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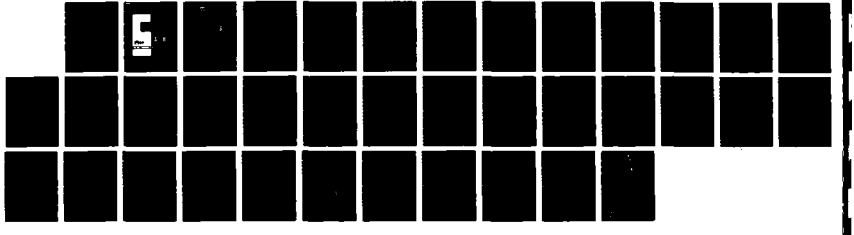

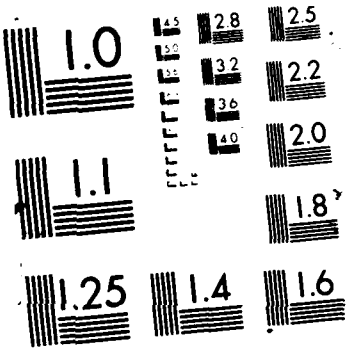
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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

Annual Technical Report

Contract No. F49620-85-C-0095
Project Task 2301/A7

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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

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REPORTED BY H. H. Michels

J. A. Montgomery, Jr.

APPROVED BY W. L. Nighan

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This technical program constitutes a theoretical research investigation of the kinetic mechanisms of negative ion formation in plasmas. This study was directed toward elucidating the mechanisms of the most important volume-dependent reactions that occur in hydrogen-ion $H^-(D^-)$ source devices, primarily of the Belchenko-Dimov-Dudnikov (BDD) type and toward evaluating other light negative anions, such as Li^-, as possible sources. The primary goal of this research program was to identify the most important reactions leading to negative ion production or destruction and to estimate these reactions rates as a function of system parameters such as density, composition and temperature. A further goal was to explore new chemical sources for the production of light mass negative atomic ions. The results of this program furnish data and provide direction for more detailed investigations into the kinetics of both gas phase and gas-surface reaction rates of importance in ion source devices and provide input for reliable modeling of such systems. This investigation

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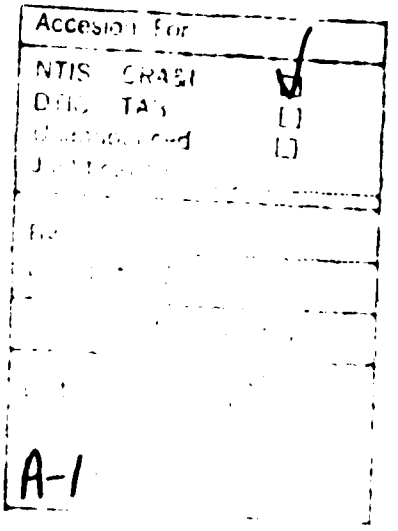
was carried out using quantum mechanical methods. Both ab initio and density functional approaches were employed in these studies.

FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Corporation, Research Center, East Hartford, Connecticut, under Contract F49620-85-C-0095, Project-Task No. 2301/A7. The performance period for the technical program was from 1 June 1986 through 31 May 1987. The project monitor was Lt. Colonel Bruce L. Smith, USAF.



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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

ABSTRACT

This technical program constitutes a theoretical research investigation of the kinetic mechanisms of negative ion formation in plasmas. This study was directed toward elucidating the mechanisms of the most important volume dependent reactions that occur in hydrogen-ion, $H^-(D^-)$, source devices, primarily of the Belchenko-Dimov-Dudnikov (BDD) type and toward evaluating other light negative anions, such as Li^-, as possible sources. The primary goal of this research program was to identify the most important reactions leading to negative ion production or destruction and to estimate these reaction rates as a function of system parameters such as density, composition and temperature. A further goal was to explore new chemical sources for the production of light mass negative atomic ions. The results of this program furnish data and provide direction for more detailed investigations into the kinetics of both gas phase and gas-surface reaction rates of importance in ion source devices and provide input for reliable modeling of such systems. This investigation was carried out using quantum mechanical methods. Both ab initio and density functional approaches were employed in these studies.

STATEMENT OF WORK

The contractor shall conduct a theoretical research investigation of the electronic structure of negative molecular ions and the kinetic mechanisms of negative ion formation in plasmas. This investigation shall include the calculation of potential energy hypersurfaces for ion-atom and ion-molecule gas phase interactions that occur in magnetron-type negative ion source devices. The contractor will perform theoretical studies of H surface adsorption to reduce the surface conversion mechanism for H^- production into a series of well characterized elementary processes. In addition, calculations shall be performed to estimate the rates of the most important volume dependent reactions leading to H^- production or destruction in such devices. Experimental data collected at LBL, LASL and AVCO-Everett from their ongoing studies with negative ion source devices shall be iteratively examined and integrated with the results generated from this theoretical investigation. The computations shall be carried out with ab initio and density functional methods using electronic structure and kinetic cross-section codes that have previously been developed or modified at this Center. Specifically, this investigation shall comprise the following:

a. Quantum mechanical calculations of the kinetic cross-sections for volume dependent reactions leading to the collisional formation and loss (destruction) of H^-.

b. Calculation of dissociative attachment cross sections for $e + Li_2 \rightarrow Li + Li^-$ as a function of collisional energy and rovibrational energy of the Li_2 molecule.

c. Development of a computer code and calculation of the electronic excitation cross sections for Li_2 via electron collisions.

d. Continued studies of negative ion formation on surfaces using large cluster representations with fractional hydrogen coverage.

BACKGROUND

Recent successes in the Tokamak program and in other controlled thermonuclear research programs (Ref. 1) have focused attention on the problem of developing an efficient high-energy particle beam source. For several applications, a neutral beam with energies above 200 keV is desired. The acceleration of negative ions (primarily H^- or D^-) to such energies, followed by neutralization through a stripping reaction, appears at the present time to be the most efficient approach for producing a high energy neutral particle beam.

In another area, the feasibility of particle beams (both charged and neutral) as military weapons has been under study. The proposed endoatmospheric applications require high intensity sources and mainly focus on the problems of beam stability and propagation characteristics. Exoatmospheric applications require lower intensity sources but of very high quality. Design goals are highly collimated beams with a narrow energy spread.

A magnetron-type negative H^- source has been reported by Belchenko, Dimov and Dudnikov (BDD) (Ref. 2) that has produced H^- current densities of several A cm^{-2}. This device operates as a plasma discharge in an atmosphere of hydrogen gas with cesium or other alkalis present at ~ 0.01 percent. The mechanism for the production of H^- is believed to involve a catalyzed surface reaction whereby H^- ions are produced by transfer of electrons from Cs atoms that are adsorbed on the cathode surface (Refs. 3, 4). The detailed kinetic mechanisms of such surface reactions are still uncertain and parametric experimental studies are currently underway at LASL, LBL, IRT and at other laboratories to elucidate the mechanisms and operating characteristics of BDD and similar devices and to develop information for their scale-up to higher current densities. Diagnostics of H^- source devices are also underway at Brookhaven (Ref. 5) using beam probe and spectroscopic techniques.

Concurrent with these surface-plasma reactions are several electron-H volume-dependent processes that may lead either to the production of H^- or, in reverse, may act as important destructive processes of the negative ions after they are formed. Photodetachment experiments by Bacal and Hamilton (Ref. 6) in hydrogen plasmas indicate H^- densities 100 times larger than that predicted from simple electron attachment mechanisms. Further, these experiments indicate a nonlinear dependence of the production of H^- on electron density, at least for densities less than 10^{10} cm^{-3}. Several mechanisms (Ref. 7) have been proposed to explain these volume-dependent H^- production processes but the cross-sections for many of the reactions leading to H^- are uncertain.

By a large margin, the major thrust of the development of particle beam technology has been experimental in nature. Theoretical studies of surface catalyzed reactions leading to H^- production have been undertaken by LLL (Ref. 4), but only a relatively small theoretical effort (Ref. 8) has been

directed toward detailed calculations of cross-sections for volume-dependent reactions. Because of the difficulty of conducting experiments to measure these unknown cross-sections, the development of a sound theoretical method for calculating these state-to-state processes appeared desirable. Although relatively little work of this nature has been done in the past, enough theoretical work is available to indicate that the development of such procedures can be made practical, particularly if good wave functions and potential energy surfaces are available for the interacting species.

The original goal of this technical program was to delineate the most important volume dependent reactions that lead to $H^-(D^-)$ production (or destruction) and to calculate the energetics and cross-sections of such reactions as a function of system parameters. Attention was also directed toward those kinetic processes that are of importance in high pressure ion source devices, particularly of the BDD type. It was intended that this theoretical program should compliment experimental studies with negative ion source devices. A cooperative program of ongoing experimental research and our theoretical studies are of mutual benefit and result in a better understanding of the fundamental physical processes occurring in ion source devices.

A further goal of this research program is to explore new chemical sources for the production of light negative atomic ions, in particular H^- and Li^-. Current studies include the formation of H^- or D^- via photodissociation of unsaturated hydrocarbon negative ions and the formation of Li^- via dissociative-attachment of electrons to molecular Li_2. This latter process appears feasible based on our current knowledge of the energetics of this system. Our recent research efforts have been directed toward three general areas: mutual neutralization and collisional dissociation reactions in negative-ion plasmas, analysis of dissociative-attachment in the $e + Li_2$ system, including the calculation of electron excitation cross sections for $e + Li_2$, and further studies of surface catalyzed reactions for the production of H^-. The negative-ion plasma studies entail analysis of the kinetics of volume reactions leading to the destruction of, for example, H^- and Li^-. The $e + Li_2$ dissociative attachment studies parallel the work of Bardsley and Wadehra (Refs. 8,9) on the $e + H_2$ reaction and are being carried out in collaboration with Professor Wadehra. Although a phenominological model for negative-ion formation on metal surfaces has been proposed by Hiskes, et al. (Ref. 4), a basic understanding of the surface state chemistry has yet to be developed. Our work in this area includes density functional calculations of tungsten and molybdenum clusters, analyzed as base metals and with the addition of cesium and hydrogen on the surface.

RESEARCH PROGRESS

During the past contract year, we have undertaken studies of several light negative ion systems. As a continuation of our work on Li^- formation, we have suggested a new kinetic route for the formation of quiescent Li^- through Rydberg atom collisions. This new mechanism is now under study by M. McGeoch at AVCO as an alternative to dissociative attachment of $e + Li_2$ as a source for Li^-. In addition to our Li^- studies we have continued an analysis of the kinetics of He_2^- autodetachment. This work is being done in collaboration with J. Peterson and Y. Bae at SRI and has resulted in several publications and joint technical papers. Finally we have examined the negative hydrogen ion cluster, H_3^-, to determine whether this system is thermodynamically stable relative to $H^- + H_2$. A summary of our research is given below. Four technical papers and seven presentations have resulted from the past year's research efforts.

Li^-

The negative ions of light atoms are currently being studied for their possible application in gaseous discharges, fusion plasmas and gas lasers (Ref. 10). One source for the volume production of atomic anions is the process of dissociative electron attachment to molecules (Ref. 11). This process has been studied experimentally for low energy electron-hydrogen molecule collisions by Allen and Wong (Ref. 12). A parallel theoretical study has been reported by Wadehra and Bardsley (Ref. 13). More recently, McGeoch and Schlier (Ref. 14) have examined dissociative attachment (DA) in electron-lithium molecule collisions and have found large DA rates for attachment to highly vibrationally excited Li_2 molecules. The effect of vibrational excitation on the DA rates has been studied by Hiskes (Ref. 15) for $e + H_2$ collisions and by Wadehra and Michels (Ref. 16) for the $e + Li_2$ system.

In the $e + Li_2$ system, it has been shown (Ref. 16) that excitation of Li_2 to the $A\ ^1\Sigma_u^+$ state, either by electron impact or by photon pumping, results in an enhanced vibrational distribution upon radiative decay of the $A\ ^1\Sigma_u^+$ state to the ground $X\ ^1\Sigma_g^+$ state of Li_2. The cross sections for vibrational excitation of Li_2 $X\ ^1\Sigma_g^+$ via low energy electron collisional excitation of the $A\ ^1\Sigma_u^+$ state exhibit a relatively flat vibrational distribution in the range $3 \leq v'' \leq 9$. This suggests that Li_2 molecules which are vibrationally excited to the DA threshold for Li^- formation should exhibit the largest attachment cross sections, a result that is indicated by the studies of McGeoch and Schlier (Ref. 14).

An alternative mechanism for negative ion formation was suggested by Lee and Mahan (Ref. 17), who proposed that ion-pair formation:

$$X^* + X \rightarrow X^+ + X^- \qquad (1)$$

should occur for systems where the energetics for ion-pair formation are competitive with associative ionization:

$$X^* + X \rightarrow X_2^+ + e. \qquad (2)$$

The alkali metals, including lithium, are therefore good candidates for such a study of ion-pair formation. Ciocca, et. al. (Ref. 18) have recently reported on the formation of Na^- ions in highly excited (n=7-40) Rydberg atom collisions. Our studies were directed toward examining the possible mechanisms for ion-pair formation in lithium atom collisions.

In order to determine the possible paths for Li excited state interactions, a series of ab initio calculations of the electronic states of Li_2 up to the $Li[^2S(3s)] + Li[^2S(3s)]$ dissociation limit was undertaken. Since the formation of the ion-pair $Li^+[^1S] + Li^-[^1S]$ can occur only for $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetries, our studies were restricted to these two representations.

Theoretical potential curves for the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetries of Li_2 were obtained from valence configuration interaction (VCI) calculations. A 64 function Slater orbital basis, containing a (2s1p) optimized valence basis augmented by a (3s3p3d2f) Rydberg basis, was used in this study. The basis was transformed to $D_{\infty h}$ symmetry orbitals and CI calculations were performed in the space of all symmetry adapted configurations having the $1\sigma_g$ orbital doubly occupied. The resulting CI expansions contained 344 and 331 configurations for the $^1\Sigma_g$ and $^1\Sigma_u$ symmetries, respectively. As the interactions in this system are very long-ranged, calculations were performed over a range of internuclear separations from 5 to 50 bohrs. The results of our theoretical calculations are shown in Fig. 1 and Fig. 2 for the $^1\Sigma_g^+$ and $^1\Sigma_u^+$ symmetries, respectively. The ionic curves which dissociate to $Li^+[^1S] + Li^-[^1S(2s^2)]$ are clearly evident in both Fig. 1 and Fig. 2, where they exhibit a nearly diabatic crossing behavior with the normal valence states of Li_2 at large internuclear separations, but show strong mixing at distances $\leq$ 10Å. Ion-pair formation may occur for long-range interactions of the type

$$Li\ [^2S(2s)] + Li^{**}[^2S(n=5)] \rightarrow Li^+\ [^1S] + Li^-[^1S] \qquad (3)$$

but clearly there are few effective curve crossing channels leading to $Li^+ + Li^-$. The curve crossing mechanism suggested by Ciocca, et al. (Ref. 18), thus appears not to be an important mechanism for ion-pair production in the Li_2 system.

A second mechanism suggested by Ciocca et al. (Ref. 18) for alkali negative ion formation would involve excited state negative ion formation via

$$Li^*[^2P(2p)] + Li^{**}(n\geq 9) \rightarrow Li^+[^1S] + Li^-[^1P(2s2p)] \qquad (4)$$

or from electron attachment to a Rydberg state of Li^{**} followed by radiative stabilization to the ground $Li^-[^1S(2s^2)]$ state. Both of these processes can be ruled out for the Li_2 system since the autoionization lifetime of the $Li^-[^1P(2s2p)]$ state is known to be very short (Ref. 19) relative to radiative

stabilization and higher autoionizing states should exhibit even shorter lifetimes.

The analysis of our calculated results given above leaves us with radiative stabilization of excited state Li_2 interactions as the most probable mechanism for ion-pair formation in this system. Three separate types of interactions leading to ion-pair production can be identified:

$$Li[^2S(2s)] + Li^{**}(n>5) \rightarrow Li_2^{**} \rightarrow Li^+ + Li^- + h\nu \quad (18.0\mu > \lambda > 2.0\mu) \tag{5}$$

$$Li^*[^2P(2p)] + Li^{**}(n>3) \rightarrow Li_2^{**} \rightarrow Li^+ + Li^- + h\nu \quad (2.8\mu > \lambda > 0.5\mu) \tag{6}$$

$$Li^{**}(n>3) + Li^{**}(n>3) \rightarrow Li_2^{**} \rightarrow Li^+ + Li^- + h\nu \quad (\lambda < 0.6\mu) \tag{7}$$

The mechanism illustrated by Eq. (7) exhibits a quadratic dependence on the Rydberg atom concentration and, similar to the studies reported by Ciocca, et al. (Ref. 18) for Na, should be distinguishable from the reactions given by Eq. (5) and (6). The latter reactions should exhibit a linear dependence on reaction rate with Rydberg atom concentration. A preliminary analysis of the radiative decay of these high-lying Li_2 states shows a strong preferential coupling to the $Li^+[^1S] + Li^-[^1S(2s^2)]$ dissociating channel. This is as expected since the transition moments are very large for covalent Rydberg interactions radiating to a lower ionic molecular state. In addition, the range for these Rydberg atom interactions is predicted to be very large (>30Å) where the radiative moments are increasing proportional to the internuclear separation.

An experiment similar to that reported by Ciocca et al (Ref. 18) has been suggested by M. McGeoch at AVCO to test this radiative mechanism for $Li^+ - Li^-$ ion-pair formation through Rydberg atom collisions. The two laser excitation mechanism:

$$Li[^2S(2s)] + h\nu \rightarrow Li^* [^2P(2p)] \quad \lambda = 671.0 \text{ nm} \tag{8}$$

$$Li^*[^2P(2p)] + h\nu' \rightarrow Li^{**} [^2S(3s)] \quad \lambda' = 812.8 \text{ nm} \tag{9}$$

should produce Rydberg Li atoms in either the $^2S(3s)$ or $^2D(3d)$ states, provided near-saturation is achieved in the first resonant line excitation. The subsequent reactions of these laser-produced Rydberg state Li atoms is illustrated in Table I. Two photon excitation by the first laser, and excitation of the $^2S(3s)$ Rydberg state by the 671 nm laser source, are both below the ionization threshold for Li, thus eliminating any first order ionization process. The suggested experiment will look for $Li^+ - Li^-$ ion-pair formation accompanied by excimer-like radiation at wavelengths < 600 nm. The ion pairs could be

electrostatically extracted from the laser reaction region and mass analyzed to identify the Li^- signal.

As mentioned above, the reaction given by Eq. (7) should exhibit a quadratic dependence on the Rydberg state density and a very large cross section for ion-pair formation. Similar volume processes to that represented by Eqs. (5)-(7) are energetically possible for $H^+ - H^-$ ion pair formation, provided that a useful mechanism for n = 2 production in H can be found. Very recently R. McFarlane (Hughes) has developed a Lyman alpha (L_α) laser source which can be used to pump the n = 2 transition in H. An analysis and possible collaboration with R. McFarlane in studying this process is in progress.

He_2^-

In recent studies of the newly discovered (Ref. 20) metastable He_2^- anion, autodetachment to the He_2 $[X^1\Sigma_g^+]$ + e repulsive continuum was observed (Refs. 20-22). A preliminary analysis (Ref. 21 and 22) of the measured intensity distribution of this autodetachment process yields a vertical separation of 15.7 ± 0.2 eV between the metastable He_2^- $[^4\Pi_g]$ state and the repulsive ground $[X^1\Sigma_g^+]$ state of He_2. This energy separation is ~0.5 eV larger than that calculated using our best estimate (Ref. 23) of the spectroscopic constants for He_2^-, and the ground state potential for He_2 as represented by the recent Monte Carlo calculations by Ceperley and Partridge (Ref. 24).

In order to determine the source of this discrepancy, we have analyzed the intensity distribution of the Hopfield helium continuum reported by Huffman, et al. (Ref. 25). This continuum emission arises from the transitions, He_2^* $[A^1\Sigma_u^+] \rightarrow [X^1\Sigma_g^+]$ and He_2^* $[D^1\Sigma_u^+] \rightarrow [X^1\Sigma_g^+]$, where several vibrational levels of the radiating states contribute owing to the nature of the discharge formation of the He_2^* excimer. The spectroscopic data for both the $A^1\Sigma_u^+$ and $D^1\Sigma_u^+$ states of He_2 are accurately known from the work of Tanaka and Yoshino (Ref. 26) and Ginter (Ref. 27), leaving any uncertainty in the analysis of the Hopfield continuum solely in the repulsive character of the ground state potential of He_2. Since the equilibrium separation of the $A^1\Sigma_u^+$ state of He_2 (1.0406 Å) is close to the predicted value for the $^4\Pi_g$ state of He_2^- (1.064 Å), an analysis of the He_2 continuum intensity should be a sensitive test of the ground state potential in a region where discrepancy between theory and experiment has existed (Refs. 28-30).

The problem of calculating the bound-free emission spectra for a diatomic molecule has been previously treated in detail (Refs. 31 and 32). For an analysis of the spectral intensity distribution arising from the $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $D^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transitions in He_2, accurate numerical wavefunctions are required for both the bound vibronic levels of the upper radiating states and the continuum dissociating state. Such wavefunctions describing the nuclear motion of the system can be accurately generated, provided reliable potential energy functions are available for the electronic states involved in the transition.

For the bound $A^1\Sigma_u^+$ and $D^1\Sigma_u^+$ states, accurate RKR potential energy functions were generated based on the latest analysis of the spectroscopic constants given by Huber and Herzberg (Ref. 33). For the ground state potential of He_2, we have used three different functional forms. The first was the exponential fit derived by Foreman, et al. (Ref. 34), based on the their careful analysis of total scattering cross sections for He-He collisions. The second potential employed was the ab initio result recently reported by Ceperley and Partridge (Ref. 24), based on quantum Monte Carlo calculations at short internuclear separations ($0.5\ \text{Å} < R < 1.8\ \text{Å}$). This theoretically derived ground state potential is reported to be accurate to ± 0.05 eV at 0.5 Å and ± 0.01 eV at 1.8 Å. The third potential is that derived by Leonas and Sermyagin (Ref. 35) from differential elastic scattering cross section measurements. For internuclear separations greater than 1.8 Å, which affect the normalization of the continuum nuclear wavefunctions, we used an accurate ab initio potential that has been reported by Liu and McLean (Ref. 36). This latter potential was smoothly joined to the Foreman, Ceperley or Leonas potentials in the region of 1.6 - 1.8 Å.

We have evaluated the Einstein A-coefficients for He_2 corresponding to the $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $D^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transitions for the wavelength region ($60\ \text{nm} < \lambda < 110\ \text{nm}$), which covers the experimental He_2 continuum emission reported by Huffman, et al. (Ref. 25). Using the A-coefficients as a direct measure of the observed continuum intensity, we show in Fig. 3 a comparison of the data of Huffman, et al. (Ref. 25) with our calculated intensity profiles. Our calculated profiles are the result of a least-squares fit of the $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $D^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ A-coefficients assuming contributions from the first four vibrational levels of both transitions.

The calculated vibrational population of the $A^1\Sigma_u^+$ and $D^1\Sigma_u^+$ states are given in Table II for the three different ground state He_2 potentials that were studied. Overall, both the Foreman (Ref. 34) and Ceperley (Ref. 24) potentials exhibit a good fit to the data of Huffman, et al. (Ref. 25). The potential given by Foreman, et al. (Ref. 34) yields a statistically better fit with $\chi^2 = 0.002$ as compared to $\chi^2 = 0.01$ for the Ceperley and Partridge potential (Ref. 24). A significantly poorer fit with $\chi^2 = 0.47$ is found for the potential proposed by Leonas, et al. (Ref. 35). All other ground state potentials that we have explored, including those reported by Jordan and Amdur (Ref. 37), yield significantly poorer statistical fits. We have not analyzed the new potential of Nitz, et al. (Ref. 38), which, as mentioned above, is similar to that of Foreman, et al. (Ref. 34).

The best fit of our calculated intensities to the experimental data of the Hopfield helium continuum requires a repulsive energy of 3.4 ± 0.1 eV for the ground state of He_2 in the vicinity of 1.04 Å internuclear separation. This result is based on an average of the Foreman and Ceperley potentials since the experimental uncertainties in the measured intensity distributions prevent us from making a statistically favored choice.

The results of this study now cast doubt on our earlier parameterization (Ref. 23) of the calculated $^4\Pi_g$ state of He_2^-, which has been shown to be the upper state in the electron autodetachment experiments of Peterson, et al. (Refs. 20 and 21) and Kvale, et al. (Ref. 22). In our theoretical study, the calculated location of the metastable $^4\Pi_g$ state of He_2^- corresponded to a predicted electron affinity of 0.182 eV, in good agreement with the experimental estimate of 0.175 eV reported by Kvale, et al. (Ref. 22). This leaves only the equilibrium internuclear separation of He_2 as an adjustable parameter to reproduce the experimental vertical separation of 15.7 eV between the lowest vibrational level of the $^4\Pi_g$ state of He_2^- and the ground state He_2 potential. We find that our predicted equilibrium separation for He_2^- (1.064 Å) must be shifted outward by ~0.08 Å to obtain a satisfactory fit to the autodetachment data. If correct, this represents perhaps the first known instance where an ab initio CI result predicted too small a value for the equilibrium separation. Further theoretical studies of He_2 and He_2^- are now in progress using a complete basis set (CBS) extrapolation (Ref. 39).

H_3^-

There have been numerous thermochemical and kinetics studies of weakly bound ionic clusters during the past decade (Refs. 40 and 41). Of particular interest are the H_n^+ cation and H_n^- anion sequences since they represent examples of the chemistry of strong chemical bonding, in H_3^+, the simplest hydrogen bonded molecular ion, in H_5^+, and the simplest atomic anion, H^-. In addition, for the first few members of these sequences, detailed ab initio quantum mechanical calculations of their equilibrium bond lengths and vibrational spectra can be carried out.

Very recently, the possibility of forming large H_n^+ clusters ($n > 1000$), that could be kept for long periods of time in a Penning trap, has been discussed (Ref. 42). Such a system is a prototype for bulk antiproton or antihydrogen storage, with uses as high energy density material or as an energy source for advanced propulsion concepts. The mechanism for formation and storage of these large cluster ions can be understood only if the thermodynamics and kinetics of the cluster growth processes are identified and analyzed in detail. The purpose of our study was to examine the thermodynamic stability of the first few members of the hydrogen cation and anion cluster sequences since their stability is a requirement for defining a useful association pathway for the growth of large clusters.

Numerous experiments (Refs. 43 and 44) have measured the stability of the odd-membered hydrogen clusters that are formed by the association reaction:

$$H_n^+ + H_2 \rightarrow H_{n+2}^+ \quad ; \quad n = 3,5,7,... \qquad (10)$$

These clusters exhibit stabilization energies of approximately 3-6 kcal/mol, in good agreement with theoretical calculations (Refs. 45 and 46). Until recently, the even-membered hydrogen clusters had not been observed, with the exception of the suggestion of a stable H_4^+ ion formed by the attachment of a H atom to the H_3^+ ion (Ref. 47). A very recent study of the even-membered clusters (Ref. 48) suggests that the H_4^+ observation could be interpreted as H_2D^+. This study also indicates a high degree of stability for H_6^+.

In contrast, the negative hydrogen ion clusters have never been observed and a recent careful search for stable or metastable H_2^- and H_3^- produced negative results (Ref. 49). There have been several theoretical studies (Refs. 50 and 51) which support the existence of stable H_3^-, and higher clusters, but more accurate ab initio calculations (Ref. 52) shed doubt on this conclusion.

In order to establish the thermodynamic stability of these hydrogen cluster ions, ab initio calculations were carried out to determine their electronic structure and stable geometries. Several Gaussian basis sets, with increasing flexibility, were employed in these studies and levels of theory up to single and double configuration interaction expansions (CISD) were examined.

The results of these calculations are summarized in Table III, which includes the H^- and H_2 constituents as well as H_3^-. It is clear from Table III that the inclusion of the vibrational zero point energy is necessary to assess the stability of H_3^-. We find with every basis and level of theory that the H_3^- ion is not stable with respect to H^- and H_2. This conclusion is supported by the results of earlier theoretical work (Refs. 51 and 52), and by the recent experimental study of Bae, Coggiola, and Peterson (Ref. 49).

Our calculations appear to rule out the formation of hydrogen anion clusters though either of the association reactions:

$$H_n^- + H \rightarrow H_{n+1}^- \qquad (11)$$

$$H_n^- + H_2 \rightarrow H_{n+2}^- \qquad (12)$$

Although previous studies by Hirao and Yamabe (Ref. 52) indicate a weak stability for H_n^- clusters, up to n = 13, the non-existence of H_2^- and H_3^- precludes formation of higher clusters through either reaction (11) or (12). There remains the possibility (albeit remote) that association of H^- with a stable Rydberg state of H_3 could produce H_4^-. Further calculations are in progress to access this association pathway.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract during the past year have been prepared for publication in technical journals or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals and Books

1. "Spectral Intensity of the Hopfield Helium Continuum: An Analysis of the Ground State Potential for He_2," H. H. Michels, R. H. Hobbs and J. R. Peterson, Chemical Physics Letters, 134, 1987, pp. 571-574.

2. "The Electronic Structure and Stability of the H_3^- Anion," H. H. Michels and J. A. Montgomery, Jr., submitted to Chemical Physics Letter, 1987.

3. "Negative Ion Formation in Lithium Atom Collisions," H. H. Michels and J. A. Montgomery, Jr., to be published in the Proceedings of the Fourth International Symposium on the Production and Neutralization of Negative Ions and Beams (Brookhaven, 1986), ed. J. Alessi, 1987.

4. "Electronic Structure and Stability of Small Cation and Anion Hydrogen Clusters," J. A. Montgomery, Jr. and H. H. Michels, to be published in the Proceedings of the 1987 Cooling, Condensation and Storage of Hydrogen Cluster Ions Workshop, 1987.

B. Technical Paper and Lecture Presentations

1. "Negative Ion Formation in Lithium Rydberg Atom Collisions." Presented at the SDIO-Neutral Particle Beam Annual Program Review, Los Alamos National Laboratory, New Mexico, September 30 - October 2, 1986.

2. "The Hopfield Helium Continuum and He_2 ($X\ ^1\Sigma_g^+$) Potential." Presented at the Thirty-ninth Annual Gaseous Electronics Conference, Madison, Wisconsin, October 7-10, 1986.

3. "Assessment of the He_2^- Potential from the Autodetachment Spectrum." Presented at the Thirty-ninth Annual Gaseous Electronics Conference, Madison, Wisconsin, October 7-10, 1986.

4. "Negative Ion Formation in Lithium Atom Collisions." Presented at the Fourth International Symposium on the Production and Neutralization of Negative Ions and Beams, Brookhaven National Laboratory, Brookhaven, Long Island, New York, October 26-31, 1986.

5. "Electronic Structure and Stability of Small Cation and Anion Hydrogen Clusters." Presented at the 1987 Workshop on the Cooling, Condensation and Storage of Hydrogen Cluster Ions, Menlo Park, California, January 8-10, 1987.

6. "Application in Computational Chemistry: Theoretical Studies of Storable Highly Energetic Molecules." Presented at the Leermaker's Symposium, Wesleyan University, Middletown, Connecticut, May 8, 1987.

7. "Assessment of the He_2^- Potential from the Autodetachment Spectrum." Presented at the 18th Annual Meeting of the Division of Atomic, Molecular, and Optical Physics, Cambridge, MA, May 18-20, 1987.

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TABLE I

LITHIUM ATOM INTERACTIONS

(1) Resonant line excitation

$$Li[^2S(2s)] + h\nu \rightarrow Li^* [^2P(2p)](\text{saturated}) \quad \lambda_{2s-2p} = 671.0 \text{ nm}$$

(2) Rydberg state excitation

$$Li^*[^2P(2p)] + h\nu' \rightarrow Li^{**}[n>3] \text{ Rydberg state excitation}$$
$$\lambda_{2p-3s} = 812.8 \text{ nm}$$

(3) Rydberg-ground state reaction

$$Li[^2S(2s)] + Li^{**}[n>5] \rightarrow Li^+[^1S] + Li^-[^1S]$$

(4) Rydberg-excited ^2P state reaction

$$Li^*[^2P(2p)] + Li^{**}(n>3) \rightarrow Li^+[^1S] + Li^-[^1S]$$

(5) Rydberg-Rydberg excited state reaction

$$Li^{**}(n>3) + Li^{**}(n>3) \rightarrow Li^+[^1S] + Li^-[^1S]$$

(6) Associative ionization reaction (loss of Li^{**})

$$Li[^2S(2s)] + Li^{**}(n>4) \rightarrow Li_2^+ [X^2\Sigma_g^+] + e$$

(7) Dissociative ionization reaction (loss of Li^{**})

$$Li[^2S(2s)] + Li^{**}(n>4) \rightarrow Li_2^+[A^2\Sigma_u^+] + e \rightarrow Li^+[^1S] + Li[^2S] + e$$

TABLE II. Least-squares vibrational population analysis of the calculated Hopfield spectral distribution

Vibrational Level		Ground State He_2 Potential		
		Foreman	Ceperley	Leonas
$A\ ^1\Sigma_u^+$	v = 0	0.706	0.739	0.628
	v = 1	0.182	0.166	0.210
	v = 2	<0.002	0.	0.029
	v = 3	0.	0.	0.133
$D\ ^1\Sigma_u^+$	v = 0	0.069	0.070	0.
	v = 1	0.031	0.022	0.
	v = 2	0.009	0.003	0.
	v = 3	0.	0.	0.

TABLE III. Calculated Electronic Energies and Bond Lengths for H_3^-.

Level	R1	R2	H_3^- electronic energy	H_3^- zero-pt. energy	H^- electronic energy	H_2 electronic energy	H_2 zero-pt. energy	D_e	D_o
SCF/small	0.7340	3.2120	-1.621341	0.01250	-0.487640	-1.132408	0.01046	1.29	-0.75
MP2/small	0.7451	2.8977	-1.668994	0.01277	-0.507128	-1.160181	0.01030	1.68	-0.79
MP4/small	0.7482	2.9607	-1.683973	---	-0.514803	-1.167750	---	1.42	---
CISD/small	0.7480	3.0933	-1.684610	0.01227	-0.517166	-1.168354	0.01005	1.25	-0.97
SCF/large	0.7385	3.2020	-1.622682	0.01236	-0.487785	-1.133502	0.01046	1.40	-0.50
MP2/large	0.7436	2.8129	-1.679633	0.01258	-0.514177	-1.163478	0.01032	1.98	-0.28
MP4/large	0.7473	2.8950	-1.697126	---	-0.524534	-1.170956	---	1.64	---
CISD/large	0.7469	2.9583	-1.696702	0.01216	-0.526268	-1.171560	0.01005	1.58	-0.53
SCF/huge	0.7383	3.2015	-1.622877	0.01234	-0.487887	-1.133598	0.01044	1.39	-0.51
MP2/huge	0.7438	2.7649	-1.682973	0.01257	-0.515161	-1.165762	0.01031	2.05	-0.21
MP4/huge	0.7476	2.8695	-1.699551	---	-0.524995	-1.172764	---	1.79	---
CISD/huge	0.7476	2.8695	-1.698957		-0.526727	-1.173376	0.01005		

Bond lengths are in angstroms, energies in hartrees, except D_e and D_o, which are in millihartrees. R1 is the H - H equilibrium separation, and R2 is the H_2 - H^- equilibrium separation.

As CISD is not size-consistent, the CISD D_e values are found from $D_e(\text{CISD}) = E[R1=H_2(R_e), R2=15\text{Å}] - E[\text{eq}]$. $D_o = D_e - \text{ZPE}(H_3^-) + \text{ZPE}(H_2)$.

FIG.1

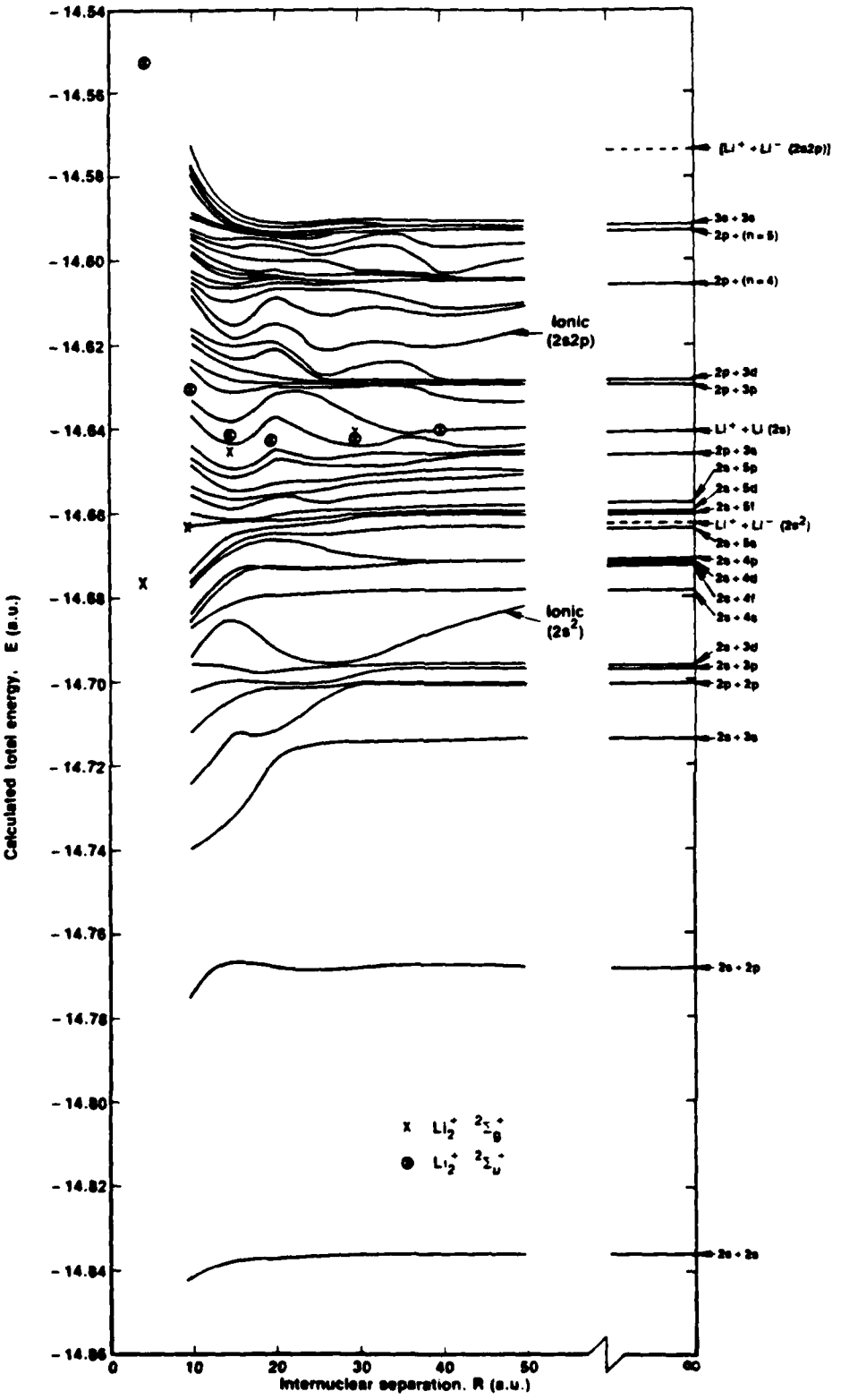

Fig. 1 Long-range behavior of excited $^1\Sigma_g^+$ states of Li_2.

FIG. 2

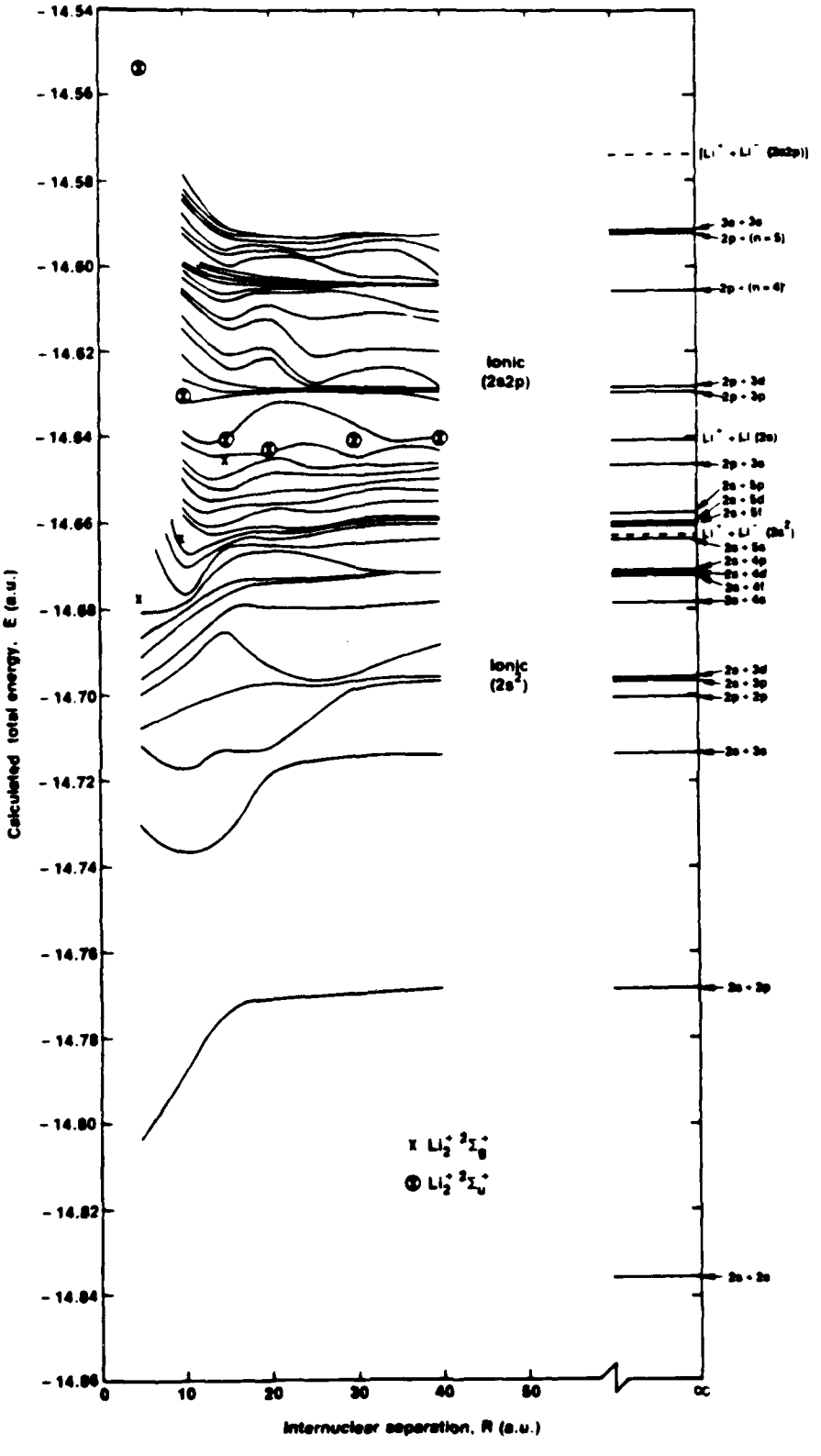

Fig. 2 Long-range behavior of excited $^1\Sigma_u^+$ states of Li_2.

FIG. 3

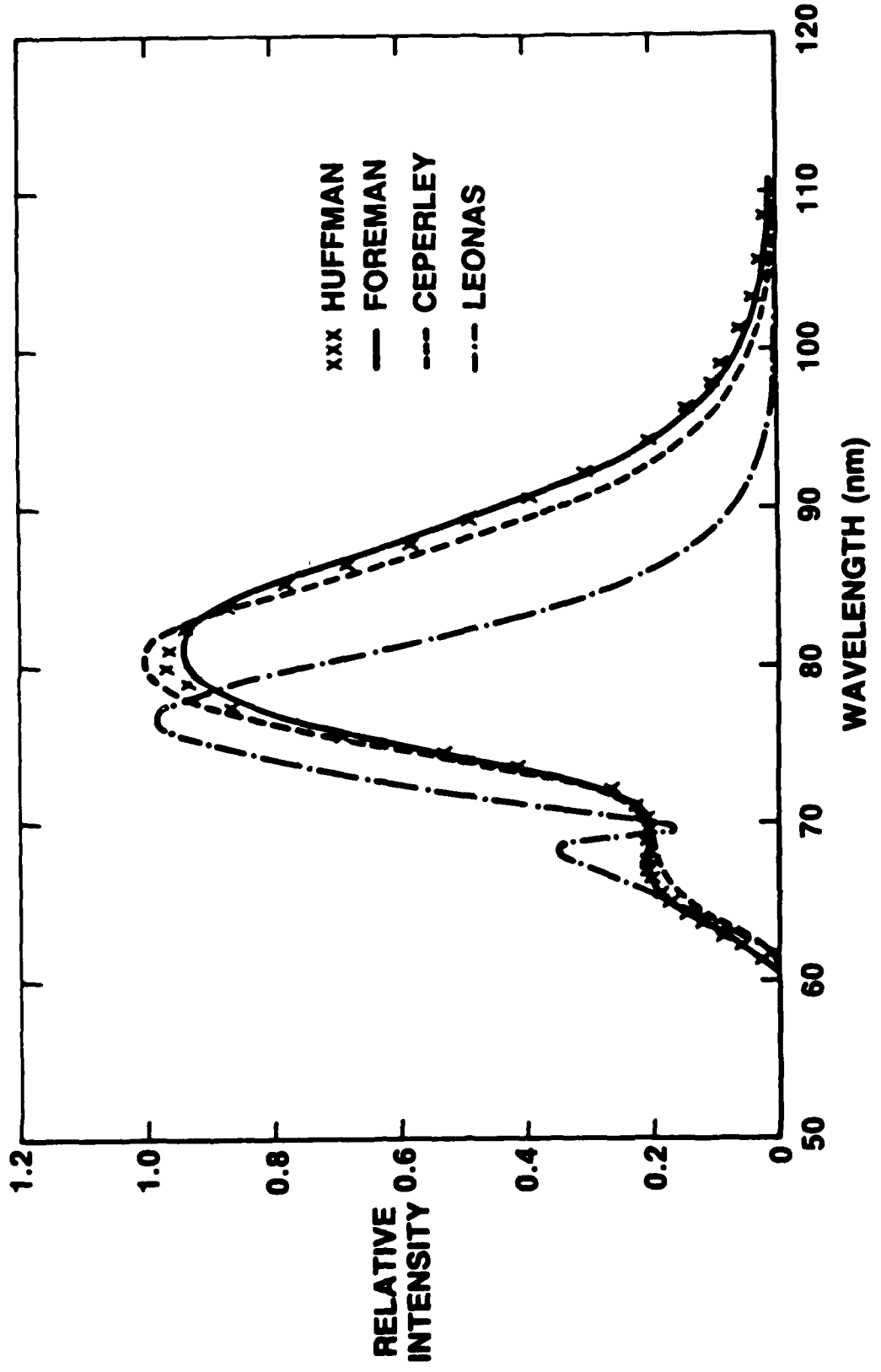

Fig. 3 Spectral intensity distribution of the Hopfield helium continuum. Comparison of experimental and calculated data.

APPENDIX A

Spectral Intensity of the Hopfield Helium Continuum: An Analysis of the Ground State Potential for He_2.*

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ABSTRACT

The intensity distribution of the Hopfield helium continuum has been analyzed using accurate numerical wavefunctions. The best comparison of our calculated intensity to the experimental continuum of Huffman, et al, yields a repulsive energy of 3.4 ± 0.1 eV for the ground $X\ ^1\Sigma_g^+$ state of He_2 in the vicinity of 1.04 Å internuclear separation.

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APPENDIX B

Negative Ion Formation in Lithium Atom Collisions*

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ABSTRACT

The formation of Li^- by dissociative attachment in e + Li_2 collisions is characterized by a large cross section for electron attachment to highly vibrationally excited Li_2 molecules. However, the electronic structure of the Li_2^- system dictates that low energy electrons ($\lesssim$ 0.2 eV) are needed to minimize loss processes. An alternate production route for Li^- is possible via direct ion-pair formation through collisions of highly excited (Rydberg) Li atoms. The mechanisms for ion-pair formation will be discussed in terms of the high-lying molecular Rydberg states of Li_2.

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To be published in the Proceedings of the Fourth International Symposium on the Production and Neutralization of Negative Ions and Beams (Brookhaven, 1986), ed. J. Alessi, 1987.

APPENDIX C

Electronic Structure and Stability of Small Cation and Anion Hydrogen Clusters

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ABSTRACT

Ab initio calculations of the electronic structure of H_n^- and H_n^+ clusters have been carried out using accurate Gaussian basis sets and with levels of theory up to fourth-order perturbation theory (MP4) and single and double excitation configuration interaction (CISD). The odd hydrogen cation addition sequence, $H_n^+ + H_2 \rightarrow H_{n+2}^+$, appears to be thermodynamically stable for large size cluster formation. The even H_6^+ cation also exhibits surprising stability in D_{2d} symmetry. In contrast, the hydrogen anion addition sequences, $H_n^- + H \rightarrow H_{n+1}^-$ and $H_n^- + H_2 \rightarrow H_{n+2}^-$, appear to be thermoneutral or unstable.

*Supported in part by AFOSR under Contract F49620-85-C-0095 and in part by AFRPL under Contract F04611-86-C-0071.

To be published in the Proceedings of the 1987 Cooling, Condensation and Storage of Hydrogen Cluster Ions Workshop, 1987.

APPENDIX D

The Electronic Structure and Stability of the H_3^- Anion*

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ABSTRACT

A systematic study of the electronic structure of the H_3^- anion has been carried out using both perturbation theory and configuration interaction. Counterpoise corrections are used to estimate the basis set superposition error in the computed dissociation energy. We find that H_3^- is not thermodynamically stable relative to $H^- + H_2$ upon consideration of the vibrational zero-point contribution to the dissociation energy. Isotopic analysis predicts weak stability for D_3^- and D_2-H^-.

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