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OBSERVATION OF LUMINESCENT SPECTRA
IN LOW ENERGY ION-NEUTRAL COLLISIONS

Progress Report
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ABSTRACT

Recent experiments on energy transfer processes in atomic and molecular interactions are described. Of particular interest are the results of studies involving energetically excited atoms. Using laser excitation, collisions between excited sodium atoms were found to form both ionic and highly excited neutral products, neither of which is energetically possible unless both reactant atoms are excited. It is shown that energy from the laser beam is "stored" in sodium atoms and returned to the system in subsequent collisions between excited species.

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I. INTRODUCTION

The work described in this Progress Report is directed toward obtaining experimental information on energy transfer and energy partitioning in collisions involving atoms and molecules. Research of this type, on microscopic systems, is fundamental to understanding energy disposal in macroscopic systems.

The major experimental technique employed in this work is that of observing collision-produced luminescence. Analysis of radiation from decay of excited species formed in the collision processes directly yields internal energy state distributions for the product species. The studies conducted during the past year may be classified conveniently in two categories:

1. Collisions involving ground state reactants.
2. Collisions involving excited reactants.

Studies of collisions involving ground state reactants are conducted by directing a beam of ions (or neutral species) into a collision cell containing neutral gas. Photons emanating from the collision region are focused onto the entrance slit of a scanning monochromator and collision produced spectra assembled by counting photons at each wavelength setting of the monochromator. This technique, which was developed in the atomic and molecular physics laboratory at UMSL for study of low energy collisions, has provided much valuable information of both a fundamental and an applied nature. Because this

experimental method directly yields state distributions, possible population inverting collision processes may be studied and the results applied to design and construction of new types of lasers.

Collisions involving excited species have been studied in a similar manner, by observing collision-produced luminescence, but in this case it is necessary to selectively excite the reactants before the collision occurs. This has been accomplished by laser excitation in our experiments. Of course, the use of intense laser light in experiments in which low light yields are detected presents formidable experimental problems, such as elimination of scattered laser light, that must be solved before high quality data can be obtained.

Two different sets of experiments will be reported here, one in each of the above categories. A previous study by us of positive ion- N_2O collisions¹ stimulated additional work by a group at Universite de Paris-Orsay. Their work² raised further questions so that, using our recent instrumental improvements further work by us seemed warranted. This subsequent work by us raised yet another group of questions.

In addition to these ion- N_2O experiments a program for experimental study of interactions involving energetically excited species was initiated. Our first such study was of energy pooling processes in collisions between two excited sodium atoms. We define an energy pooling process as one in which two excited species collide and pool their internal

energy to form products. Our studies of these energy-rich systems have been among the first to yield detailed information of a state-to-state nature. Briefly, our observations to date may be summarized as follows: Yellow light (Na D line) of wavelength 589 nm, or 2.1eV per photon, irradiates a cell containing Na vapor. We observe radiation from high-lying excited states of atomic sodium. We also observe Na^+ and Na_2^+ ions. Thus, illumination by 2.1eV photons results in radiation from levels lying higher than 2.1eV; we also observe small yields of light from levels lying slightly higher than 4.2eV above the ground state. In addition to the radiation, the 2.1eV photons produce Na^+ (the Na ionization potential is 5.1eV) and Na_2^+ . The data obtained in these experiments are used to deduce the mechanisms for formation of the observed species. These mechanisms will be discussed later in this report; additional information can be found in our first publication on the subject.³

II. EXPERIMENTAL

The experimental setup used in the positive ion-N₂O work is basically the same as that described in the last Progress Report (Report No. COO-2718-5). Improvements in the vacuum system and electronic circuitry made it possible to extend the energy range of the primary ion beam down to 1 eV. Improvements in the data acquisition system were also made during the last year. Briefly, ions are produced in an electron impact source and subjected to magnetic mass selection before being decelerated (or accelerated) to the desired collision 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 gas at 1 mtorr pressure has a slot oriented parallel to the ion beam trajectory from which photons emerge and pass through a scanning monochromator. Detection, over the range 180 - 850 nm, is accomplished by counting output pulses from a cooled photomultiplier tube.

The apparatus is controlled and data is acquired by a PDP-8/E minicomputer which repetitively steps the monochromator through the spectral range of interest, and stores both the number of photon counts and the projectile ion current for each channel.

The apparatus used for the energy pooling [Na(3p) - (Na(3p))] experiments is shown schematically in Figure 1. The vacuum system is the same as that for the other experiments, but the

luminescence and ion detection systems have been modified. In these experiments a beam from a cw dye laser tuned to one of the D lines is directed into a collision cell containing Na vapor at density $\sim 10^{13} \text{ cm}^{-3}$. A "notch" filter, which reduces the 589 nm photon signal by a factor of 10^7 , is interposed between the collision cell and the optical system to protect the sensitive photomultiplier from the intense laser induced fluorescence at this wavelength. Thus, luminescence spectra resulting from collisions occurring in the cell may be obtained. Even with this filter in place 589 nm photons from the laser-induced fluorescence can be detected. That is, although the filter reduces this signal by a factor of 10^7 the reduced signal can still be detected (without harming the photomultiplier tube). This effect provides a convenient check of the laser wavelength and the relative Na(3p) population.

Figure 1. Schematic diagram of the apparatus.

Opposite the photon exit slot in the collision cell is a 3 mm diameter hole for sampling ions with a quadrupole mass filter; ion detection is accomplished with a particle...

multiplier. Mass spectra were obtained by scanning the quadrupole and storing the signal in a multichannel analyzer. Sodium vapor is introduced into the collision cell from below by indirectly heating a graphite crucible containing solid sodium. Care must be taken to shield blackbody radiation from the sensitive optical system to minimize background counts. Under our conditions dimer molecules should constitute only about one percent of the vapor. Using the Ar ion laser for a crude laser-induced fluorescence experiment no evidence of Na_2 was detected so that it is assumed that the effects observed with the dye laser tuned to one of the D lines are due only to atomic sodium.

III. RESULTS AND DISCUSSION

A. Positive ion- N_2O studies: Our previous studies of collisions involving N_2O molecules¹ were undertaken because this species is a potential source of several excited fragments. Thus, competition between the various accessible reaction channels could be investigated. These experiments showed that in the kinetic energy range 20-1000eV all of the singly charged ions used except He^+ and Ne^+ produced spectra dominated by $N_2O^+(\tilde{A} \rightarrow \tilde{X})$ emissions. The spectra produced by He^+ or Ne^+ impact contained both $N_2O^+(\tilde{A} \rightarrow \tilde{X})$ and $N_2^+(B \rightarrow X)$ emissions, and these spectra changed very little as a function of collision kinetic energy. In addition the He^+ and Ne^+ results were very similar. Since these ions are the only singly charged ions with electronic recombination energy (RE) in excess of the energy needed to yield the $N_2^+(B) + O(^3P)$ exit channel it was suggested that conversion of kinetic energy to internal energy was of little importance in determining fragmentation in charge-transfer excitation (CTE) processes involving N_2O molecules. Experiments with doubly charged ions such as Ar^{++} yielded spectra similar to those from He^+ or Ne^+ impact supporting this conclusion.

As a result of our work Gerard, Govers and Marx² began a study of positive ion- N_2O collisions at thermal energies using a pulsed ion cyclotron (ICR) apparatus. Their results for $He^+ - N_2O$ were identical to our superthermal data, but they observed no radiation from $Ne^+ - N_2O$ collisions. Our subsequent work, using our improved apparatus, was undertaken to bridge

the gap between the near thermal studies and our previous superthermal experiments. We found that while the relative amounts of $N_2^+(B)$ and $N_2O^+(\tilde{A})$ that we observed changed as we decreased the collision kinetic energy to 1 eV, the absolute emission cross sections for both the N_2^+ and N_2O^+ radiation increased as the kinetic energy was lowered.

These results do not provide a link between the earlier superthermal and the ICR data. While the fractional shift toward $N_2O^+(\tilde{A})$ production with decreasing relative energy demonstrates the importance of kinetic energy conversion in Ne^+-N_2O CTE, this trend does not extrapolate to the total absence of radiating excited states at thermal energy. Indeed, the rising emission cross section with decreasing kinetic energy observed in our work coupled with the ICR result indicates a rather precipitous drop in both $N_2^+(B)$ and $N_2O^+(\tilde{A})$ production between 1 eV and thermal energy. In the absence of the ICR data a low energy barrier to the $N_2^+(B)$ exit channel might have been assumed, and led to the conclusion that as the relative energy was further decreased the preferred (radiating) product would be $N_2O^+(\tilde{A})$. This is however not the case, and it must be concluded that the N_2^+ and N_2O^+ fragments observed in earlier ICR experiments⁴ are formed in their respective ground states. This work has been submitted for publication.

B. Energy pooling processes: As discussed previously in this report we have observed three different product species resulting from laser irradiated Na vapor. Below are brief descriptions of the deduced production mechanisms for each.

Figure 2. Partial term diagram of Na. The heavy arrow indicates absorbed laser radiation (589 nm). The other transitions shown were observed in this work in emission.

1. Formation of $Na(n\ell)$: Figure 2 shows a partial term diagram for the Na atom. The absorbed laser wavelength is indicated by a heavy arrow. The other transitions shown were observed in emission in our experiment. The combined signal from emission from these states is roughly 10^7 times smaller than the observed laser-induced fluorescence signal. The dashed line in the figure represents twice the internal energy of $Na(3p)$. Our proposed mechanism for production of these high-lying states is the energy pooling reaction

It is proposed that production of those states that lie higher than 4.2 eV above the ground state is effected by converting $Na(3p)$ kinetic energy in reaction 1 to internal energy to make up the deficit. The highest deficit is 0.14 eV, about three times thermal energy at the approximate temperature of the Na cell, 500 K. At 500 K approximately ten percent of the atoms

have kinetic energy in excess of 0.14eV. Because the Na(3s→3p) transition saturates with only modest laser power density, approximately half of the Na atoms that reside within the laser "cylinder" can be excited to this level. We may estimate the cross section for the observed processes using the following notation, parameters, and data:

$$n_0 = \text{Na atom density} \cong 10^{13} \text{ cm}^{-3}$$

$$n_1 = \text{Na}^+ \text{ density} \cong 10^8 \text{ cm}^{-3}$$

$$n_2 = \text{Na}_2^+ \text{ density} \cong 10^9 \text{ cm}^{-3}$$

$$n_2 = \text{Na}(n\ell) \text{ density [excluding Na(3p)]} \cong 10^6 \text{ cm}^{-3}$$

$$n_p = \text{Na(3p) density} \cong 1/2 n_0$$

$$I_p = \text{photon flux density/sec} \cong 3 \times 10^{20} (\text{sec cm}^2)^{-1}$$

The cross section for the energy pooling process may be estimated by examining the rate equation for formation under steady state conditions, that is when $\dot{n}_3 = 0$

$$\begin{aligned} \dot{n}_3 &= (\text{formation by energy pooling}) - (\text{radiation loss}) \\ &\quad - [\text{photoionization of Na}(n\ell)] - (\text{quenching}) \\ &= \sigma_{23} v n_p^2 - A n_3 - n_3 I_p \sigma_i - \sigma_q v n_3 n_0 = 0 \end{aligned}$$

where

$$\sigma_{23} = \text{energy pooling cross section}$$

$$\sigma_i = \text{photoionization cross section}$$

$$\sigma_q = \text{quenching cross section}$$

$$A = \text{Einstein coefficient}$$

$$v = \text{average atomic speed} \cong 10^5 \text{ cm/sec}$$

Solving for n_3 gives

$$n_3 = \frac{\sigma_{23} v n_p^2}{[A + \sigma_i I_p + \sigma_q v n_0]} \quad (2)$$

Now for the strongest of the observed transitions⁵, $4p \rightarrow 3s$ at 330 nm, $A = 3 \times 10^6 \text{ sec}^{-1}$ and the other two terms in the denominator may be compared to this value.

$$\sigma_q v n_o \approx (10^{18} \sigma_q)(\text{cm}^2 \text{sec})^{-1} \quad (3)$$

and

$$\sigma_i I_p \approx (\sigma_i 3 \times 10^{20})(\text{cm}^2 \text{sec})^{-1} \quad (4)$$

so that in order for these terms to be significant compared to A , σ_q and σ_i would have to have values of 10^{-12} cm^2 and 10^{-14} cm^2 . The former is unreasonably large so that quenching is clearly unimportant compared to radiation. Although we are unaware of and cross section measurements or calculations for photoionization of an excited atom, the photoionization cross sections for ground state Na are⁶ $\sim 10^{-20} \text{ cm}^2$. Thus, photoionization is also probably an unimportant loss mechanism for $\text{Na}(n\ell)$ compared to radiation. Solving equation 2 for σ_{23} and inserting numbers we obtain

$$\begin{aligned} \sigma_{23} &\cong \frac{n_3 A}{v n_p^2} \\ &\cong 10^{-18} \text{ cm}^2 \end{aligned} \quad (5)$$

2. Formation of Na_2^+ : To establish the origin of the observed ions the $\text{Na}(3p)$ population was varied by slightly detuning the laser and observing the resulting ion signals. Figure 3 shows plots of these data; the relative $\text{Na}(3p)$ population was determined by observing the (filtered) laser induced fluorescence at 589 nm. As may be seen both the Na^+ and Na_2^+ signals increase in a nonlinear fashion as the $\text{Na}(3p)$ concentration is

increased. This suggests that $\text{Na}(3p) - \text{Na}(3p)$ processes are important, just as for the production of high-lying states. We believe that the dimer ions are formed by associative ionization:

Figure 3. Na^+ and Na_2^+ ion signals as functions of $\text{Na}(3p)$ population. Data were taken for Na_2 for two different values of Na atom density: $n_0 = 5 \times 10^{13} \text{ cm}^{-3}$ (1) and $3 \times 10^{13} \text{ cm}^{-3}$ (2). The zeros on the ordinates are shifted for clarity.

Figure 4. Potential energy curves for Na_2 and Na_2^+ . Data for Na_2 taken from Reference 7 and data for Na_2^+ from Reference 8.

Figure 4 shows relevant potential energy curves^{7,8} for Na_2 and Na_2^+ . For sodium, as contrasted to other alkali metals, no additional energy, either from the laser field or reactant kinetic energy is required for reaction 6 to proceed. Associative ionization in this system has been observed in a beam experiment⁹ supporting our hypothesis that reaction 6 is responsible for production of Na_2^+ . Using our data we may estimate the cross section for this process.

$$\begin{aligned}
 \dot{n}_2 &= (\text{rate of formation}) - (\text{loss to drift out of the laser cylinder}) - (\text{loss to photodissociation}) \\
 &= \sigma_{02} v n_p^2 - n_2 v \left(\frac{2}{r}\right) - n_2 I_p \sigma_{21} \\
 &= 0 \quad \text{in steady state}
 \end{aligned} \tag{7}$$

where

σ_{02} = associative ionization cross section

σ_{21} = photodissociation cross section = $2 \times 10^{-17} \text{ cm}^2$ (calculated)¹⁰

and r = laser spot radius $\approx 10^{-1} \text{ cm}$.

The drift term in Equation 7 may be derived as follows:

A = area of laser "cylinder" (neglect caps)

V = volume of laser cylinder

then $n_2 A v$ = Flux/sec through the cylinder

and $n_2 A v / V$ = Flux density/sec

$$\begin{aligned}
 &= n_2 v \frac{2\pi r \ell}{\pi r^2 \ell} \\
 &= n_2 v \left(\frac{2}{r}\right)
 \end{aligned}$$

Solving Equation 7 for σ_{02} and inserting numbers yields

$$\sigma_{02} \approx 10^{-15} \text{ cm}^2$$

3. Formation of Na^+ : Among the processes considered as the origin of the atomic ions are

two photon ionization of $\text{Na}(3p)$

laser induced Penning ionization

photoionization of highly excited atoms

and photodissociation of Na_2^+

Geltman¹¹ has considered processes 8 and 9 in a theoretical study. Using his results it can be shown that, under our experimental conditions, n_1 would be about 0.1 cm^{-3} and 10 cm^{-3} for 8 and 9 respectively; the experimental value was $n_1 \approx 10^8 \text{ cm}^{-3}$.

In order for process 10 to be significant the photoionization cross section of $\text{Na}(n\ell)$ would have to be $\sim 10^{-12} \text{ cm}^2$ so it too seems unlikely. We may calculate n_1 for photodissociation using the experimentally determined dimer ion density, $n_2 \approx 10^9 \text{ cm}^{-3}$.

$$\begin{aligned} \dot{n}_1 &= (\text{rate of formation}) - (\text{loss to drift}) \\ &= \sigma_{21} n_2 I_p - n_1 v \left(\frac{2}{r} \right) = 0 \end{aligned} \quad (12)$$

from which

$$n_1 \approx 3 \times 10^5 \text{ cm}^{-3}$$

Although this value is roughly 30 times lower than the value estimated from the data, however it is much closer than the alternatives, so that we believe photodissociation of Na_2^+ to be the major source of Na^+ .

In addition to the observations described above, we searched for evidence of superelastically heated electrons. That is electrons which have undergone $e - \text{Na}(3p)$ "quenching" collisions.

In an attempt to explain apparently anomalous data in two other experiments^{12,13} on phenomena related to those observed here it was hypothesized^{11,14} that fast electrons, heated by reaction 13, were present in the vapor. In one of the experiments¹², which was conducted under substantially different conditions than ours, that is, using a pulsed laser with $\sim 1 \text{ MW}$ peak power and with $n_0 \approx 10^{16} \text{ cm}^{-3}$, this explanation seems plausible. However, in the other experiment¹³ both the laser power density and the atom density were very close to those employed by us. Since there was some question as to the existence of hot electrons in this experiment, it was considered important to test for their presence in our system.

If superelastically heated electrons are present in the cell then the observed radiation and the Na^+ ions could both result from electron impact processes. However, at the atom densities of our experiments the electron mean free path through $\text{Na}(3p)$ is about 25 cm, roughly 40 times the cell diameter, so it seems unlikely that any appreciable heating by multi-collisional processes could occur. This mean free path was estimated from the Na atom density and the cross section for reaction 13. To check for the presence of hot electrons, potassium was added to the oven. No KI radiation was detected.

From the $4s+np$ electron impact cross-sections¹⁵, the K atom density, and the known efficiency of the optical system it is calculated that if 3-5 eV electrons are present the $4p+4s$ KI resonance line (770nm) count rate should be about 10^3 times background; the $5p+4s$ (405nm) count rate should be about 5×10^3 times background. The absence of these lines eliminates the possibility that hot electrons play an important role in our experiments. Since the atom densities and laser power densities of the experiments of Allegrini et al¹³ were similar to ours, it may be inferred that hot electrons did not contribute to their observations. However, our results do not rule out hot electrons in the experiments of Lucatorto and McIlrath¹², since they observed almost total ionization with considerably higher atom and laser power densities.

IV. SUMMARY

Two different kinds of atomic and molecular energy transfer processes have been studied during the past year. The first, a study of energy partitioning among accessible product states in positive ion - N_2O collisions, was designed to bridge the gap between thermal energy studies in another laboratory and previous experiments conducted in the atomic and molecular physics laboratory at UMSL. While important new information resulted from our recent study of this interesting system still other questions were raised.

In the second series of experiments collisions involving internally excited reactant species were begun. Experiments of this type have not been feasible in the past, but the availability of contemporary dye lasers has made it possible to produce excited species in sufficient quantity to attempt such studies. The results we have obtained over the past year were confined to systems involving sodium atoms. Of particular interest was the production of high lying excited states of Na (higher than 2.1eV above the ground state) and atomic and molecular ions by irradiating Na vapor with laser light tuned to one of the Na D lines (589nm). Since light of wavelength 589nm corresponds to 2.1eV per photon these effects must involve more than one photon. It was deduced that direct multiphoton processes are unlikely with the low laser power density of our experiment. Rather, a unique "energy pooling" mechanism,

in which two 2.1eV photons are "stored" in Na atoms by forming Na(3p), was found to be responsible for the observed phenomena. The effects ultimately were the result of energy transfer in collisions between two Na(3p) atoms.

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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

G. D. Myers - Research Associate

M. Mlynczak - Undergraduate Assistant

During the Summer of 1978 the principle investigator devoted 50% of his time to the project. During the academic year 1978-1979 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.