MASTER

~~COO-2718-8~~

COO-2718-8

DISCLAIMER

This book was prepared as an account of work sponsored by or for the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors included herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OBSERVATION OF LUMINESCENT SPECTRA
IN LOW ENERGY ION-NEUTRAL COLLISIONS, 34

Progress Report,
For Period June 1, 1979 - May 31, 1980

J. J. Leventhal

University of Missouri - St. Louis
St. Louis, Missouri 63121

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

February, 1980

Prepared For

THE U. S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-AS02-76-ER02718

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENT

	<u>Page</u>
ABSTRACT	i
I. INTRODUCTION	1
II. LASER-ASSISTED CHARGE TRANSFER	2
III. TRAPPED LIFETIME EXPERIMENTS	6
IV. ENERGY TRANSFER MODELLING.	9
V. PERSONNEL.	12
VI. REFERENCES	13
VII. APPENDIX	14
FORM ERDA-427.	18

ABSTRACT

This report describes work performed during the past year. Apparatus was constructed for the purpose of studying laser-assisted charge transfer and work was begun on developing a novel method of measuring metal atom densities in the vapor phase. Modelling of energy transfer in molecular systems was continued and new results obtained.

I. INTRODUCTION

This Progress Report describes work done in the past year in the Atomic and Molecular Physics Laboratory at UMSL. The primary objective in this work is to obtain data on energy transfer and energy partitioning in inelastic atomic and molecular collisions. Although a variety of techniques are employed, major emphasis is placed in obtaining these data by observing luminescence from the decay of excited species formed in the collisions.

During the past year progress has been made in three aspects of this program:

1. Laser-assisted charge transfer
2. Trapped lifetime experiments
3. Energy transfer modelling.

These topics will be discussed separately.

II. LASER-ASSISTED CHARGE TRANSFER

Experiments of this type have generated considerable recent interest in a number of laboratories. This interest is due in part to the prospect of using state-selective reactions for isotope separation and/or producing inverted state distributions, especially those leading to xuv or soft x-ray superradiance. Of course the availability of tunable dye lasers, facilitating such experiments, has also been an important factor.

In our experiments we are attempting to answer the questions: Is there a significant difference in the charge exchange cross section for $H^+ - Na(3p)$ as compared to $H^+ - Na(3s)$? Based on current concepts of the nature of the evolution of a molecular system from reactants to products it is expected that the reaction

will have a considerably lower cross section than

Reaction (1) is endothermic by 1.73eV while reaction (2) is exothermic by 0.37eV. From the point of view of reaction energetics reaction (2) is expected to have the higher cross section (at a given collision energy) than reaction (1).

In terms of molecular potential energy functions the situation may be described by stating that the entrance channel potential energy curve for reaction (2) lies closer to that for the exit channel than reaction (1) so that the transition from reactants to products is expected to be more favorable for reaction (2). In our experiment the $\text{Na}(3p)$ is to be produced by laser excitation, and the difference between $\text{H}^+-\text{Na}(3s)$ and $\text{H}^+-\text{Na}(3p)$ charge transfer assessed by comparing the detected Lyman α signal with the laser on and off. Indeed in a related experiment¹, in which a moving hydrogen plasma collided with a sodium cloud which could be excited by a pulsed dye laser tuned to one of the Na D lines, an 80% increase in $L\alpha$ was detected when the laser was on. This, of course, strongly suggests the preference of reaction (2) over reaction (1).

We are attempting to study the H^+-Na system under well-defined conditions, and have constructed apparatus for this purpose. A schematic diagram of the apparatus is shown in Figure 1. A mass selected beam of protons at the desired kinetic energy is directed into a cell containing sodium vapor at about 10^{13} atom/cm³. The proton beam is collected with an open ended "Faraday cup". The cw laser beam, which can be mechanically chopped, passes through the ion collector and enters the collision cell antiparallel to the proton beam. There is a slot in one side of the collision cell leading to an optical system consisting of a focusing lens, monochromator and cooled photomultiplier tube sensitive over the

wavelength range $1800\text{\AA}$ - $8500\text{\AA}$. This optical system may be used to detect radiation from the decay of excited collision products, but in our initial experiments has been used to monitor the $5890\text{\AA}$ laser-induced fluorescence so that we may be assured that the laser is properly tuned to the $3s+3p$ Na transition. On the side of the collision cell opposite the optical system is a hole through which vuv radiation may pass. A Lyman α filter and a channeltron are used to select and detect $1216\text{\AA}$ radiation. Pulses from the channeltron are amplified into a discriminator, the output of which is fed into a dual channel counter. This counter is synchronized with the chopped laser beam so that one channel registers only when the laser is on and the other only when the laser is off.

Figure 1. Schematic diagram of apparatus used in laser-assisted charge transfer experiments.

Although the apparatus represented in Figure 1 is essentially complete and preliminary experiments have been performed we have not as yet detected any difference in the "laser off" and "laser on" Lyman α signals. This result is preliminary and more work is required. Although the $3s+3p$ Na transition should easily be saturated with the laser power

density of our experiment, if it is not a low relative $\text{Na}(3p)/\text{Na}(3s)$ population would account for the null result. It is also possible that the lower limit of $\text{L}\alpha$ detectability with our current setup is higher than the actual signal--enhanced or otherwise. We intend to improve our detection system by using a photomultiplier tube rather than a channeltron; this should increase the $\text{L}\alpha$ sensitivity by about a factor of ten. Further, we have ascertained that the nude channeltron is picking up counts from stray charged particles; the enclosed photomultiplier tube should eliminate this problem.

It is, of course, also possible that there really is no significant difference in $\text{L}\alpha$ production between reactions (1) and (2). We are not, however, prepared to make such a declaration at this time.

III. TRAPPED LIFETIME EXPERIMENTS

One of the most important parameters in our work is the atom density, n , in a crossed beam or cell experiment. For experiments with metal atoms in the vapor phase n cannot be determined using a McLeod gauge or capacitance manometer as is customarily done for gases. In the past we have employed two methods for determination of n . In the first², Na^+ resulting from electron impact on Na vapor is measured and, using the "known" electron impact ionization cross section, the atom density deduced. In the second³, a conventional surface ionization detector (a "hot wire") is employed. Because of uncertainties associated with each of these methods an alternative method has been devised. This alternative method, based on resonance trapping of radiation, comprises a separate research effort in order to develop it to a point at which it will be useful.

Briefly, it is known that the apparent lifetime of the upper state of an atomic resonance transition will depend on the atom density.^{4,5} We intend to use this "trapped lifetime" effect to determine n by comparing an in situ measurement of the apparent lifetime, τ^* , to a calibration curve of τ^* vs. n obtained previously. This calibration curve is to be obtained using time resolved spectroscopy in a separate cell of sodium vapor that replicates the geometry of our collision cell. Unlike our collision cell, the replica will be in equilibrium with its surroundings. Although it is not yet complete, we have begun construction of apparatus needed for this project. It is shown schematically in Figure 2.

Figure 2. Schematic diagram of apparatus used in trapped lifetime experiments.

A cylindrical cell made of alkali resistant glass and containing approximately 1 gm. of distilled sodium is embedded in an aluminum block containing several resistance heaters. The cell and block are maintained within .2K of a constant temperature with an electronic temperature controller. Several thermocouples at various locations in the block are used to monitor the temperature to ensure equilibrium. Light from a pulsed tunable dye laser tuned to one of the D lines irradiates the cell and resonant fluorescence is detected with a photomultiplier (PMT) tube perpendicular to the incident laser light. The PMT output is coupled to a 50 Ω constant impedance tee splitter to produce two in phase pulses of equal amplitude. Each output is independently applied to a fast discriminator (100 MHz). The threshold of one discriminator is fixed at voltage V_0 while that of the second is set to V_0/C . The first discriminator starts a time multichannel analyzer and the second stops it. After many laser pulses a distribution is accumulated in the analyzer which measures the time difference Δt between the start and stop signals. For the case $C=e$, the base of natural logarithms, the position of the peak in the distribution directly represents

the (time resolved) lifetime, but the computed lifetime $\tau^* = \frac{\ln C}{\Delta t}$ should be independent of the chosen value of C, for exponential decay, and we will test to be certain that this is the case. Data may then be transferred to a PDP8/E computer for analysis, storage, and display.

During the past year construction began on the apparatus described above. Although it is not yet completed to a stage at which calibration data may be acquired, we have observed the trapped lifetime effect that we wish to use for the accurate determination of n in our other experiments.

IV. ENERGY TRANSFER MODELLING

Our experimental studies of vibronic excitation of molecular systems on collision with ions led us to propose a model⁶ for the vibrational state distribution in the electronically excited state of the product species, an alternative superior to the polarization-distortion model⁷ considered previously. Our original work contained several simplifying assumptions that made the problem analytically tractable. This work has been extended in the last year by three dimensional, "quasi-classical" curve-crossing trajectories⁸ for the system

This study was "quasi-classical" in the sense that, while the exact classical solution of the motion on the potential surfaces was obtained numerically, the initial diatomic conditions were selected from a quantized 300K vibrational-rotational distribution. The potential energy surfaces were constructed as pairwise sums of Morse potentials for N_2^+ in its ground or excited states, and an exponentially repulsive interaction between the helium atom and each nitrogen atom of the molecule.

These two-surface trajectory calculations successfully rationalized both the trends in the energy dependence of the total cross section and in the vibrational distribution of the upper electronic state. The most interesting feature of the latter trend is that the vibrational temperature of the product molecule decreases with increasing relative kinetic energy in

the collision; at the highest energy explored (6400 eV), no excitations above $v=2$ were observed, and only one above $v=1$. This distribution is consistent with excitation of $N_2^+(X, 300K)$ in a Franck-Condon process. In our model, high energy collisions at the small impact parameters necessary to cause vibrational excitation often dissociate the molecule, so that significant vibrational excitation occurs only at moderate energies. This is the same behavior observed experimentally.

The success of this curve-crossing "quasi-classical" trajectory approach to energy transfer problems suggests that it may well be useful in contexts more general than the collision-induced excitation problem. Our first thought was that the formally similar process

would be another good test of the model, but it appears that a significant fraction of the $N_2^+(B)$ emission intensity from this reaction results from cascading from $N_2^+(C, v=3 \text{ or } 4)$.⁹

A system which does appear to meet the criteria of being a well-characterized process which involves only two potential energy surfaces is E-V transfer in the quenching of excited mercury atoms by carbon monoxide:¹⁰

While this process has had several approximate dynamic treatments,¹¹ it was felt likely that a three dimensional exact classical solution of the dynamics of this reaction could provide an improved insight into the physics of the problem, as well as acting as an additional test of our surface-crossing

model for vibronic energy transfer. This study is now under way; potential energy surfaces which reflect the available knowledge about the real molecular interaction have been synthesized, and tests of the dynamical behavior of the model prior to "production runs" of trajectories are under way.

V. PERSONNEL

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

J. J. Leventhal - Principle Investigator

H. H. Harris - Faculty Associate

V. Kushawaha - Research Associate

M. Mlynchak - Undergraduate Assistant

During the Summer of 1979 the principle investigator devoted 50% of his time to the project. During the academic year 1979-1980 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.

VI. REFERENCES

1. N. Dutta, R. Tkach, D. Frohlich, C. L. Tang, H. Mahr, P. L. Harman, *Phys. Rev. Lett.*, 42, 175 (1979).
2. G. H. Bearman and J. J. Leventhal, *Phys. Rev. Lett.*, 41, 1227 (1978).
3. M.A.D. Fluendy and K. P. Lawley, Chemical Applications of Molecular Beam Scattering (Chapman and Hall, New York, 1973) and S. Dutz and E. H. Taylor, *J. Chem. Phys.*, 25, 389 (1955).
4. B. P. Kibble, G. Copley and L. Krause, *Phys. Rev.*, 153, 9 (1967).
5. A. Corney, Atomic and Laser Spectroscopy (Clarendon Press, Oxford, 1977).
6. J. D. Kelley, G. H. Bearman, H. H. Harris, and J. J. Leventhal, *J. Chem. Phys.* 68, 3345 (1978).
7. M. Lipales, *J. Chem. Phys.* 51, 1252 (1969).
8. J. D. Kelley and H. H. Harris, *J. Phys. Chem.*, 83, 936 (1979). (Appendix of this report).
9. V. G. Ancich, J. B. Laudenslager, W. T. Huntress, Jr., and J. H. Futrell, *J. Chem. Phys.* 67, 4340 (1977) and references therein.
10. G. Karl, P. Kruus, and J. C. Polanyi, *J. Chem. Phys.*, 46, 224 (1967).
11. For examples, see R. D. Levine, and R. B. Bernstein, *Chem. Phys. Letters*, 15, 1 (1972); M. A. Gonzalez, G. Karl, and P.J.S. Watson, *J. Chem. Phys.*, 57, 4054 (1972); A. D. Wilson, R. D. Levine, *Mol. Phys.*, 27, 1197 (1974).

reprint removed