Progress Report No. 7

MASTER

to

Office of Basic Energy Sciences

U. S. Department of Energy

from

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for

Contract No. DE-AS05-76ER04676

"Atomic and Molecular Sciences"

(Contract Period, April 1, 1980 through March 31, 1981)

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"Atomic and Molecular Sciences"

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TABLE OF CONTENTS

	Page
I. Abstract	1
II. Scientific Progress - Experimental	4
A) Gaseous Electronics	4
B) Spin-Polarized He^+ and $\text{He}(2^3\text{S})$ Beams for Probing Atom- and Molecule-Surface Interactions	9
C) Surface Atomic Structure Studies by Polarized Low Energy Electron Diffraction (PLEED)	12
III. Scientific Progress - Theoretical	14
A) Charge Exchange Collisions	14
B) Electron-Ion Inelastic Scattering in Dense Plasmas	18
C) Highly Excited "Rydberg" Atom Scattering	23
D) Electron Scattering from Molecules--Vibrational Excitation	28
E) Inner Shell Photoabsorption and Photoionization of Atoms and Molecules	29
F) Exchange and Correlation in Electron-Scattering and Photon Processes Involving Atoms and Molecules	30
IV. List of References	33
V. Personnel	39
A) List of Personnel Working on Project During Year to March 31, 1981	39
B) Changes in Personnel	39

	Page
C) Time Devoted by Faculty Investigators	40
VI. Publications Arising from the Contract	41
VII. Expenditure Report (1980-81)	44

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Atomic and Molecular Sciences

I. Abstract

The atomic and molecular physics program at Rice University addresses fundamental problems in structure, radiation-induced gas- and condensed-phase reaction kinetics and dynamics, and the mutual interactions of radiation, atoms, molecules, electrons and ions, particularly in highly unusual or exotic environments. The program emphasizes fundamental studies relating to new sources of energy, with close interaction between experimental and theoretical aspects of the research.

Progress in the experimental program is reported in three principal areas, A) gaseous electronics, B) spin-polarized He^+ and $\text{He}(2^3\text{S})$ beams for probing atom- and molecule-surface interactions, and C) surface atomic structure studies by polarized low energy electron diffraction (PLEED).

The gaseous electronics project is oriented toward the study of fast reaction kinetics, radiative lifetimes and energy pathways in e-beam and photon excited dense gas systems (both pure and with dopants) of laser interest. During the current contract year i) reaction pathways and kinetic processes pertinent to XeF^* exciplex lasers were identified and the reaction rates measured at the Stanford Synchrotron Radiation Laboratory, and studies there were extended to XeCl^* and the Xe_2Cl triatomic system; ii) the Rice University-based experiments on radiative charge transfer in heteronuclear rare gas ions focused on a comprehensive survey of ion emission bands in binary rare gas mixtures that should be completed during the current contract year.

An intense spin-polarized $\text{He}(2^3\text{S})$ atomic beam with polarization ~50% has been successfully completed and tested, and is being installed, along with the polarized He^+ ion beam reported last year,

in a new apparatus for studying the mechanism of ion neutralization and atomic de-excitation at solid surfaces. These novel probe beams will be used to study the properties of adsorbed atoms and molecules as well as the underlying substrate. Diagnostics being incorporated in the apparatus include low energy electron diffraction (LEED), Auger analysis, and a Stern-Gerlach system for monitoring the $\text{He}(2^3\text{S})$ beam polarization.

In a separate project, spin polarization studies in low energy electron diffraction (PLEED) are being extended to nickel surfaces with tellurium adsorbates. This system is of interest because the polarization properties of the diffracted beams should be dominated by the higher-Z adsorbate. Measurements on clean $\text{Ni}(001)$ surfaces confirm theoretical expectations that the polarization effects induced by Ni are quite small (polarizations of scattered beams $\approx 1\%$). A tellurium oven has been installed in the PLEED apparatus, and preliminary polarization results on the composite Ni/Te system are expected during the current contract year.

Areas of progress in the theoretical program include the following research topics: radiative and non-radiative charge-transfer in collisions of He^{++} with H and D atoms; charge transfer and excitation in collisions of $\text{He}^+(n1)$ ions with protons; excitation and de-excitation of atomic ions by electron impact in dense hot plasmas; elastic and inelastic electron-molecule scattering; exchange effects in photoabsorption, photoionization and electron scattering from atoms and molecules; energy transfer in collisions of molecules with highly excited ("high-Rydberg") atoms; interaction of "high-Rydberg" atoms with background black-body radiation.

The principal focus of the theoretical program this past contract year has been the refinement and further extension of our detailed collision dynamics studies include collisional-radiative studies of the HeH^{++} one-electron system. New results include

reliable cross sections for radiative charge transfer in collisions of He^{++} with $\text{H}(1s)$. The radiative process is found to dominate charge transfer at energies much below 50 eV (c.m.) In all cases, the calculated cross sections (scaled appropriately) also apply to the analogous processes of muon transfer and excitation in collisions of H^+ with $(\text{He}^{++}\mu^-)_{nl}$.

Excitation of highly stripped ions by electron impact in a dense hot plasma is found to be sensitive to characteristics of the plasma. Continuing theoretical studies using the Born and close-coupling approximations and a simple Debye screening model of plasma effects are being refined and extended to include a more realistic treatment of the plasma environment.

A continuing study of exchange and correlation effects in electron-molecule scattering and in photoabsorption and photoionization of atoms and molecules involves the application of various local approximations systematically to a number of systems. A screened Free-Electron-Gas approximation based on the Random Phase Approximation in many-body theory has been found to be particularly successful in photoionization. Formal as well as computational efforts are being continued with the goal of better defining reliable exchange approximations for use in complex systems.

The interaction of "high-Rydberg" atoms with photons, atoms and molecules probes the details of atoms with a highly excited electron and of the interaction of very slowly moving Rydberg electrons with atoms and molecules. Classical calculations of energy transfer in collisions of highly excited atoms with molecules are underway. Results, so far, are consistent with measurements and provide enlightening physical interpretations. Studies of photoionization by black-body radiation have been completed.

II. Scientific Progress - Experimental

A) Gaseous Electronics

We have employed the delayed-coincidence single photon counting technique described in preceding Progress Reports and publications,¹⁻³ for monitoring the time evolution of transient atomic and molecular species concentrations in dense gases, in a systematic study at the Stanford Synchrotron Radiation Laboratory (SSRL) of several systems of electronic transition laser interest. The results of definitive studies on kinetic and radiative processes involving xenon and krypton excimers excited by monochromatized synchrotron radiation at SSRL, both in the pure gases and with argon buffers, are complete and were published this year.^{4,5}

During 1980, experiments at SSRL, conducted in collaboration with a group headed by Dr. D. C. Lorents from the Molecular Physics Laboratory of SRI International, have focused on rare gas-halide systems. A comprehensive investigation of photolysis of XeF_2 to produce XeF^* (B, C, and D) states (see Fig. 1), including measurements of quantum yields and pertinent rate coefficients for kinetic and radiative processes was completed and the results are being prepared for publication. A summary of the measured rates appears in Table I.

The work at SSRL is now being extended to include other rare gas halides, both diatomics and triatomics. Preliminary results have been obtained on the $\text{XeCl}/\text{Xe}_2\text{Cl}$ system, and are presented in Table II for the reaction pathways indicated in Fig. 2.

Our last two experimental runs at SSRL have been hampered by unavailability of beam for about 70% of our scheduled time.

Because we have given priority to the SSRL-based program described above, progress at Rice on e-beam excited systems has been modest. However, the accelerator control- and data-acquisition systems

Figure 1

TABLE I

Measured radiative lifetimes and reaction rates for collisional processes involving the B and C states of XeF*

a) Radiative lifetimes

XeF*(B)	13.3 ± 0.2 nsec
XeF*(C)	101 ± 5 nsec

Reaction	Rate Coefficient (cm ³ /sec)
XeF(C) + XeF ₂ → Quenching	(4.75 ± 0.08) × 10 ⁻¹⁰
XeF(C) + Xe → Quenching	~1.9 × 10 ⁻¹⁰
XeF(C) + Ar → Quenching	(7 ± 7) × 10 ⁻¹⁵
XeF(C) + N ₂ → Quenching	≤ 2.5 × 10 ⁻¹⁴
XeF(C) + SF ₆ → Quenching	≤ 9 × 10 ⁻¹⁵
XeF(B) + XeF ₂ → Quenching	~7.4 × 10 ⁻¹⁰
XeF(B) + Ar → XeF(C) + Ar	(1.4 ± 0.2) × 10 ⁻¹¹
XeF(B) + Xe → XeF(C) + Xe	~1.5 × 10 ⁻¹⁰
XeF(B) + Ne → XeF(C) + Ne	~3.5 × 10 ⁻¹²
XeF(B) + N ₂ → XeF(C) + N ₂	(5.7 ± 0.3) × 10 ⁻¹¹
XeF(B) + SF ₆ → XeF(C) + SF ₆	(8 ± 1) × 10 ⁻¹¹
XeF(B) ⇌ XeF(C)	Equilibrium Constant = 22.8 ± 2.5

XeF(B) vibrational relaxation rate is comparable to B → C relaxation rates.

Quantum yield of XeF*(B,C, and D) from photolysis of XeF₂ is
≈ 1.0 across the 145-175 nm absorption band.

XeCl / Xe₂Cl Reaction Pathways

in Synchrotron Radiation Excited Xe / Cl₂ Mixtures

Figure 2

TABLE II

Measured radiative and collisional rates for XeCl*

<u>Reaction</u>	<u>Rate Constant</u>
$\text{Xe}^* + \text{Cl}_2 \rightarrow \text{XeCl}^*$	$7.6 \pm 7 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$
$\text{Cl}_2^* + \text{Xe} \rightarrow \text{XeCl}^*$	$1.1 \pm 0.1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$
$\text{XeCl}^* \rightarrow \text{XeCl} + \text{Hv}$	$2.5 \pm 0.3 \times 10^7 \text{ sec}^{-1}$
$\text{XeCl}^* + \text{Cl}_2 \rightarrow \text{Quenching}$	$5.0 \pm 0.4 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$
$\text{XeCl}^* + 2 \text{Xe} \rightarrow \text{Xe}_2\text{Cl}^*$	$7.3 \pm 0.7 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}$
$\text{Xe}_2\text{Cl}^* \rightarrow 2 \text{Xe} + \text{Cl} + \text{Hv}$	$4.9 \pm 0.4 \times 10^6 \text{ sec}^{-1}$
$\text{Xe}_2\text{Cl}^* + \text{Cl}_2 \rightarrow \text{Quenching}$	$4.5 \pm 0.4 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$
$\text{Xe}_2\text{Cl}^* + \text{Xe} \rightarrow \text{Quenching}$	$\leq 4.0 \pm 0.5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$

have been substantially upgraded, and a systematic spectral survey of heteronuclear ion fluorescence bands in e-beam excited rare gas binary mixtures is in progress. The 4900Å band resulting from the reaction

is by far the most prominent we have observed to date. The spectral survey should be completed during the current contract year, and time resolved measurements initiated on the $(\text{KrXe})^+$ system, and/or other strong bands identified by the survey. The heteronuclear ion transitions are quite interesting examples of radiative charge transfer processes, the nature and dynamics of which remain relatively obscure.⁶

B) Spin-Polarized He^+ and $\text{He}(2^3\text{S})$ Beams for Probing Atom- and Molecule-Surface Interactions

Over the years, this DOE (alias AEC, ERDA)-sponsored program at Rice has addressed a variety of research problems involving the need for spin-polarized atoms, ions and electrons. Our earlier work focused on optical pumping of metastable $\text{He}(2^3\text{S})$ atoms in electrical discharges, to elucidate the atomic and molecular processes governing ion- and metastable formation and destruction.⁷ These studies led to the development of techniques for producing nuclear-spin polarized ^3He targets⁸ and $^3\text{He}^+$ ion beams⁹ which we then exploited in pioneering research on spin-dependence of nuclear forces.¹⁰ More recently, we extended the optical pumping method to produce an intense spin-polarized electron beam¹¹ which has most recently been used in a definitive search for possible polarization effects in asymmetric degradation of chiral molecules.¹² Finally, an important component of our on-going program is a pioneering project on the study of spin-polarization effects in low energy electron diffraction (LEED) from solid surfaces, which is the subject of the following section of this Progress Report.

During the course of these studies we have advanced not only the technologies associated with production of spin-polarized beams, but also those associated with detection and accurate measurement of electron spin polarization.¹³

This year we have initiated yet another project in this sequence --the application of spin-polarized beams of helium ions and 2^3S metastable atoms to a) investigate the dynamics of ion-neutralization and atomic de-excitation at solid surfaces,^{14,15} b) study basic properties of the surfaces themselves,¹⁶ and c) probe electronic structure, bonding and reaction channels of atoms and molecules adsorbed on surfaces.^{17,18}

During the contract year, we have completed and demonstrated an apparatus shown in Fig. 3 that produces an intense beam of spin-polarized $He(2^3S)$ atoms suitable for use in beam-surface investigations. The beam flux is $\sim 10^{14}$ per second per steradian, and the polarization is $\sim 50\%$ as determined by the homemade Stern-Gerlach analyzer indicated in the figure.* A manuscript on this unique source has been submitted for publication.

In addition, an ultra-high vacuum-compatible version of the spin-polarized He^+ ion beam reported last year has been constructed,

*For spin-one systems such as $He(2^3S)$ polarized in the z-direction, one must specify two components of the polarization tensor

$$P_z = \langle S_z \rangle = \frac{n_+ - n_-}{n_+ + n_0 + n_-} \quad (\text{polarization})$$

$$\text{and} \quad P_{zz} = 3\langle S_z^2 \rangle - 2 = \frac{(n_+ + n_-) - 2n_0}{n_+ + n_0 + n_-} \quad (\text{alignment})$$

where n_+ , n_0 and n_- are respectively the populations of the $m_s = 1, 0$ and -1 magnetic sublevels of $He(2^3S)$. For the beam reported here, we measure $P_z \approx 50\%$ and $P_{zz} \approx 16\%$.

Figure 3

with improved ion transport optics that will permit beam-surface studies for incident ion energies as low as 20 ev (a factor ten improvement).

We are now in the process of assembling the completed apparatus for beam-surface studies in an ultra-high vacuum environment ($\sim 10^{-10}$ Torr). The apparatus is complex, requiring two stages of high-speed differential pumping to overcome the helium gas load associated with production of the beams. We are hopeful, nevertheless, that the first beam-surface experiments can be initiated in the first half of 1981.

C) Surface Atomic Structure Studies by Polarized Low Energy Electron Diffraction (PLEED)

Measurements of spin-polarization in LEED have become feasible only in very recent years, and experiments to date suggest that they will significantly enhance the power of LEED in surface structure determinations.¹⁹⁻²⁸ Polarization measurements complement intensity measurements in a number of ways: (a) polarization studies probe a different region of the muffin-tin scattering potential, since the spin-orbit interaction responsible for polarization effects is proportional to $(1/r)(dV/dr)$ and falls off as r^{-3} in contrast to the r^{-1} decrease of the Coulomb potential, (b) polarization effects tend to be largest in the vicinity of intensity minima in the diffracted LEED beams,⁴ whereas structure determinations have thus far emphasized the positions of intensity maxima, (c) polarization has been shown to be particularly sensitive to the presence and locations of adsorbates,²⁴ and (d) excellent laboratory-to-laboratory reproducibility has been demonstrated,²⁵ pointing up an inherent advantage of polarization measurements--namely that polarization is a ratio measurement in which instrumental and beam-geometrical problems inherent in measuring absolute intensity profiles approximately cancel out.

Until this year the PLEED project has focused on clean tungsten surfaces, and tungsten/adsorbate systems. In recent months we have overhauled the apparatus to make it suitable for cleaning and investigation of a wider variety of surfaces. In particular, an argon ion bombardment gun has been installed, as has a quick-cool and refrigeration capability (of our own design and construction) for the target crystal. A PLEED study of the nickel (001) surface with ordered tellurium overlayer^{29,30} has been initiated in the new apparatus. This should serve as a model system for evaluating the potential of PLEED as a diagnostic in cases where the adlayer can be expected to dominate the polarization behavior. In contrast to the tungsten-adsorbate systems, it is scattering from the higher-Z tellurium adsorbate rather than from the nickel substrate that is expected to dominate the polarization behavior. (Polarization effects are a consequence of the spin-orbit interaction, which increases rapidly with the atomic number Z of the scatterer.) To date, our measurements have confirmed that the clean Ni(001) surface is ineffective in producing polarization in the scattered beams ($\lesssim 1\%$). A tellurium oven has been installed for depositing the adlayer, and preliminary results on the composite system are expected during the current contract year.

Professors A. Ignatiev of the University of Houston, and R. Feder of the Universität Duisburg (W. Germany), respectively, are collaborating with us on the experimental and theoretical aspects of this work.

III. Scientific Progress - Theoretical

A) Charge Exchange Collisions

Charge transfer collision processes, e.g.

are of practical importance to research on advanced energy systems and at the same time of considerable fundamental interest, as an example of a class of only partially understood rearrangement collision processes. In particular, charge transfer processes (1) involving one electron target atoms, H and D, are especially important in determining the radiation losses and neutral beam heating properties in Tokamak plasmas as well as the spectral features of X-ray sources in the interstellar media, and even the possibility of providing a pumping mechanism for an X-ray laser.³¹ From a fundamental point of view, the theoretical description of such transfer and excitation processes is complicated by the existence of "avoided crossings" (and actual crossings) of the adiabatic potential energy curves, which are particular to a given system and do not permit generalization.³²⁻³⁵ In addition, the dynamical problem of properly accounting for the spatial "translation" of the electrons in circumstances where the electron transfers to the other nuclei remains a significant challenge to the theory.^{35,36}

In this group, we set out several years ago to calculate accurate cross sections for the collision processes

over an energy range where "molecular" effects were felt to be important and where experimental measurements were especially difficult and the results ambiguous. We chose the one-electron HeH^{++} system so that highly accurate electronic matrix elements could be calculated,

thus eliminating one chronic theoretical uncertainty in such studies. Moreover, for this system, there are no "avoided crossings" tending to eliminate electronic transitions during the collision³⁷; thus, attention could be focused on the "electron translation" problem and various approaches to handling it. This work is essentially completed.³⁸

In the current contract year, emphasis is being placed on:

(i) further study of alternative simple approximations to the electron translation factors; (ii) a more precise handling of the long-range 2s,2p coupling associated with the near degeneracy of these He^+ states; (iii) application of the Eikonal approximation³⁹ to calculate differential cross sections for some of the processes (2). We have also performed preliminary calculations of cross sections for the radiative charge transfer process

which we have found to be the dominant charge transfer process at energies much below 50 eV (c.m.).

Calculations of the total charge-transfer cross section (at all impact parameters) in the perturbed stationary state (pss) formalism holding the equal potential point (EPP) fixed are in excellent agreement with calculations in the plane wave translational factor (PWTF) formalism. Since the EPP calculations are many times easier than PWTF calculations considerable effort was made to develop other relatively simple formalisms which accurately determined not only the total exchange probability, but also transition probabilities into individual final states. All these alternative formalisms were pss in nature. The coupling elements were altered from the pss elements in simple ways to satisfy basic physical pictures. For example, in one method the exchange elements were the pss elements evaluated at the EPP, and the direct elements were the plane wave translational factor elements (which are the same as the pss elements evaluated at

the appropriate nucleus). Calculations were carried out with the phases all evaluated at one point, with the phases evaluated at the appropriate nucleus, and with combinations of these ways. All of the methods conserved unitarity; however, none agreed with the full plane wave translational factor treatment as well as the pss formalism holding the equal potential point fixed. Thus, we find the EPP method to be by far the simplest and essentially equivalent in accuracy to the more complicated P WTF approach. However, so far we have tested this only on the HeH^{++} collision system. Moreover, aside from a qualitative physical argument, we have no rigorous basis for selecting the EPP approach; certainly, the comparison needs to be made on other asymmetric systems. While we do not plan to do this at present, we may follow up in the future.

The probabilities of excitation from the metastable $\text{He}^+(2s)$ to the $\text{He}^+(2p_0)$ and to the $\text{He}^+(2p_{\pm 1})$ in collisions with He^+ are shown in Fig. 4 for energy 8 kev. The interactions between these states are strong over a relatively large range. At large internuclear separations the relativistic Lamb shift must be included.

The radiative charge transfer process (3), which is significant at low energies,⁴⁰⁻⁴¹ is expected to dominate at low energies simply because the non-radiative cross sections begin to fall off so rapidly for energies below 1 kev (c.m.).³⁸ The latter is due to the large (coulomb) electronic energy separation between the $2p\sigma$ (correlates to $\text{He}^{++} + \text{H}(1s)$) and $3d\sigma$, $2p\pi$, $2s\sigma$ states (correlate to $\text{He}^+(2s, 2p) + \text{H}^+$) at intermediate and small internuclear separations.³⁷ In addition to our fundamental interest in the radiative charge transfer process, an immediate objective of this study is to calculate accurate cross sections for this reaction and to determine at what energies this process begins to dominate as the primary mechanism for charge transfer.

Figure 4

In preliminary studies of this reaction we have computed cross sections applying the JWKB approximation and incorporating an optical potential approach recently used by Cohen and Bardsley⁴⁰ in a similar problem. Exact wave functions of the $(\text{HeH})^{++}$ molecule³⁷ were used to compute the relevant dipole matrix elements. Total cross sections were computed for center of mass energies of 0.1 to 1000 eV. These results are illustrated in Fig. 5. The deviation from smooth behavior at the lower energies is the result of the "centrifugal barrier" present in the effective potential energy which determines the relative nuclear motion. In Fig. 6 the situation is illustrated for energy 0.25 eV (c.m.) and partial waves $\ell = 46$ and 47. In the semi-classical (JWKB) method, there is an abrupt cut-off when the colliding partners are unable to get past the barrier (as occurs for $\ell = 47$ in the case shown). This gives rise to small discontinuities in the cross section. Of course, in a quantum mechanical description, tunneling will take place, thereby smoothing out the effect. However, in the latter case, "vibrational resonances" will appear at energies corresponding to predissociating rotational-vibrational states of the HeH^{++} molecule. We do plan to carry out the quantum mechanical calculations in the future. In Fig. 7 the radiative and non-radiative cross sections are compared. To the best of our knowledge there are no other theoretical or experimental results for the radiative cross section, and below 200 eV (c.m.) there is no information on the magnitude of the non-radiative cross section, although our theoretical studies suggest that it will continue to fall rapidly toward lower energies. Trajectory effects are undoubtedly very important at the lower energies as shown by Winter and Lane.³⁸

B) Electron-Ion Inelastic Scattering in Dense Plasmas

Diagnostics of dense high-temperature plasmas such as those occurring in inertial confinement fusion experiments require detailed

Figure 5.

Figure 6

Figure 7

knowledge of spectroscopic and collision properties of ions under extreme conditions. The interpretation of line emission from such plasmas requires quantitative data on the radiative transition probabilities and cross sections for ionization, recombination, and other collision processes for stripped ions present in the plasma.⁴²⁻⁴⁴

Indeed progress has been made in determining the influence of the dense plasma on atomic structure^{45,46} and on various radiative processes.⁴⁷ However, very little is known about such effects on rates for relevant collision processes. Since the inelastic cross sections for unscreened ions are finite at threshold,⁴⁸⁻⁵⁰ it is likely that plasma interactions will be important there.

In order to obtain some indication of the magnitude of the effect, Born approximation calculations were performed for the $1s \rightarrow 2s, 2p$ and $2s \rightarrow 2p$ transitions in a one-electron ion, where the influence of the dense-hot plasma was approximated by (Debye) screening the electron-ion interaction. The lowering of the cross sections (in comparison with the unscreened coulomb case) was found to be appreciable, especially near threshold. This was reported in last year's PROGRESS REPORT, and a paper is being submitted for publication.

In the current year, we are investigating the importance of "distortion" and "strong coupling" effects--both neglected in the Born approximation studies. To this end, Dr. Barbara Whitten (new Research Associate) is modifying a particularly flexible coupled-channels computer code to treat the inelastic electron-ion problem. One objective of these early studies is to obtain some measure of the influence of the plasma on the larger partial waves, which in the pure coulomb case contribute so strongly to the inelastic cross sections just above threshold.⁴⁸⁻⁵⁰ (In a rough way, this could be done by comparing partial-wave, coulomb-Born (unscreened) cross sections with Born (screened) cross sections.⁵⁰ However, the latter are likely to be quite inaccurate near threshold, especially for intermediate and weak screening, where

distortion effects will be important.) In this way, it may be possible to develop a simple scaling (due to the plasma screening) of the partial-wave contribution corresponding to ℓ greater than some "cut-off" value ℓ_c . If the smaller- ℓ partial waves are found to be not so much influenced by the plasma, then it may be possible to "adapt" existing accurate theoretical or experimental electron-ion cross sections (small- ℓ contributions) to the dense-plasma environment by simply adding in the appropriate plasma density-, and temperature-dependent, higher- ℓ , partial wave contributions. In the current year we expect to have at least a preliminary test of this potentially powerful procedure.

C) Highly-Excited "Rydberg" Atom Scattering

Very impressive recent experimental studies of highly-excited atoms by Stebbings et al. (at Rice)⁵¹⁻⁵³ and in other laboratories⁵⁴ have demonstrated that an electron in an outer "Rydberg" orbit, on the average very far from the nucleus, interacts with colliding atoms and molecules rather like a free electron. By an intricate process of state selection "before" and state inquiry "after" the collision, the Rice group has been able to demonstrate excitation-transfer from rotational energy of the molecule (NH_3 , HCl , etc.) to orbital energy of the excited atom.⁵² While the "free-electron" model of the electron-molecule encounter is probably not very accurate, still it provides some guidance towards a more realistic description.⁵⁵⁻⁵⁷ The "highly-excited" nature of the atom, and the "long-range dominance" of the electron-molecule interaction make a classical approach attractive. We are currently carrying out a classical calculation of the atom-molecule collision process, using a cut-off dipole model for the electron-molecule interaction. The justification for a fully classical treatment is not completely clear. However, there are several sound reasons for performing the classical calculations,⁵⁵ at least initially: (i) A classical description of the

high-Rydberg atomic states is certainly appropriate; (ii) The long-range dipole interaction of the orbital electron with a polar molecule permits a classical description under certain conditions^{58,59}; (iii) A classical description of the molecular rotation is appropriate for large rotational angular momentum; and (iv) The relative motion of the molecular center of mass and the nucleus of the atom can be adequately described using a classical trajectory. There is some analogy with Olson's fully classical calculation of ionization cross sections for collisions between two "high-Rydberg" atoms.⁶⁰

Moreover, one principal finding of the experimental measurements⁵² lends itself to a classical, intuitive explanation; viz. the data (for NH_3) show a marked propensity for rotational de-excitation (and electronic excitation) in the collisions (the atoms are initially in states $26 \leq n \leq 40$ and $\ell = 3$). The effect is less dramatic for HF which, in comparison with NH_3 , has a larger dipole moment and smaller moment of inertia. These data suggest that the cross section is dominated by electron-molecule encounters at the "far reaches" of the eccentric orbit, where the electron has very little kinetic energy to "give up" in the collision. We expect to be able to test this hypothesis with the classical calculation. In the current contract year, we are performing 2-dimensional classical calculations where the orbiting electron, rotating nuclei, and relative motion of the molecular center of mass and the atomic nucleus are all confined to a plane, as illustrated in Fig. 8. The classical equations of motion are solved for the electronic and molecular-rotational and center-of-mass coordinates, subject to some arbitrarily chosen initial conditions, including the parameter b , orbital orientation α , etc. In the classical Hamiltonian, the electron-molecule interaction is represented by a cut-off dipole potential of the form

$$V_{\text{em}}(\vec{r}_{\text{em}}) = - \frac{\vec{d} \cdot \vec{r}_{\text{em}}}{(r_{\text{em}})^3} [1 - \exp(-r_{\text{em}}^2/a^2)] , \quad (4)$$

Figure 8

where $\vec{r}_{em}$ is the position vector of the electron relative to the molecule (c.m.), $\vec{d}$ is the molecular dipole moment orientated along the molecular axis, and a is a parameter chosen to remove the unphysical r_{em}^{-2} divergence as $r_{em} \rightarrow 0$. By monitoring the closest electron-molecule approach in a given collision (i.e. for a given set of initial conditions b , d , etc.) it will be possible to identify "unacceptable cases" where the electron comes too close to the molecule so that not only is Eq. (4) inaccurate, but the classical description of the electron-molecule encounter fails in any case. This is one aspect of the problem that will require a quantum mechanical description in subsequent work. In Fig. 9, a sample of our preliminary results is illustrated. The final electronic energy (atomic units) of the Rydberg electron is plotted against impact parameter for one set of initial conditions. The initial electron position momentum and energy are consistent with the state $n = 25$, $\ell = 3$; the molecule has initial rotational energy $E_j \approx 3$ mev corresponding to angular momentum $j \approx 5$ of NH_3 ; the initial relative velocity of the molecular c.m. corresponds to $E_{cm} \approx 2$ ev; and the orbital orientation is $\alpha = 45^\circ$. While details of the shapes of these curves are not yet fully understood, it is clear that in this particular atomic molecule collision, the electron had three close encounters with the molecule. (Of course, the b at which the encounter occurs will vary with certain of the initial conditions.) Also, atomic excitation as well as de-excitation are evident at different impact parameters. In order to extract a cross section, it will be necessary to perform calculations at a large number of (random) initial conditions and average the results.⁶¹ Moreover, some form of "binning" or other approximation must be employed to relate the classical results to quantum transitions.⁶² Finally, since these are two-dimensional results, an approximate weighting with respect to impact parameter is necessary. The objective for the remainder of this contract year

Figure 9

is to obtain approximate cross sections for atomic and molecular excitation and de-excitation collisions and atomic ℓ -changing cross sections in the two-dimensional classical model.

A study of the avoided crossings of the energy levels of the relativistic hydrogen atom in an electric field will be initiated in the contract year. The states under consideration cross in the non-relativistic hydrogen atom,⁶³ and consequently the avoided crossings are entirely a result of relativistic effects. The matrix elements necessary to carry out the calculation are obtained analytically, and combined by a computer to determine the relativistic energy curves. The experimental study (being carried out in the Yale group) has not as yet obtained results. Collaborative research with Dr. Stebbings' group on black-body radiative photoionization of "hot-Rydberg" atoms is now complete and has been submitted for publication.⁶⁴

D) Electron Scattering from Molecules -- Vibrational Excitation

Earlier work in this group on slow electron collisions with CO_2 molecules indicates that the low-energy elastic scattering is strongly enhanced by a "virtual state" present in the electron- CO_2 effective potential.⁶⁵ Very recent, high-resolution electron- CO_2 elastic scattering measurements by the Bielefeld group show excellent agreement with our theoretical calculations.⁶⁶ Moreover, Morrison has extended the calculations to lower energies, and by fitting an effective-range expansion about a virtual-state zero in the complex k plane, has obtained a position for the virtual state pole.⁶⁷ We also showed that the $000 \rightarrow 100$ (symm. stretch) vibrational-excitation cross section near threshold was enhanced by this virtual-state mechanism.⁶⁸ However, the vibrational impulse approximation used in these calculations fails very near threshold, so the precise behavior of the cross section there is not known. In the current contract year, we are resolving this threshold ambiguity. Our intention was to extract

an R matrix (at several R_{co} separations and at an electron radius of about $4 a_0$) from the large coupled channel calculations performed previously.⁶⁵ These could then be transformed to a vibrational basis and a few-channel vibrational close-coupling calculation carried out from $4 a_0$ to the asymptotic region. However, we found we simply did not have sufficient information from the earlier calculations to construct the R matrix. Therefore, we have adopted an alternative procedure. Since the low-energy scattering is dominated by s-wave (asymptotically) contributions to the S matrix, we are simply representing the e-CO₂ interaction by spherically symmetric potentials adjusted so as to reproduce the accurate phase shifts over a range of low energies. These will then be chosen as the "distortion potentials" (diagonal potential matrix elements) in a two-vibrational-state close coupling (CC) calculation. The vibrational coupling matrix element is represented by an effective polarization potential "adjusted" so that the CC cross sections for the 000 $\rightarrow$ 100 transition agree with the vibrational-impulse results⁶⁸ well above threshold (but still low energy) where the latter are felt to be reliable. The two-state CC results, then, will provide a proper extrapolation down to threshold. We expect to have results by the end of the contract year.

E) Inner Shell Photoabsorption and Photoionization of Atoms and Molecules

The objectives of this project have been twofold: (1) to develop and test reliable approximations for exchange and correlation (XC) contributions that can be used reliably in photoabsorption, photoionization, and electron-scattering studies, and (2) using these XC approximations, to initiate a study of inner-shell photoabsorption and photoionization of relatively small symmetric molecules such as CH₄, CCl₄, etc., using the multiple scattering method (MSM).⁶⁹ Indeed,

we have made progress on the XC approximations, showing that taking into account "screening" of the exchange "fermi-hole" in a local free-electron-gas exchange approximation considerably improves both photoionization and electron-scattering cross sections for the atomic cases studied. (This is reported in the next section, "Exchange and Correlation in Electron-Scattering and Photon Processes Involving Atoms and Molecules.")

We have postponed application to inner-shell photoabsorption and photoionization of the molecules for two reasons: (1) our research, so far, suggests that it will probably be more profitable to focus on attempting to improve the XC approximations further (see next section) than to perform extensive calculations at the present time; (2) Dr. Huang's group (Rice) is interested in carrying out experimental (synchrotron absorption) and theoretical (multiple scattering method MSM) calculations on KO_4^+ and related molecules,⁷⁰ and hence will be in a position to help us with the testing of various XC approximations. We will maintain a close interaction with Dr. Huang's group over the next year or so.

F) Exchange and Correlation in Electron-Scattering and Photon Processes Involving Atoms and Molecules

The theoretical study of photoabsorption, photoionization and electron collision processes involving complex molecules, clusters, adsorbed atoms or molecules, etc. requires reliable approximations to exchange and correlation (XC) effects. In recent years, a number of local density (LD)⁷¹⁻⁷⁷ exchange approximations have been studied, and in a number of instances, with surprisingly good results. The Hara⁷⁷ version of the Free-Electron-Gas (HFEG) has been particularly useful in electron scattering^{65,69,75,76} and photoionization⁶⁹ of molecules. In last year's PROGRESS REPORT we reported atomic photoionization cross sections for Li, C, O, Ne and Ar obtained by applying

the X ALPHA, HFEG, and a screened version of HFEG ("Screened Hara"). A comparison for $3p \rightarrow ks$ of Argon with the Hartree-Fock (HF) result⁷⁸ is illustrated in Fig. 10. In all cases the local charge density used the calculation was taken to be that of the Hartree-Fock neutral Ar, with one electron removed. We concluded that taking into account "screening" of the fermi hole (Screened Hara or SHFEG) represents an improvement over HFEG in all cases studied (the agreement for $3p \rightarrow kd$ of Argon not shown, is not as good; nevertheless the screened Hara approximation is still an improvement). More recently, we have found that the SHFEG approximation can be derived as a local approximation to the "mass operator" in the many-body theory of the free electron gas,⁷⁹ where the fermi momentum k_F is defined as in the Hara theory.⁷⁷ This, then, suggested a systematic way of further improving the SHFEG procedure by employing higher-order perturbation theory corrections the exchange energy. (Because of this development we chose not to proceed with publication as implicated in last year's PROGRESS REPORT.) Preliminary results suggest that the second-order corrections are small, so that the SHFEG approximation is quite good. However, there are remaining questions to resolve. The ad hoc definition of fermi momentum k_F , while seeming to work well in a variety of circumstances, is not on a very solid foundation. For smaller atomic and molecular systems, some modification of the electron-gas approximation is surely required, e.g. as described by Rae⁸⁰ in his modification of the Gordon-Kim theory.⁸¹ In the current contract year efforts will be directed toward improved XC approximations, perhaps in the context of "density functional theory."⁷¹⁻⁷³

Figure 10

IV. List of References

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V. Personnel

A) List of Personnel Working on Project During Year to March 31, 1981:

1) Experimental Program

G. K. Walters
F. B. Dunning
D. Helms, Research Associate
J. Lang, Research Associate
M. Durrett (M.S., San Diego State), Research Assistant
K. Giberson (B.S., Eastern Nazarene College), Research Assistant
A. Harrison (B.A., Sam Houston State), Research Assistant
K. Jamison (B.S., Indiana U. of Penn.)
M. Onellion (B.S., West Virginia U.)
T. Riddle (M.A., Rice), Research Assistant

2) Theoretical Program

N. F. Lane
G. J. Hatton
J. S. Cohen
B. Whitten, Research Associate
A. Day (B.A., Cornell U.)
J. O'Connell (part-time; no direct support from contract)
S. Preston (B.A., Rice)
B. West (B.A., Univ. of Oklahoma)

B) Changes in Personnel

- 1) Dr. Jürg Kurt Lang (Ph.D. Swiss Federal Institute of Technology (ETH-Zurich), 1979) joined the experimental program as a postdoctoral Research Associate in January 1980.
- 2) Dr. D. Helms resigned his position as Research Associate in November 1980, to accept a research position with Texaco, Inc.
- 3) Dr. G. Hatton has accepted a position with Texaco, Inc., following his appointment as Visiting Assistant Professor.

- 4) Dr. Barbara Whitten (Ph.D. Univ. Roch., 1977) joined the theoretical program as postdoctoral Research Associate in September 1980.

C) Time Devoted by Faculty Investigators

Professor G. K. Walters devoted 2-1/2 months of full-time effort to the contract during the summer of 1980, and 30% time during the academic year.

Professor F. B. Dunning devoted 1 month of full-time effort during the summer of 1980, and 15% time during the academic year.

Professor N. F. Lane devoted 1/2 month of full-time effort during the summer of 1980 (upon his return from a year's leave at the NSF), and 30% time during the academic year 1980-81.

Professor G. J. Hatton devoted 3-1/2 months of full-time effort from May 16 through August 31 and 30% time during the 79-80 academic year.

Professor J. S. Cohen has contributed significantly to the group's effort during the 79-80 academic year.

VI. Publications Arising From the Contract

Published

- 1) "Production and Decay of the 0_u^+ and 1_u States of Kr_2 Excited by Synchrotron Radiation," T. D. Bonifield, F.H.K. Rambow, G. K. Walters, M. V. McCusker, D. C. Lorents, and R. A. Gutcheck, Chem. Phys. Letters, 69, 290 (1980).
- 2) "Time Resolved Spectroscopy of Xenon Excimers Excited by Synchrotron Radiation," T. D. Bonifield, F.H.K. Rambow, G. K. Walters, M. V. McCusker, D. C. Lorents, and R. A. Gutcheck, J. Chem. Phys. 72, 2914 (1980).
- 3) "Effects of Adsorbates on Electron Spin Polarization in Low Energy Electron Diffraction from Tungsten (001). III. Nitrogen Overlayer," Surface Science 93, 550 (1980).
- 4) "Plane-Wave Factors in a Molecular-State Treatment of Electron-Transfer in Collisions of He^{++} Ions with H Atoms," T. G. Winter and G. J. Hatton, Phys. Rev. A 21, 793 (1980).
- 5) "Molecular-State Treatment of Collisions between Protons and He^+ Ions," T. G. Winter, G. J. Hatton, and N. F. Lane, Phys. Rev. A 22, 930 (1980).

Accepted

- 1) "Time Resolved Spectroscopy Using Synchrotron Radiation," G. K. Walters and T. D. Bonifield, IEEE Transactions on Nuclear Science.

Submitted

- 1) "A Polarized $He(2^3S)$ Thermal Metastable Atom Source," T. W. Riddle, M. Onellion, F. B. Dunning, and G. K. Walters, Rev. Sci. Instr.
- 2) "Inelastic Electron-Ion Collisions in a Dense Plasma," G. J. Hatton, J. C. Weisheit, and N. F. Lane (submitted to J. Phys. B.)

- 3) "The Interaction of Black-Body Radiation with Xenon Rydberg Atoms,"
G. F. Hildebrandt, E. J. Beiting, C. Higgs, G. J. Hatton, and
K. A. Smith (submitted).

In Preparation

- 1) "XeF* Quantum Yields by Photolysis of XeF₂ Using Synchrotron Radiation," G. Black, D. C. Lorents, D. L. Huestis, R. L. Sharpless, D. A. Helms, M. Durrett, and G. K. Walters.
- 2) "Time Resolved Spectroscopy of XeF* Excited by Synchrotron Radiation," G. Black, D. C. Lorents, D. L. Huestis, R. L. Sharpless, D. A. Helms, M. Durrett, and G. K. Walters.
- 3) "A Study of XeCl/Xe₂Cl Excited State Kinetics Using Synchrotron Radiation Excitation," K. Y. Tang, D. C. Lorents, R. L. Sharpless, D. L. Huestis, D. A. Helms, M. Durrett and G. K. Walters.
- 4) "Molecular Cluster Approach to Single Hydrogen Impurity in a Nickel Crystal," R. W. Simpson, R. Chaney, and N. F. Lane.
- 5) "Local Exchange Approximations in Photoionization and Electron Scattering," J. O'Connell, G. J. Hatton, and N. F. Lane (see discussion in Section III.F).

Papers Presented

- 1) "Time Resolved Spectroscopy of Rare Gas- and Rare Gas-Halide Excimers Excited by Synchrotron Radiation," G. K. Walters.
Invited paper American Physical Society, New York, N.Y., March 28, 1980. Bull. Am. Phys. Soc. 25, 405 (1980).
- 2) "Study of XeCl/Xe₂Cl Excited State Kinetics Using Synchrotron Radiation Excitation," K. Y. Tang, D. C. Lorents, R. L. Sharpless, D. L. Huestis, D. A. Helms, M. Durrett, and G. K. Walters.
"Long" paper presented by K. Y. Tang at 33rd Gaseous Electronics Conference, Norman, Oklahoma, October 8, 1980.

- 3) "Time Resolved Spectroscopy Using Synchrotron Radiation," G. K. Walters. Invited Paper. Sixth Conference on the Application of Accelerators in Research and Industry, Denton, TX, Nov. 5, 1980.
- 4) "Collisions of Metastable $\text{He}(2s)^+$ with H^+ ," G. J. Hatton, N. F. Lane, and T. G. Winter; DEAP meeting of APS, Bull. Amer. Phys. Soc. 24, 1176 (1979).
- 5) "Cross Sections for Electron Transfer and Excitation in p-He^+ Collisions," T. G. Winter, N. F. Lane, and G. J. Hatton, DEAP meeting of APS, Bull. Amer. Phys. Soc. 24, 1187 (1979).
- 6) "Local Exchange Potentials in Photoionization," J. O'Connell, N. F. Lane, and G. J. Hatton, DEAP meeting of APS, Bull. Amer. Phys. Soc. 24, 1201 (1979).

VII. Expenditure Report (1980-81)

	Rice University Expense Total Estimated 4/1/80 to 11/30/80	DOE Expense Total Estimated 4/1/80 to 11/30/80	DOE Expense Total Estimated 4/1/80 to 3/31/81
1. Salaries & Wages	\$19,174	\$35,098	\$ 39,605
2. Equipment	- 0 -	- 0 -	36,675
3. Materials & Supplies*	12,000	12,000	47,600
4. Travel	- 0 -	- 0 -	3,175
5. Fringe Benefits	3,260	5,967	5,318
6. Indirect Costs	<u>12,913</u>	<u>19,899</u>	<u>35,887</u>
Totals	\$47,347	\$72,964	\$168,260

*Includes funds for shop charges and computer services.

Estimated Expenses April 1, 1980 to March 31, 1981

Rice Contribution	\$ 72,964	(25.3%)
DOE Contribution	<u>215,000</u>	(74.7%)
Total Budget	\$287,964	(100%)

DOE Support Ceiling for current contract period (4/1/80-3/31/81):

\$215,000

Accumulated DOE Support Ceiling: \$1,303,000

Estimated DOE Funds remaining

3/31/81:

- 0 -

G. K. Walters
Principal Investigator