimental and theoretical work. These studies have been stimulated by the importance of such processes in high temperature plasmas² and the potential of multiply charged ions for soft x-ray lasers.⁹ Although some work has provided absolute cross sections very few experiments which yield final state energy level distributions have been conducted. Since our experimental technique provides an ideal opportunity to study these state distributions under single collision conditions we undertook such a study. A detailed investigation of final state energy partitioning was conducted for single charge transfer in $\text{CO}^{++} - \text{H}_2$ collisions¹⁰ (reaction (2)). Motivation for study of systems involving CO^{++} was provided by

the opportunity to compare our data to theoretical predictions based on an available semiempirical potential energy curve¹¹ for this species. H_2 was chosen as the electron donor because the $CO^{++}-H_2$ system provides a favorable mass ratio permitting the reaction to proceed with minimum contribution from kinetic energy converted to internal energy. For example, the center-of-mass kinetic energy for laboratory kinetic energy 7.5eV is 0.5eV; most data were acquired at this energy.

The data showed clearly that both the $CO^+ A^2\pi$ and $B^2\Sigma^+$ state were formed when an electron was transferred to CO^{++} . The identification of these final states was made by observing radiation from $B \rightarrow X$, $B \rightarrow A$, and $A \rightarrow X$ transitions. (Comparison of the $A \rightarrow X$ signal to the $B \rightarrow A$ signal established that the $A^2\pi$ state was formed both directly and by $B \rightarrow A$ cascading.) Because the $B \rightarrow A$ and $A \rightarrow X$ radiation occurs in the same spectral region (3500-4500Å) overlap of these two emission systems prevented accurate determination of vibrational distributions within the product $CO^+(A)$ electronic state. However, it was established that the ground vibrational level of the $CO^+(B)$ state was preferentially populated in these collisions. That is, the preponderant $B \rightarrow X$ emission bands originated in $CO^+[B(v'=0)]$. This observation is in disagreement with calculated spectra obtained from a model based on the well-known CO^+ potential energy curves and the aforementioned semiempirical CO^{++}

curve. It is concluded, therefore, that either the semi-empirical curve or the model (based on vertical transitions) is inadequate. Some interest has been expressed by theorists in obtaining an accurate ab initio curve for CO^{++} thus eliminating the uncertainty associated with the semiempirical curve. As will be discussed later in this report, however, there is a need for a more general model than has previously been used.

C. Model calculations and experiments

One of the goals of the study of energy conversion processes at the microscopic level (single collision processes) is the formulation of general "selection rules" or "propensity rules" that govern energy disposal in these fundamental processes. Toward this goal it is desirable to have theoretical models available for comparison with our experimentally determined internal energy state distributions. The results of work performed in this program have demonstrated that the two most popular models are inadequate to explain our observed state distributions and the variation of these distributions with available initial kinetic and potential (internal) energy. Therefore, we have developed a model which may be applied to a variety of energy transfer processes of the type with which this work is concerned.

Before outlining this model it is useful to briefly describe the two alternate models. In order to do this a specific collision system ($\text{Ar}^+ - \text{N}_2$) and a specific process (CTE) will be considered; the reaction is

Vibrational state distributions within $\text{N}_2^+(B)$ product ions are obtained from collision-produced emission spectra from $\text{N}_2^+(B \rightarrow X)$ radiative decay. Changes in these state distributions are observed by comparing spectra obtained at a variety of incident ion (Ar^+) kinetic energies.

As a starting point, state distributions predicted from the Franck-Condon (FC) model, in which electronic excitation is assumed to proceed vertically,¹² can be compared to observed state distributions. This model is illustrated in Figure 4 (left panel). It is assumed that electron transfer from $\text{N}_2(X)$ to Ar^+ takes place without any change in N_2 internuclear separation. Therefore, the state distribution should be in accord with FC factors¹³ calculated from the accurately known N_2 and N_2^+ potential energy curves. While photoionization and electron impact ionization processes are known to proceed in this vertical fashion, state distributions observed for reaction (4) deviate substantially from these predicted by this model. In fact, as the relative kinetic energy is decreased the deviations from the model become more severe. This is illustrated in Figure 5 which shows a series of collision-produced spectra taken at

Figure 4. Potential energy curves for N_2 and N_2^+ representing the FC ionization model and the polarization distortion model.

different relative kinetic energies. In order to compare the data to the model, a calculated emission spectrum, based on the predicted $N_2^+(B)$ vibrational population, is included in the figure (bar graph). The radiative decay processes are known to proceed vertically. According to the FC model about 90% of the $N_2^+(B)$ should be in the lowest vibrational level,

Figure 5. $N_2^+(B \rightarrow X)$ emission spectra from $Ar^+ - N_2$ collisions at several kinetic energies. A bar graph representing the spectrum predicted from the Franck-Condon model is also shown.

so that the height of the (0,0) band may be taken as a measure of the FC character of the distribution. Note that at the lowest kinetic energy shown in Figure 4 this band is nearly absent; as the kinetic energy increases the (0,0) band increases and approaches the model spectrum. Comparison of the observed (1,0) band intensity with the (1,0) bar in the model spectrum shows that even at 1000eV kinetic energy (lab) the data are substantially different from the model spectrum. Earlier work¹⁴ at considerably higher kinetic energies shows that the distributions do not agree with the FC model distributions until the kinetic energy

reaches several thousand electron volts. These trends are characteristic of our observations for many CTE systems involving a variety of reactant ions and target molecules* (N_2 , CO, O_2 , etc.). It is clear that for ion-molecule collisions of this type the FC picture does not adequately describe the electron transfer process. An additional inadequacy with respect to these collision systems is that there is no kinetic energy dependence in the model.

The second model that has been proposed¹⁵ depends crucially on the fact that one of the reactant species is an ion rather than a neutral atom or molecule. It is presumed that the target molecule is distorted by the electric field of this incoming ion; that is, electrical polarization (of the N_2 in the example of reaction (4)) stretches the N_2 bond. Vertical ionizing transitions from the stretched molecule would then produce vibrational distributions different from an undistorted molecule. This is illustrated in Figure 4 (right panel) where the dashed curve schematically represents the potential energy function of the stretched N_2 . Vertical ionization from the stretched N_2 favors states other than $v=0$. Further, it is assumed that as the relative kinetic energy is increased

* the exceptions to the propensity of CTE systems to behave in this fashion are the extraordinarily large cross section processes involving He_2^+ and Ne_2^+ reactant ions where FC distributions are observed at kinetic energies as low as 1 eV. This phenomenon is consistent with our model and will be discussed.

the target molecule does not have time to adjust to the presence of the incoming ion and vertical transitions from an undistorted (or less distorted) molecule occur. Therefore, the trend toward the FC picture can be rationalized with this model. While this concept of a distorted molecular target is a significant contribution to understanding the underlying mechanisms of these energy transfer processes, the use of isolated ion-molecule charge distributions at such small separations is questionable. In order to test the polarization-distortion model we have performed a series of experiments designed to eliminate the effect of the electric field on the target molecule. In one set of experiments a beam of neutral H or He atoms (formed by charge transfer of H^+ or He^+ beam prior to the collision cell) was directed at neutral target molecules.¹⁶ Collision-produced emission spectra resulting from these neutral-neutral collisions were then obtained. For example, Figure 6 shows a portion of the spectrum from the ionizing collisions

Figure 6. Spectrum from 2keV H-CO collisions.

Although the FC model spectrum is not displayed in Figure 6 the vibrational distributions of $\text{CO}^+(\text{A})$ from reaction (5) are not in accord with the FC distributions, but tended toward the FC picture with increasing kinetic energy, displaying the same general character as the CTE systems. In another set of experiments CIE processes of the type

were studied. Figure 7 shows a series of spectra for reaction (6) taken at several kinetic energies. Note the increasing prominence of the (0,0) band of the $\text{N}_2^+(\text{B} \rightarrow \text{X})$ emission system with increasing kinetic energy, illustrative of the trend of the distributions toward the FC picture. Again this is the same behavior as was observed in CTE systems (compare Figure 7 to Figure 5).

Figure 7. $\text{N}_2^+(\text{B} \rightarrow \text{X})$ emission spectra from $\text{N}_2^+(\text{X}) - \text{Ar}$ collisions at several kinetic energies. A bar graph representing the spectrum predicted from the Franck-Condon model is also shown.

The deviations from FC model predictions observed by us in a number of ion-molecule energy transfer processes, and the inadequacy of the (electric) polarization-distortion model for description of a number of other collision systems (typified by reactions (5) and (6)) established the need for a more general model. The model which we have developed¹⁷ is based on the assumption that deviations from FC behavior are caused by direct translational-vibrational (T-V) excitation in both the initial and final electronic states of the electronically excited molecule. For specificity we have applied the model to N_2^+ -He CIE to vibrational levels of product $N_2^+(B)$, that is:

It is assumed that the T-V transfer proceeds via short range interactions. The potential hypersurfaces describing $N_2^+(X)$ -He and $N_2^+(B)$ -He are taken to have avoided crossing for some value of R , the N_2^+ -He separation (see Figure 8).

Figure 8.
Coordinates used
in applying the
model to N_2^+ -He
collisions.

For simplicity, we have assumed that these two hypersurfaces, $V_X(r, \theta, R)$ and $V_B(r, \theta, R)$, are independent of the N_2^+ -He orientation angle θ , and that the dependence on N-N separation, r , can be approximated as

$$V_{X,B}(r, R) \approx V_{X,B}(r_e, R) + (r - r_e) \frac{\partial V_{X,B}(r_e, R)}{\partial r} + \frac{1}{2} (r - r_e)^2 \frac{\partial^2 V_{X,B}(r_e, R)}{\partial r^2} \quad (8)$$

The term $\frac{\partial^2 V_{X,B}(r_e, R)}{\partial r^2}$ can be written as $k_0 + k_1(R) \approx k_0$,

the unperturbed N_2^+ force constant. In this study, we have replaced the adiabatic surfaces with diabatic surfaces which cross at R_c ; these diabatic states are coupled by a potential operator. For mathematical convenience, these surfaces are taken to vary as $\exp(-R/L)$. A number of calculations were performed in which the important parameters were varied; these parameters are: the range parameter, L ; the X-B coupling matrix element; and the potential energy at the crossing point, V^* . Figure 9 shows the functions V_X and V_B and the relevant parameters. R-motion was treated classically, but all other calculations were quantum mechanical.

Two conclusions can be drawn from the calculations. First, for a given center-of-mass kinetic energy $E_{\text{COLL}} > V^*$, the opacity function $P_{X \rightarrow B}(b)$, which represents the total electronic transition probability as a function of impact parameter b , rises as b increases from $b=0$ to $b=R_c$; in the latter case, the transition proceeds by tunnelling through

an energy gap which increases rapidly with b .

Figure 9. The functions $V_X(R)$ and $V_B(R)$ as described in the text.

The second conclusion is that the average vibrational energy, $\overline{\Delta E_{VIB}}$, transferred to $N_2^+(X)$ by T-V coupling, is a decreasing function of E_{COLL} for $b \approx R_C$ ($\Delta E_{VIB}(b \approx R_C) \propto 1/E_{COLL}$). This occurs because E_{COLL} is much greater than the N_2^+ vibrational spacing ($\hbar\omega_{VIB} \approx 0.25$ eV) and also because the trajectories are approximately rectilinear for large b . For small b , however, $\Delta E_{VIB}(b)$ increases with E_{COLL} , and can become so large that the $N_2^+(B)$ formed from such highly excited $N_2^+(X)$ immediately dissociates [$D_e(N_2^+(B)) \approx 5$ eV]. The experimental technique does not

allow observation of such collision-induced dissociation, so that a calculation for comparison with data need only consider b greater than some value b^* for which $\Delta E_{VIB}(b^*) = 5$ eV. Note that we are inferring the extent of β -state vibrational excitation from the χ -state excitation in a given collision; a full calculation requires a more complex treatment than afforded by our present model. Figure 10 shows the form of $P_{\chi \rightarrow \beta}(b)$ when $E_{\text{COLL}} > V^*$; superimposed are $\Delta E_{VIB}(b)$ curves for two values of E_{COLL} . Since

$$\overline{\Delta E_{VIB}} = \int_{b^*}^{\infty} P(b) \Delta E_{VIB}(b) b db / \int_{b^*}^{\infty} P(b) b db, \quad (9)$$

the observed decrease in $\overline{\Delta E_{VIB}}$ with increasing E_{COLL} can be qualitatively understood.

Figure 10. Total relative $N_2^+(X+b)$ transition probability, $P_{\chi \rightarrow \beta}(b)$, and vibrational energy transfer to $N_2^+(X, v=0)$, $\Delta E_{VIB}(b)$. The potential parameters are: $L = 0.02 \text{ nm}$, $V^* = 4 \text{ eV}$, $R_c = 0.2 \text{ nm}$. The $P_{\chi \rightarrow \beta}(b)$ curve shown accurately represents results for E_{COLL} between 25 and 125 eV.

Although these calculations have been applied specifically to N_2^+-He CHE, the model is applicable to any atom-diatom process having electronically-excited molecular products. The decrease in $\overline{\Delta E}_{VIB}$ with increasing E_{COLL} is not peculiar to the present system but rather is to be expected for systems with an accessible avoided surface crossing, provided l_{COLL} is high enough. Since this T-V excitation is superposed on the usual vertical (FC) distribution, such systems will tend toward the FC picture at high collision energy.

As mentioned in the footnote on page 18, the exceptions to the general behavior of vibrational state distributions discussed in this section are the huge cross section processes involving He_2^+ and Ne_2^+ reactant ions. Without exception the vibrational state distributions resulting from these high cross section processes are consistent with the FC picture and do not exhibit any kinetic energy dependence. These observations are consistent with the model discussed above. For large cross section processes the avoided crossing of the surfaces occurs at large values of R , and, since

$$\lim_{R \rightarrow \infty} \frac{\partial V(R, r_e)}{\partial r} = 0 \quad (10)$$

the linear term in equation (8) vanishes. It is precisely this term in the Hamiltonian that mixes the initial vibrational states. In the absence of this term only the ground vibrational state of the reactant molecule is present, and overlap integrals (FC factors) from higher initial vibrational states consequently make no contribution to the final state distribution in accord with the FC model - consistent with our observation for very large cross section processes.

Although this model has been effective in describing qualitative features of most of the energy transfer processes we have investigated¹⁸ there are some as yet unexplained observations. After developing the technique to extend our investigations to neutral-neutral systems, a thorough study of a number of such systems was conducted. In such systems the absence of electrical charge permits observation of vibronically excited neutral molecules to be relatively more prominent than in ion-molecule systems. For example, the energy transfer process

is not observed although $\text{N}_2(\text{C} \rightarrow \text{B})$ emissions are readily observed by us under other circumstances. What is observed in $\text{H}^+ \cdot \text{N}_2$ collisions is the CTE process

However, emissions from $\text{N}_2(\text{C})$ are the dominant features resulting from low energy collisions between H-atoms and N_2 . That is

is observed. At elevated kinetic energies $\text{N}_2^+(\text{B} \rightarrow \text{X})$ emissions are observed from H- N_2 collisional ionization. We have observed that while the vibrational distribution within the $\text{N}_2(\text{C})$ state from reaction (13) exhibits FC behavior at all kinetic energies the vibrational distribution within $\text{N}_2^+(\text{B})$ produced in H- N_2 collisions is not in accord with the FC

distribution. This is a very surprising result since the electron that is promoted in ground state N_2 to form $N_2(C)$, a $2\sigma_u$ electron, is the same electron that must be removed to form $N_2^+(B)$. Thus, reaction (13) and collisional ionization to $N_2^+(B)$ may be visualized as different degrees of the same process. Although this phenomenon may be rationalized in the context of our model it is clear that additional data and refinements to the model are necessary.

IV. SUMMARY

The research described in this Progress Report has provided information on energy redistribution among accessible quantum states of products species resulting from ion-molecule or atom-molecule collisions. Internal energy state distributions were determined under single collision conditions from data obtained using our apparatus which combines ion beam techniques with spectroscopic methods. Several classes of inelastic collisions were studied. One unique type of dissociative charge transfer process, which is the operative mechanism for achieving population inversion in the N_2^+ laser, was exhaustively studied; other similar collision systems which are potentially useful as laser pumping mechanisms were also investigated. In an effort to test theoretical models which are used to predict internal energy state distributions resulting from molecular collision processes a number of different ion-molecule and atom molecule systems were studied. Our data clearly demonstrate the inadequacy of these models, and establish the need for further theoretical work. We have developed a simple model based on the assumption that T-V excitation of the molecular reactant occurs in both the initial and final electronic state of the molecular species. This model requires further refinement, but does have the virtue that it is qualitatively consistent with all of the data. In addition, our model, unlike the most popular previous model,

does not depend crucially on having an electrically charged reactant (an ion.)

V. REFERENCES

- *1. a) J. J. Leventhal, J. D. Earl and H. H. Harris, Phys. Rev. Lett. 35, 719 (1975).
- * b) G. H. Bearman, J. D. Earl, R. J. Pieper, H. H. Harris and J. J. Leventhal, Phys. Rev. A13, 1734 (1976).
2. See for example D. H. Crandall, R. E. Olson, E. J. Shipsey, and J. C. Browne, Phys. Rev. Lett. 36, 858 (1976).
3. See for example J. B. Laudenslager, T. J. Pacala, and C. Wittig, Appl. Phys. Lett. 29, 580 (1976).
4. R. A. Gerber, G. F. Sauter and H. J. Oskam, Phys. Letters 19, 656 (1966).
- *5. G. H. Bearman, H. H. Harris and J. J. Leventhal, Appl. Phys. Lett. 28, 345 (1976).
6. W. J. Price, Nuclear Radiation Detection (McGraw-Hill, New York, 1958).
- *7. G. H. Bearman, J. D. Earl, H. H. Harris and J. J. Leventhal, Appl. Phys. Lett. 29, 108 (1976).
8. J. S. Cohen and B. Schneider, J. Chem. Phys. 61, 3230 (1974); 61 3240 (1974).
9. W. Louisell, M. O. Scully and W. B. McKnight, Phys. Rev. A11, 1989 (1975).

- *10. G. H. Bearman, F. Ranjbar, H. H. Harris and J. J. Leventhal, Chem. Phys. Lett. 42, 335 (1976).
11. A. C. Hurley, J. Chem. Phys. 54, 3656 (1976).
12. G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, New York, 1950).
13. R. W. Nicholls, J. Research (NBS), 65A, 451 (1961).
14. J. H. Moore, Jr. and J. P. Doering, Phys. Rev. 177, 218 (1969).
15. M. Lipeles, J. Chem. Phys. 51, 1252 (1969).
- *16. G. H. Bearman and J. J. Leventhal, Phys. Rev. A (in press).
- *17. J. D. Kelley, G. H. Bearman, H. H. Harris and J. J. Leventhal, Chem. Phys. Lett. 50, 295 (1977); also ACS Symposium Series, 56, 171 (1977).
- *18. a) G. H. Bearman, J. D. Earl, H. H. Harris, P. B. James and J. J. Leventhal, Chem. Phys. Lett. 44, 471 (1977).
- * b) G. H. Bearman, H. H. Harris and J. J. Leventhal, J. Chem. Phys. 66, 4111 (1977).

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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

S. D. Alspach - Undergraduate assistant

J. G. Ambrose - Undergraduate assistant

During the summers of 1976 and 1977 the principle investigator devoted 50% of his time to the project. During the academic years 1976-1977 and 1977-1978 the principle investigator has (will) devote approximately 30% 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.

0