Semi-Annual Report

# RESEARCH ON METASTABLE SPECIES IN ATOMIC AND MOLECULAR BEAMS PRODUCED BY CHARGE TRANSFER

Sponsored by: ADVANCED RESEARCH PROJECTS AGENCY
PROJECT DEFENDER
ARPA ORDER NO. 553

Monitored by: U.S. ARMY RESEARCH OFFICE - DURHAM
CONTRACT DA-31-124-ARO-D-446

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

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*SRI Project PAU-5962*

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## SYNOPSIS

Methods of performing laboratory studies of excited-state reactions important to ionization and optical effects in reentry physics are being studied. Near resonance charge exchange reactions are being used to convert beams of ions to beams of neutrals containing a large fraction of excited particles. The high cross sections of these charge exchange reactions allow efficient conversion of ions to neutrals. Present studies are devoted to identification and detection of excited states of the neutrals in the beam. First results of this work are reported here. One of the significant results is the realization of a direct and practical method of measuring radiation lifetimes of diatomic molecules.

CONTENTS

## ILLUSTRATIONS

# I INTRODUCTION

It is clear that excited atomic and molecular species play an important role in reentry physics. The short-lived excited species manifest themselves by the visible radiation they emit in the shock wave and in the wake of a reentering body. Much of the excitation energy, however, remains imprisoned in the hot gas for a long time, either because it is absorbed and re-emitted rapidly or because it is trapped in nonradiating states. This trapped energy is released via a variety of energy transfer reactions which influence the chemistry of the development and relaxation of a reentry shock wave as well as its radiative signature. To understand the role of this excitation energy in shock wave phenomena, a knowledge of the direct interactions between excited- and ground-state particles as well as of the radiation transfer is needed. For these reasons, cross sections of many energy transfer reactions involving excited species are needed along with radiative transition probabilities.

It is the purpose of the research described here to develop new methods of studying important collision processes involving long-lived excited neutrals. Suitable methods of producing, identifying, and detecting excited neutrals, particularly metastables, are needed. We are studying near-resonant electron capture reactions as a means of efficiently converting beams of ions to beams of excited neutrals. An interesting example of this type of reaction was recently reported: metastable hydrogen atoms in the 2S state were produced by electron capture of protons in cesium.[1] We have measured total electron capture cross sections for a number of similar closely resonant reactions ($He^+ + Cs$, $Ar^+ + Rb$, $N_2^+ + Na$), involving both atoms and molecules, and have found them to be extremely high.[2] These results indicated that excited-state capture readily occurs, and studies of methods of determining the state populations of neutral beams produced were begun.

This report describes the initial results of excited-state studies now under way. Two aspects of the problem of detecting metastables and

of determining the states populated by the charge exchange reactions are being studied. The radiation emanating immediately from the charge exchange reaction zone is being observed and provides information concerning capture into optically allowed excited states. It also reveals any excitation of the incident ions, target atoms, and ions resulting from electron transfer.

A new apparatus, designed to convert ions to excited neutrals with high efficiency, has been constructed and is presently being used in the investigation of metastable detection problems.

The present studies demonstrate the electron capture technique as a practical means of producing beams of excited neutrals useful for studies of energy transfer reactions. Excitation of optically allowed, as well as metastable states, is observed, and the technique is found to be particularly suitable for the measurement of radiative lifetimes of diatomic molecules.

## II OPTICAL RADIATION MEASUREMENTS

The crossed beam apparatus used for the total charge transfer cross section measurements, described in the final report of the preceding[2] contract, is now in use for the optical studies. The slow ion trap has been removed. Photons emanating from the beam intersection region in a direction perpendicular to the plane of the beams are observed. Wavelength measurements reported here were obtained with a grating spectrograph using Kodak 103aO film. The observed resolution in the wavelength range of interest was about 5Å. A mercury lamp provided a calibration spectrum.

To allow proper adjustment of the optics, several exposures of the $CO^+$ comet tail bands were obtained. These bands are efficiently excited with $Ar^+$ or $N_2^+$ ions by electron capture reactions. The reaction $N_2^+ + CO$ giving comet tail bands was initially observed by Utterback and Broida,[3] who found that the cross section remains large to very low energies. Our observations show that the rotational excitation of the

$CO^+$ is larger for incident $Ar^+$ than for $N_2^+$. We have no explanation for this surprising effect.

$He^+$ + Rb and $N_2^+$ + Na spectra obtained with the spectrograph are shown in Figs. 1 and 2. These are two very distinctive examples of near-resonant charge exchange.

The $He^+$ + Rb reaction is of particular interest because two types of near resonance reactions can occur:

(1) $He^+ + Rb \rightarrow He(\text{excited}) + Rb^+$

(2) $He^+ + Rb \rightarrow He(1^1S) + Rb^+(\text{excited})$

The spectral observations (Fig. 1) obtained at 1040 eV indicate that reaction (2) occurs readily and excites several states of $Rb^+$. For the purpose of producing a beam of excited atoms, reaction (2) is undesirable because it produces ground state He atoms. The cross sections for reactions (1) and (2) have not yet been measured, so their relative contributions cannot be assessed. Reaction (2) will be strongly suppressed if Na is used, since excitation of the $Na^+$ requires a reaction endothermic by more than 6 eV.

It is noteworthy that one He transition corresponding to excitation of the $3p^3P$ state is observed. Excitation of this state is weak, but it leads directly to the metastable $2^3S$ state. None of the other n = 3 states are observed, probably because the transitions do not lie in a wavelength region detectable with the film used.

Several lines of the Rb II spectrum are excited, although the line at 4244 Å stands out as the most strongly excited. It should be noted that the intensity scale is logarithmic and small differences in peak intensity of dark lines correspond to large differences in intensity. The excited levels populated by the charge exchange interaction are listed in Table I, using the notation of Moore together with the energy defect $\Delta E$. The states are labeled consecutively from highest to lowest intensity, and cascade transitions are indicated. The predominant

Table I

MAJOR LEVELS OF Rb II EXCITED BY $He^+$

| λ Wavelength of Transition | Core Config. | State Desig | J | ΔE (eV) | Relative Strength | Cascade Routes |
|---|---|---|---|---|---|---|
| 3595 | $4p^5(^2P^0_{01/2})$ | $5d'[1\frac{1}{2}]^0$ | 1 | -3.02 | 10 | |
| 4469 | $4p^5(^2P^0_{11/2})$ | $5d\ [1\frac{1}{2}]^0$ | 1 | -2.82 | 16 | |
| 4377 | " | $6s\ [1\frac{1}{2}]^0$ | 2 | -1.88 | 2 | |
| 3926 | " | " | 2 | -1.88 | 6 | |
| 4347 | " | " | 2 | -1.88 | 15 | |
| 4755 | " | " | 2 | -1.88 | 13 | |
| 4530 | $4p^5(^2P^0_{01/2})$ | $5p'[0\frac{1}{2}]$ | 1 | -0.06 | 14 | |
| 4104 | " | $5p'[1\frac{1}{2}]$ | 2 | -0.04 | 9 | |
| 4648 | " | " | 2 | -0.04 | 11 | |
| 3796 | $4p^5(^2P^0_{11/2})$ | $5p\ [0\frac{1}{2}]$ | 0 | +0.42 | not observed | |
| 4193 | " | $5p\ [1\frac{1}{2}]$ | 2 | +0.73 | 12 | |
| 3940 | " | " | 2 | +0.73 | 4 | |
| 4294 | " | " | 1 | +0.80 | 7 | |
| 4244 | " | $5p\ [2\frac{1}{2}]$ | 3 | +0.96 | 1 | |
| 4273 | " | " | 2 | +0.97 | 8 | |
| 4572 | " | " | 2 | +0.97 | 3 | |
| 4776 | " | $5p\ [0\frac{1}{2}]$ | 1 | +1.28 | 5 | |

excitation occurs in the $4p^5(^2P_{1\,1/2}^{\,0})5p$ states, although the 6S state is also strongly populated. The 5p' states are weakly populated, although they are most closely resonant. Energy resonance is therefore clearly not the major factor determining the state population, although it does give a crude indication of the region in which the excitation occurs. These observations may provide a clue as to what factors other than energy resonance are important, and from this point of view, the reaction warrants further study.

One peculiarity which is not understood is the lack of observation of the 3796 Å line. This is the only transition of the $4p^5(^2P_{1\,1/2}^{\,0})5p$ group not observed; furthermore, a cascade transition into the state is observed.

The reaction

(3) $N_2^+ + Na \rightarrow N_2^* + Na^+$

is extremely interesting and important in several respects. A spectrum obtained at an energy of 950 eV is shown in Fig. 2. The superimposed $CO^+$ comet tail spectrum was used for calibration. All the observed $N_2$ bands except one (an $N_2^+$ first negative) belong to the second positive system ($C^3\Pi_u \rightarrow B^3\Pi_g$). Moreover, all vibrational levels of the C state (v = 0 to 4) are observed to be excited. Not shown in Fig. 2 are the (1,0), (2,1), (3,2) and (2,0), (3,1), (4,2) sequences of transitions which appeared in the second-order spectrum. The endothermicity of the reaction varies from 0.7 eV for v = 0 to 1.7 eV for v = 4. To observe the energy dependence of the C-state excitation from reaction (3), the second positive radiation was observed with a photomultiplier viewing through a broad-band uv filter. The wavelength range of the filter is 3100 to 3850 Å, and therefore the (0,2), (0,1), (0,0), and (1,0) sequences are transmitted. The excitation cross section is found to increase with decreasing energy. The observed energy dependence shown in Fig. 3 closely resembles the energy dependence of the total capture cross section previously measured. A crude estimate of the cross section for C-state excitation was obtained by calibrating the photomultiplier filter combination on the first negative (0,0) band excited

by $N_2^+ + N_2$ collisions. Cross sections for this process were measured by Doering.[4] The results obtained indicate that the C-state excitation comprises between 10% and 30% of the total electron capture of reaction (3). More definitive measurements of both the total and radiative cross sections are needed to clarify this point.

Other states likely to be populated in reaction (3) are the $a^1\Pi_g$ and $a'^1\Sigma_u^-$ metastable states and the $w^1\Delta_u$ and $B'^3\Sigma_u^-$ states of unknown lifetimes. These states are as closely resonant as the C state, but are exothermic rather than endothermic. On the basis of energy resonance, potassium is a better choice than sodium for populating the C state.

C-state capture is pertinent to the problem of producing metastables because it decays to the long-lived $A^3\Sigma_u$ state via the B state. The mean radiative lifetime of the C state is $5 \times 10^{-8}$ sec. The B state radiates to the A state in turn in 3 to $10 \times 10^{-6}$ sec, depending on the vibrational state. It is unlikely that the A state is significantly populated directly by electron capture because it is out of resonance by 4.2 eV. Assuming no direct capture, the A-state population of the beam in each vibrational level can be determined from the relative intensity of the first positive bands ($B \rightarrow A$). In the beam velocity range of $10^6$ to $10^7$ cm/sec (15 to 1500 eV), the B-state population will persist for a long distance beyond the region of charge exchange. Therefore, it is possible to use either the B state or the A state in certain experiments by varying the beam velocity or the distance from the charge exchange region.

The determination of radiative lifetimes of diatomic molecules suggests itself as a straightforward measurement using near-resonant charge exchange as an excitation mechanism. The decay in intensity of a particular band can be measured as a function of distance down the beam, and the distance scale is converted to time scale through the beam velocity. As an example, the lifetimes of the first positive bands could readily be measured using a beam of $10^7$ cm/sec (1500 eV).

There is good reason to believe that the technique is quite general and can be used to obtain radiative lifetimes of a wide variety of diatomic molecular states.

## III DETECTION OF METASTABLES

### A. The Auger Effect

One of the major problems associated with the experimental study of metastable collision processes is the lack of a practical, efficient, and universal method of detection. A commonly used detector for thermal beams of metastables is the Auger ejection of an electron from a metal surface.[5] In this process the metastable is de-excited to the ground state and an electron in the metal is ejected; an incident ion is in a similar manner neutralized and the energy is released to a second electron. Recent studies of the electron emission from a clean metal surface by energetic ions and neutrals have shown that up to energies of several hundred volts the emission is essentially independent of energy and due only to the Auger process.[6] In this region the emission is referred to as potential emission. At higher energies, in the region of kinetic emission, the emission increases with kinetic energy due to other processes. In the potential emission region, electron ejection by ground-state neutrals is extremely inefficient, whereas ejection by metastables, depending on their excitation energy, can be nearly as efficient as ejection by ions. Thus, the Auger process will distinguish between ground-state neutrals and excited neutrals if the excitation energy is sufficient and the kinetic energy low. For emission from clean refractory metal surfaces, a practical lower limit for the excitation energy is about 10 eV and upper limit on kinetic energy is about 400 eV.

An apparatus designed to efficiently convert a beam of ions to excited neutrals has been constructed and is being used to study the metastable detection problems. The ion beam, after mass analysis, passes through an alkali oven where charge exchange with the alkali vapor converts it to a neutral beam with an efficiency of 10% to 30%

After passing through the charge exchange oven, the beam enters a detection chamber where an ambient pressure in the $10^{-8}$ torr range can be maintained. Here the ions can be separated from the neutrals before entering the Auger detector where the particles impinge on a tungsten surface which can be heated to 2300°K to remove adsorbed gases. The beam passes through apertures in a series of four plates directly in front of the tungsten surface. These plates serve to define the beam and allow application of electrical fields to ensure collection of the electrons. At present, Auger emission due to ions is being studied to determine the conditions necessary to obtain reproducible results. We are convinced this detector will be useful as a monitor for beam metastables for kinetic energies up to a few hundred volts and excitation energies above 10 eV. Other methods must be employed to identify the excited states.

## B. Photodetection Methods

Perhaps the most direct method of detecting and identifying metastable states is by the radiation they emit. In some cases, particularly in molecular systems, the radiative lifetime is in a range ($10^{-6}$ to $10^{-1}$ sec) that allows detection of the radiation by a photomultiplier filter combination for beam intensities attainable in our apparatus. This applies, for example, to the $a^1\Pi_g$ state (lifetime $1.7 \times 10^{-4}$ sec) and $a'^1\Sigma_u^-$ state (lifetime $\sim 4 \times 10^{-2}$ sec) of $N_2$. In those cases where the radiative lifetime is known or can be measured, the population of the radiating state can be determined absolutely, otherwise the method is useful on a relative basis.

Another method under consideration as a detector is the use of resonance fluorescence. The metastables are passed through a gas and transfer their energy to selected molecules which can radiate the energy. This process is of interest both as a metastable detector and as an important physical process, but it needs further study.

## IV DISCUSSION

The results presented here, though somewhat fragmentary and preliminary, serve to demonstrate that near-resonance charge exchange is a practical means of converting ion beams to excited neutrals. Both long-lived (metastables) and short-lived (radiative) excited states can be produced in quantities sufficient to perform energy transfer studies with many species and excited states. The problems of identification and detection of individual metastable states are under study, and it appears that several methods will be required, no one method being suitable for all species or states.

One of the most obvious and direct measurements possible with the electron capture technique is the determination of radiative lifetimes of allowed transitions in diatomic molecules. The technique should be applicable to a large number of diatomic species obtainable from an ion source.

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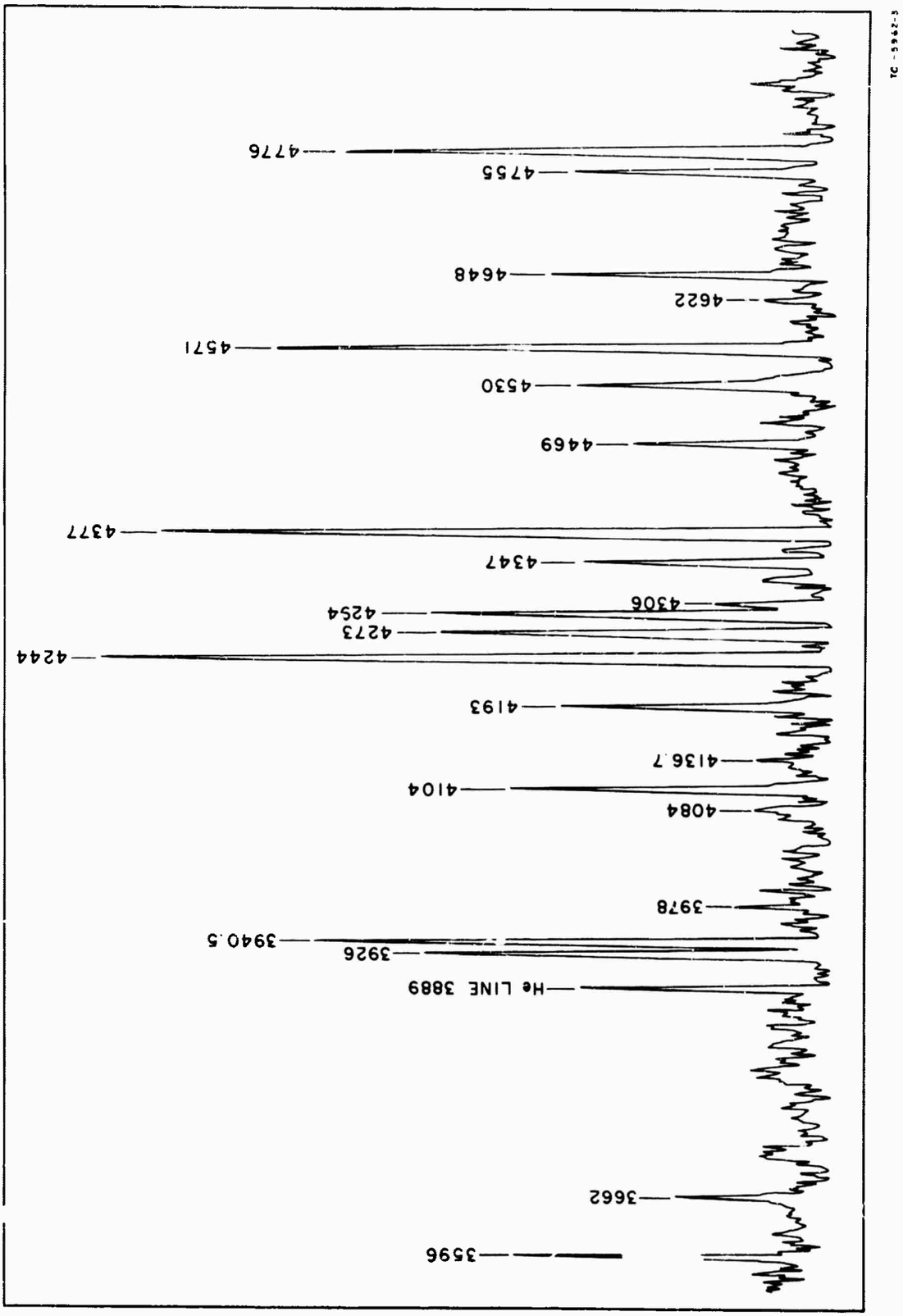


FIG. 1 $He^+ + Rb$ SPECTRUM AT 1040 eV. All of the observed lines originate from the electron capture reaction $He^+ + Rb \rightarrow He + Rb^+$. All except the 3889 He line originate from Rb II

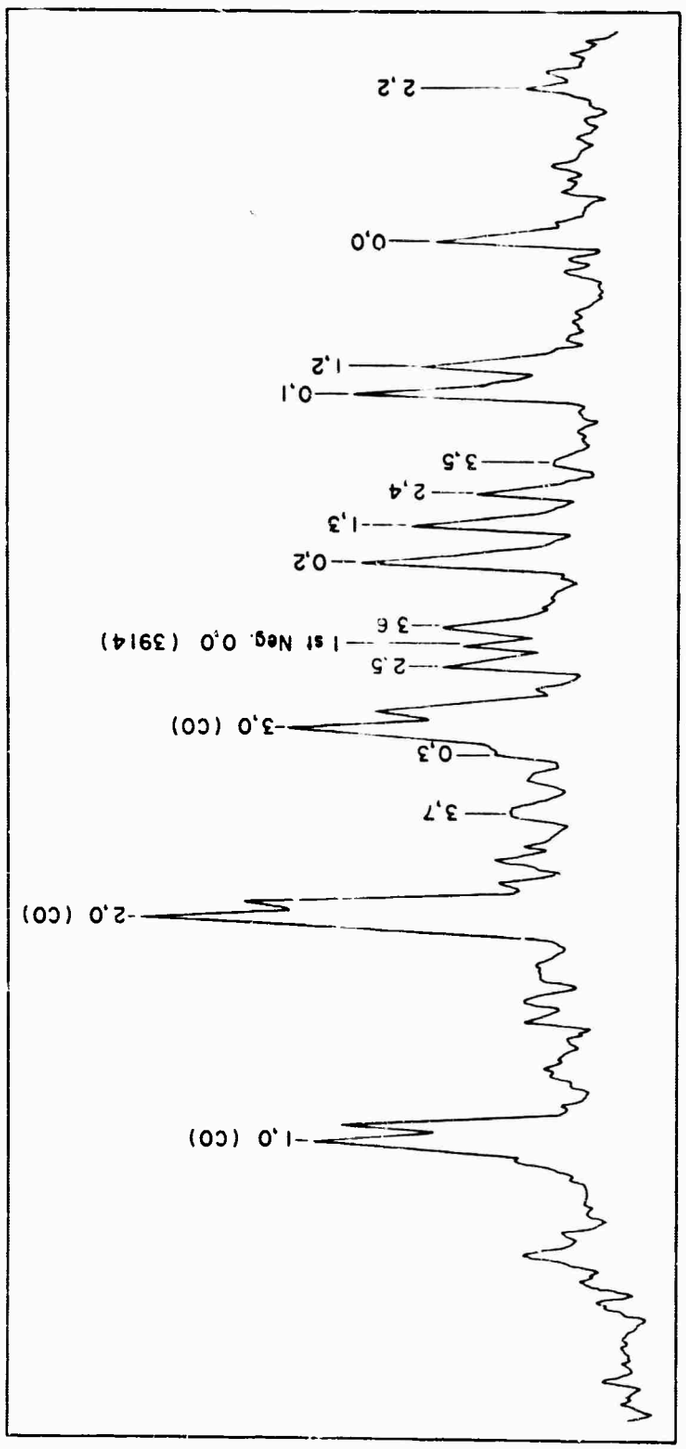


FIG. 2 $N_2^+$ + Na SPECTRUM AT 950 eV. The bands labeled CO are the comet tail bands of $CO^+$ excited by charge exchange with $N_2^+$. This spectrum was superimposed for calibration of the wavelength scale. All of the bands except the 1st negative 3914 belong to the second positive system of $N_2$. The bands are labeled according to initial and final vibrational levels.

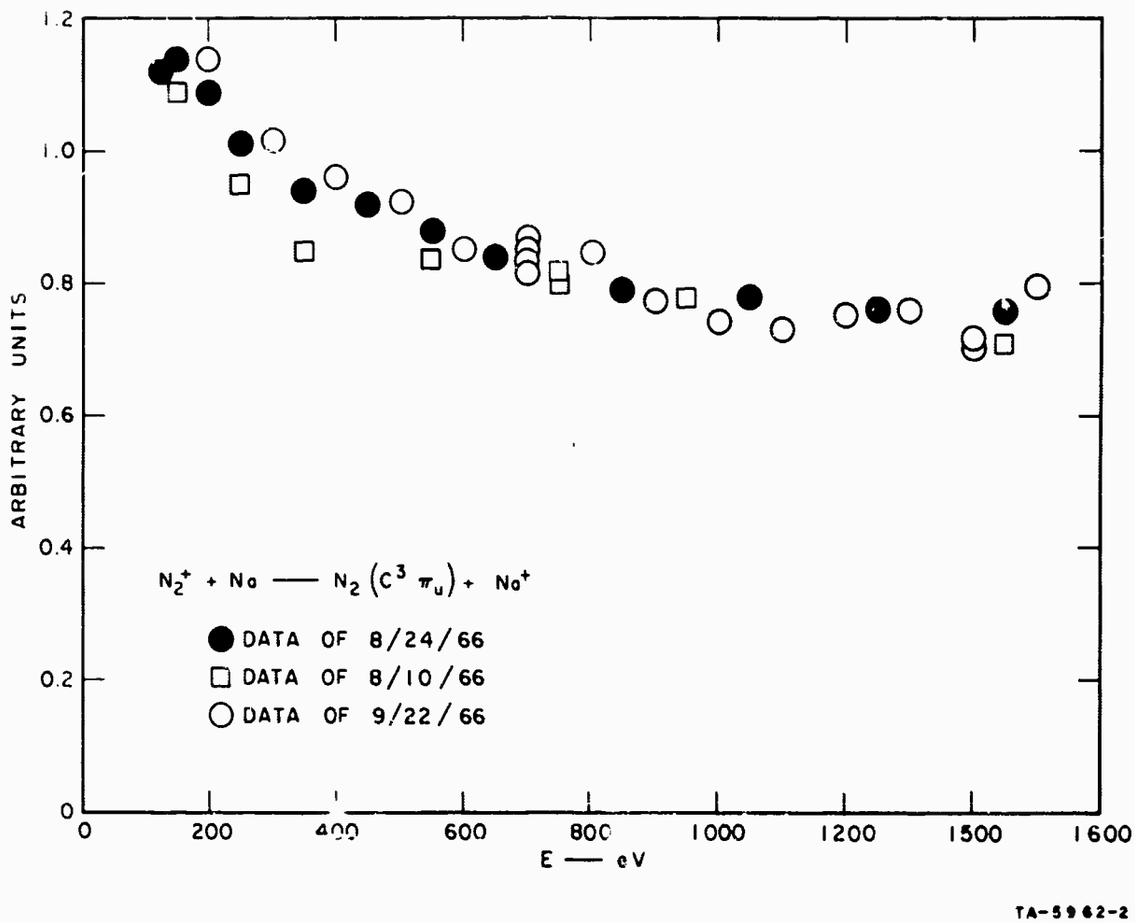


FIG. 3 ENERGY DEPENDENCE OF C STATE EXCITATION. Energy dependence of cross section for excitation of $N_2$ 2nd positive system in the charge exchange of $N_2^+$ in Na.


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