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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

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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. A 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 cross sections and product branching ratios. 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.

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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

Final Technical Report

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

H. H. Michels
R. H. Hobbs
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FOREWORD

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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. A 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 cross sections and product branching ratios. 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.

In addition to studies of thermodynamically stable negative ions, there has been recent interest in the metastable or resonant states in these systems. Compound states of atomic negative ions have been a subject of interest in atomic physics for over forty years. The first observation of a compound negative ion state was the detection of long-lived He^- ions in a mass spectrometer by Hiby (Ref. 10) in 1939. Holoien and Midtdal (Ref. 11) theoretically showed that $He^-(1s2s2p)\,^4P°$ was stable relative to $He(1s2s)\,^3S$ and thereby offered an explanation of Hiby's observation of long-lived He^- ions. In 1963, Schulz (Ref. 12) reported evidence for a scattering resonance in He at ~ 19.3 eV which was attributed to $He^-(1s2s^2)\,^2S$. This was the first experimental observation of an electron scattering resonance in an atomic system. Since that time, compound states of atoms have been seen in many elastic and inelastic channels in electron-atom scattering (Ref. 13), in ion-atom scattering cross sections (Ref. 14), in laser photodetachment cross sections (Ref. 15), and in dissociative electron attachment studies (Ref. 16, 17). Compound states of doubly charged negative ions have also been detected (Ref. 18).

The spectroscopy of metastable negative ions has been the subject of several experimental and theoretical investigations (Refs. 19-23). Although much attention has been given to the problem of atomic anion formation, more recent studies have examined diatomic anions, especially those of the lighter elements (Refs. 24-27). In a recent study (Ref. 25), the electronic structure of the newly discovered (Ref. 24) metastable He_2^- ion was examined using CI wavefunctions. This study indicated that only the $^4\Pi_g$ state of He_2^- was metastable relative to $He_2\ [a\,^3\Sigma_u^+]$ + e. More recently, by double charge exchange of He_2^+ ions in lithium vapor, Kvale, et al (Ref. 28) have examined the autodetachment spectrum for $^4He_2^-$ and $^3He_2^-$ ions and have observed two autodetachment peaks. The first (low-energy) peak was identified as autodetachment from the first vibrational level of $He_2^-[^4\Pi_g]$ to $He_2\ [a\,^3\Sigma_u^+]$ + e and the second as autodetachment to the $He_2\ [X\,\Sigma_g^+]$ + e repulsive continuum, similar to that observed by Bae, et al (Ref. 24).

The coupling of this experimental data to theoretical studies of the electronic structure of the He_2^- anion has yielded a good understanding of the spectroscopy of this system. Because of the difficulties in conducting experiments to measure kinetic processes in these metastable and compound ion systems, the development of sound theoretical methods for calculating the positions and widths from analysis of their electronic structure appears desirable. In this direction, we have undertaken a series of calculations for the $He/He^-/He_2^-$ and $Li/Li^-/Li_2^-$ systems in an effort to understand their resonance structure.

The calculations for the He^-/He_2^- system were carried out to gain a better understanding of the experiments of Bae, Coggiola and Peterson (Ref. 24), who were the first to report observations of the metastable He_2^- ion, and the more recent autodetachment experiments reported by Kvale, et al (Ref. 28) for this system. Our results show that only the lowest $^4\Pi_g$ of He_2^- is metastable relative to He_2 $[a^3\Sigma_u^+]$ + e and that the lowest lying $^4\Pi_u$, $^4\Sigma_g^+$ and $^4\Sigma_u^+$ states are all autoionizing. However since the $^4\Pi_{5/2g}$ spin-orbit state has a long (~ 400 μsec) lifetime, it should be possible to laser induce transitions from this level to the upper resonant negative ion states. Such an experiment, using a tunable laser, is now under development by Compton and co-workers at Oak Ridge National Laboratory. A complementary experiment would involve the possible production of thermodynamically stable negative ions by stimulated radiative attachment of electrons to neutral atoms or molecules. An alkali system would appear to be a good choice for such studies since both Li^- and Li_2^- are stable and exhibit an electronic structure which includes resonances that could be reached by conventional tunable lasers.

In a related area, there is now considerable interest in understanding ion-pair production in low energy collisions of Rydberg atoms. Ciocca, et al (Ref. 29) and Cheret and Barbier (Ref. 30) have reported efficient ion-pair formation in laser excited alkali systems. In contrast, McGeoch and Schlier (Ref. 31) find no ion-pair production, as a primary process, in thermal energy collisions between lithium Rydberg atoms. Conventional curve-crossing mechanisms are not capable of explaining these results and new theoretical developments are needed. An experiment to study ion-pair formation in the reaction of $He(^3S)$ atoms and alkali Rydberg atoms has been suggested by Peterson (SRI). This system would be an ideal candidate for a collaborative experimental and theoretical study of the mechanism of ion-pair production.

The goals of this research program are to identify the electronic and resonance structure of atomic and molecular positive and negative ions, to study the effects of high laser fields on stimulated autodetachment and radiative electron attachment in such systems, and to carry out theoretical studies of atomic Rydberg state interactions leading to ion-pair production. This theoretical research effort should complement the experimental studies of ion formation processes that are being carried out by Peterson and co-workers at (SRI), by McGeoch (AVCO) and by several European research groups.

RESEARCH PROGRESS

During the course of this contract, 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 undertaken 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. Six technical papers and nineteen presentations have resulted from the research efforts under the present contract.

Li^-

The negative ions of light atoms are currently being studied for their possible application in gaseous discharges, fusion plasmas and gas lasers (Ref. 32). One source for the volume production of atomic anions is the process of dissociative electron attachment to molecules (Ref. 33). This process has been studied experimentally for low energy electron-hydrogen molecule collisions by Allen and Wong (Ref. 34). A parallel theoretical study has been reported by Wadehra and Bardsley (Refs. 8 and 9). More recently, McGeoch and Schlier (Ref. 35) 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. 36) for $e + H_2$ collisions and by Wadehra and Michels (Ref. 37) for the $e + Li_2$ system.

During the past several years, we have undertaken a series of calculations of Li_2^- in order to assess the energetics of this anion. McGeoch (Ref. 38) has suggested that a Li^- source should be possible through a series of reactions similar to those found for H_2. The initial step involves the formation of the Li_2 dimer and excitation to low-lying excited states via fast electron collisions or photon pumping. The latter process is that currently being investigated by McGeoch. The reactions are:

$$e\ (\text{fast}) + Li_2\ [X\ {}^1\Sigma_g^+] \rightarrow Li_2^*\ [A\ {}^1\Sigma_u^+,\ B\ {}^1\Pi_u] + e \qquad (1)$$

or

$$\mathrm{Li}_2\ [X\ {}^1\Sigma_g^+] + h\nu \rightarrow \mathrm{Li}_2^*\ [A\ {}^1\Sigma_u^+,\ B\ {}^1\Pi_u] \qquad (2)$$

The A $^1\Sigma_u^+$ and B $^1\Pi_u$ states both exhibit fast radiative decay back to the ground X $^1\Sigma_g^+$ state but the Franck-Condon transitions favor a shift in the population of Li_2 to higher vibrational states:

$$\mathrm{Li}_2^*\ [A\ {}^1\Sigma_u^+,\ B\ {}^1\Pi_u] \rightarrow \mathrm{Li}_2^{\ddagger}\ [X\ {}^1\Sigma_g^+\ (v > 5)] + h\nu \qquad (3)$$

Our present understanding of the energetics of the $\mathrm{Li}_2/\mathrm{Li}_2^-$ system is shown in Figs. 1 and 2. The dashed curves in Fig. 1 were estimates based on H_2^- and the known molecular orbital structure of Li_2^-. Our most recent *ab initio* calculations, which indicate that the lowest $^2\Sigma_g^+$ state of Li_2^-, is slightly attractive all the way into the curve-crossing with the ground state of Li_2, are shown in Fig. 2. This suggests that electron dissociative-attachment is possible for this system for vibrationally excited Li_2 molecules:

$$e\ (\mathrm{slow}) + \mathrm{Li}_2^{\ddagger}\ [X\ {}^1\Sigma_g^+] \rightarrow \mathrm{Li}\ [{}^2S] + \mathrm{Li}^-[{}^1S] \qquad (4)$$

The final potential energy curves governing reaction (4) are shown in Fig. 2. There is still considerable uncertainty in the location of the excited reasonant states of Li_2^-, especially in the auto-ionizing region above Li_2 + e. The ground $[X\ {}^2\Sigma_u^+]$ state is well characterized theoretically (Refs. 39 and 40) but little is known about the location of the low-lying excited electronic states which connect to Li $[{}^2P]$ + $\mathrm{Li}^-[{}^1S]$. In addition, by analogy with H_2^-, low-lying electronic states of Li_2^- with MO configuration $(1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g 1\pi_u^2)[{}^{2,4}\Sigma_g^+]$ may, in fact, actually lie lower than some of the states shown in Fig. 1. Such states dissociate to very high atom-ion limits and their general characteristics are uncertain. The curves shown in Fig. 2 represent our best estimates at the present time but more definitive calculations are required to define the curve-crossing regions for dissociative-attachment.

The lowest $^2\Sigma_g^+$ state of Li_2^- has the molecular orbital configuration

$[1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_u^2\ 2\sigma_g]$ for large separations. At short internuclear separations, this state mixes with a second bound $^2\Sigma_g^+$ state arising from $Li[^2P] + Li^-[^1S]$ with a molecular orbital configuration $[1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 3\sigma_g]$. This mixing at intermediate separations results in a lowering of the interaction potential for the lowest $^2\Sigma_g^+$ state. Our preliminary calculations, as shown in Fig. 1, indicate that this mixing is stronger than expected from MO considerations and lowers the $^2\Sigma_g^+$ potential curve into a feasible region for dissociative-attachment to occur.

The resonance structure associated with electron scattering by the hydrogen molecule has been the subject of many theoretical and experimental studies (Refs. 41-43). In contrast, electron scattering by Li_2 has received relatively little attention. Miller, et al. (Ref. 44) have measured total cross sections for e + Li_2 scattering in the 0.5-10.0 eV region and find a very large (~ 500 Å^2) and rising total cross section for the low-energy region. These results suggest that some sort of shape resonance may be found in this system corresponding to a low-lying state of Li_2^-. Such resonant states have been observed in electron impact excitation of Na_2 (Ref. 45).

In order to clarify the electronic structure of the Li_2 anion, a series of detailed ab initio calculations of the parent $^1\Sigma_g^+$ state of Li_2 and of several possible symmetries of the anion were undertaken. The calculational framework that was chosen was a configuration-interaction (CI) expansion built from orthonormal Slater-type orbitals (STO's). An extended (14σ, 6π, 2δ) basis was optimized using several methods of approach. Complete orbital optimization was possible only for Li_2 and the ground X $^2\Sigma_u^+$ state of Li_2^- since the excited anion states are either autodetaching at some critical internuclear separation or are pure resonant states. The lowest $^2\Sigma_g^+$ state of Li_2^-, which is the principle channel for DA of e + Li_2, is variationally stable for large internuclear separations, and a smooth extrapolation of optimized orbital exponents for this state was carried out into the autodetaching region. The purely resonant states of Li^- and Li_2^- were treated using a modified nuclear charge hamiltonian, similar to that described by Nestmann, et al. (Ref. 46). In this method the resonant states are variationally stabilized by an increased nuclear charge and an analytic extrapolation is carried out to determine the real part of the expectation value of the unperturbed hamiltonian.

Our calculated electron affinity for Li_2, derived from our location of the X $^2\Sigma_u^+$ state of Li_2^-, is 0.42 eV, in good agreement with previous theoretical studies. The A $^2\Sigma_g^+$ state of Li_2^- exhibits a complex potential energy for inter-nuclear separations smaller than 3.45 Å, where a crossing with the X $^1\Sigma_g^+$ state of Li_2 is found. This resonant state of Li_2^- is mainly of the Feshbach type and has a long lifetime against autoionization. We find a small width for decay to the ground state of Li_2, $\Gamma(R) \approx 0.01\ k(R)$. Of special interest is the low-lying $^2\Pi_u$ resonant state which lies approximately 150 meV above the ground state of Li_2. This anion state has a dominant MO configuration of $(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 1\pi_u)$, indicating a relatively large capture width for low-energy electron scattering, and is probably responsible for the large scattering cross sections observed by Miller, et al. (Ref. 44) for low collisional energies. The character of this $^2\Pi_u$ state is similar to the $^2\Pi_g$ resonant state of N_2^- in that the anion state lies lower than the corresponding neutral parent for a wide region of internuclear separations ($3.5 \lesssim R \lesssim 9.0$ Å).

Further theoretical studies of these interaction potentials are required to define the overall reactive kinetics leading to Li^- production. A study parallel to that reported by Hiskes (Ref. 36) for H_2 has been carried out to estimate the overall cross sections for production of vibrationally excited Li_2. In this study, cross-sections for vibrational excitation (VE) of the $X^1\Sigma_g^+$ state of Li_2 via formation of the excited A $^1\Sigma_u^+$ or B $^1\Pi_u$ electronic states were reported. For vibrational excitation through the A $^1\Sigma_u^+$ state, the cross sections are nearly constant for forming $3 \lesssim v'' \lesssim 9$ via electron collisional excitation. For photon pumping ($670\ \text{nm} \lesssim \lambda \lesssim 700\ \text{nm}$) of the A $^1\Sigma_u^+$ state, levels $v'' \lesssim 9$ are predominantly formed. Vibrational excitation via the B $^1\Pi_u$ state has a lower probability. In addition, theoretical studies are in progress to estimate the low-energy electron dissociative attachment cross-section for $e + Li_2^\ddagger \rightarrow Li + Li^-$. Our initial results are shown in Fig. 3 which indicate an attachment cross section $> 10^{-16}$ cm^2 for vibrationally excited Li_2. The enhancement in the attachment cross section with vibrational energy is similar to that found for the $e + H_2^\ddagger$ attachment.

An alternative mechanism for negative ion formation was suggested by Lee and Mahan (Ref. 47), who proposed that ion-pair formation:

$$X^* + X \rightarrow X^+ + X^- \tag{5}$$

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

$$X^* + X \rightarrow X_2^+ + e. \tag{6}$$

The alkali metals, including lithium, are therefore good candidates for such a study of ion-pair formation. Ciocca, et al. (Ref. 29) have recently reported on the formation of Na^- ions in highly excited (n=7-40) Rydberg atom collisions. In a similar experiement, Cheret and Barbier (Ref. 30) have reported efficient ion-pair formation in collisions between ground state and Rydberg Rb atoms formed by laser excitation. A curve crossing mechanism was suggested to explain these results.

More recently, McGeoch and Schlier (Ref. 31) have looked for ion-pair formation in collisions between two Rydberg Li atoms (n = 5-9). The most prominent processed observed was associative ionization:

$$Li^{**} + Li^{**} \rightarrow Li_2^{+} + e \tag{7}$$

rather than ion-pair production, which was not observable at a rate ~ 300 times less than associative ionization. McGeoch and Schlier followed the time dependence for the formation of Li^- and find that it follows the production route by associative ionization of e + Li_2. These results, for the first time, rule out direct ion-pair formation as an important process, at least in Li atom collisions, and suggest that the earlier work of Ciocca, et al. (Ref. 29) and Cheret and Barbier (Ref. 30) may be subject to a different interpretation.

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

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-range, calculations were performed over a range of internuclear separations from 5 to 50 bohrs.

The results of our theoretical calculations are shown in Fig. 4 and Fig. 5 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. 4 and Fig. 5, 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 <10Å. Ion-pair formation may occur for long-range interactions of the type

$$Li\ [^2S(2s)] + Li^{**}[^2S(n=5)] \rightarrow Li^+\ [^1S] + Li^-[^1S] \qquad (8)$$

but clearly there are few effective curve crossing channels leading to $Li^+ + Li^-$. The curve crossing mechanism suggested by Ciocca, et al. (Ref. 29), 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. 29) for alkali negative ion formation would involve excited state negative ion formation via

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

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. 48) relative to radiative stabilization and higher autoionizing states should exhibit even shorter lifetimes.

As mentioned above, McGeoch and Schlier (Ref. 31) have recently found that the most prominent process occurring in lithium Rydberg atom collisions is associative ionization:

$$Li^{**} + Li^{**} \rightarrow Li_2^+ + e \qquad (10)$$

This reaction has excess exothermicity beyond the dissociation energy of Li_2^+. Some mechanism for disposing this excess energy must be developed, either by radiation or by internal modes. It is very unlikely that the excess energy is released as kinetic energy since very hot electrons would be formed which would result in secondary ionization processes. An alternate possibility is that an excited metastable state of Li_2^+ is formed with sufficient lifetime to be detected and mass analyzed. Detailed studies of such mechanisms are proposed as part of a new research program.

He_2^-

In addition to our studies of the Li_2/Li_2^- system, calculations were carried out on the He_2^- metastable anion. The existence of metastable negative ions has been the subject of several recent experimental and theoretical investigations

(Refs. 49-51). Although much attention has been given to the problem of atomic anion formation, more recent studies have examined diatomic anions, especially those of the lighter elements (Refs. 52-55). In a recent study (Ref. 53), we have examined the electronic structure of the newly discovered (Ref. 52) metastable He_2^- ion using CI wavefunctions. This study indicated that only the $^4\Pi_g$ state of He_2^- was metastable relative to He_2 $[a\ ^3\Sigma_u^+]$ + e, with an indicated electron affinity of 0.233 eV and a vibrational frequency (ω_e) of 1783.0 cm^{-1}. A low-lying $^4\Sigma_g^+$ resonance state of He_2^- was also found but it was not possible, within the error of the calculations, to ascertain whether or not this state might also be metastable.

More recently, by double charge exchange of He_2^+ ions in lithium vapor, Kvale, et al. (Ref. 56) have examined the autodetachment spectrum for $^4He_2^-$ and $^3He_2^-$ ions and have observed two autodetachment peaks. The first (low-energy) peak was identified as autodetachment from the first vibrational level of He_2^- $[^4\Pi_g]$ to He_2 $[a^3\Sigma_u^+]$ + e and the second as autodetachment to the He_2 $[^1\Sigma_g^+]$ + e repulsive continuum, similar to that observed by Bae, et al. (Ref. 52). This experiment by Kvale, et al. suggested that either the low-energy autodetachment was from the first excited vibrational level of the $^4\Pi_g$ state as postulated, or from a second metastable electronic state (possibly $^4\Sigma_g^+$) lying in this same energy range. In either case, our earlier results, which indicated that the first excited vibrational level of the $^4\Pi_g$ state was non-autodetaching and that the lowest $^4\Sigma_g^+$ state was purely resonant in character, were in disagreement with these experimental observations.

In order to clarify the spectroscopy of He_2^-, a re-examination of both the a $^3\Sigma_u^+$ state of He_2 and the low-lying symmetries of He_2^- was carried out. Our previous studies of this system were based on CI wavefunctions constructed from a (14σ, 6π, 2δ) STO-MO basis. The atomic orbital parameters were taken from optimized calculations for the $^4P°$ state of He^-. In these new calculations, a complete non-linear orbital optimization was carried out at the equilibrium internuclear separations. This non-linear optimization was performed separately for both the neutral and negative ion states in an attempt to quantitatively characterize the small energy shifts arising from polarization effects in the formation of the anion. This approach permitted examination of smaller changes in the charge distribution, upon anion formation, than would have been possible by fixed basis set expansions with exponents chosen to insure freedom from linear dependency problems.

For studies of the lowest $^4\Sigma_g^+$ state, a modified nuclear charge hamiltonian was employed similar to the method described by Nestmann and Peyerimhoff (Ref. 57). Stabilization of this state (relative to He_2 $[a\ ^3\Sigma_u^+]$ + e) was realized by increasing the nuclear charge by ~ 0.1%. A careful study of the non-linear parameters as a function of increased nuclear charge clearly indicated that the lowest $^4\Sigma_g^+$ state is purely resonant in character and that this state is autoionizing relative to He_2 $[a^3\Sigma_u^+]$ + e. We find that this lowest $^4\Sigma_g^+$ state lies 0.074 eV above He_2 $[a^3\Sigma_u^+]$ and has a dominant MO structure of $(1s\sigma_g^2 1s\sigma_u\ 2s\sigma_u)$. A preliminary analysis of the complex part of the potential indicates that this state has a large width for decay to the He_2 $[a\ ^3\Sigma_u^+]$ + e continuum and is unlikely to be observable on the time scale of the detection apparatus in the double charge exchange experiments. Further calculations on the $^4\Sigma_g^+$ and other low lying resonances in He_2^- are required to define the real and complex behavior of these states.

The lowest $^4\Pi_g$ state of He_2^- was found to be variationally stable for all internuclear separations that were examined. Our final potential curve for this state is displayed in Fig. 6. We find an electron affinity of 0.182 eV for the $^4\Pi_g$ state of He_2^-, a value ~ 50 meV smaller than in our previous calculations which employed an STO basis that was optimized for the $^4P°$ (1s2s2p) state of He^-. We attribute this smaller calculated electron affinity to our observation that the use of optimized basis functions resulted in a larger improvement in the calculated energy of He_2 $[a\ ^3\Sigma_u^+]$ than to the corresponding $He_2^-[^4\Pi_g]$ anion. Our predicted electron affinity, coupled with a calculated vibrational spacing of 1702 cm^{-1}, now indicates that the first excited vibrational level of the $^4\Pi_g$ state of He_2^- is autoionizing and is probably responsible for the observed low energy peak in the electron detachment studies of Kvale, et al. (Ref. 56). Their experimental estimate (0.175 eV) of the electron affinity of the $^4\Pi_g$ state of He_2^-, relative to He_2 $[a\ ^3\Sigma_u^+]$, and our calculated value (0.182 eV) are within the uncertainties of both the experimental measurements and calculations.

In a related study at SRI, Bae, Coggiola and Peterson (Ref. 52) have measured the energy spectrum resulting from electron autodetachment from the lowest $^4\Pi_g$ state of He_2^-. This continuum spectrum exhibits a single peak at 15.7 eV resulting from a vertical transition from He_2^- to the repulsive ground state of He_2. Both the shape and position of this autodetachment spectrum were verified in later studies reported by Kvale, et al. (Ref. 56). However, neither the shape or position of the experimental spectrum seemed to fit predictions based on our He_2^- calculations and the generally accepted ground state He_2 potential reported by Foreman, et al. (Ref. 58).

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. 60). 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. 61) and Ginter (Ref. 62), 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. 63-65).

The problem of calculating the bound-free emission spectra for a diatomic molecule has been previously treated in detail (Refs. 66 and 67). 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. 68). 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. 69), 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. 70), based on quantum Monte Carlo calculations at short internuclear separations (0.5 Å $< R <$ 1.8 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. 71) 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. 72). 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 nm $< \lambda <$ 110 nm), which covers the experimental He_2 continuum emission reported by Huffman, et al. (Ref. 60). Using the A-coefficients as a direct measure of the observed continuum intensity, we show in Fig. 7 a comparison of the data of Huffman, et al. (Ref. 60) 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. 69) and Ceperley (Ref. 70) potentials exhibit a good fit to the data of Huffman, et al. (Ref. 60). The potential given by Foreman, et al. (Ref. 69) yields a statistically better fit with $\chi^2 = 0.002$ as compared to $\chi^2 = 0.01$ for the Ceperley and Partridge potential (Ref. 70). A significantly poorer fit with $\chi^2 = 0.47$ is found for the potential proposed by Leonas, et al. (Ref. 71). All other ground state potentials that we have explored, including those reported by Jordan and Amdur (Ref. 73), yield significantly poorer statistical fits. We have not analyzed the new potential of Nitz, et al. (Ref. 74), which, as mentioned above, is similar to that of Foreman, et al. (Ref. 69).

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.

On the basis of this study of the He_2 continuum spectra reported by Huffman et al. (Ref. 60), Michels and Peterson concluded that the Foreman ground state potential for He_2 was essentially correct. An exhaustive study by Michels and Peterson (Ref. 75) of possible shapes of the potential energy curves for He_2^- resulted in the conclusion that the He_2^- beam must have been rotationally hot in the SRI experiments. A suitable fit to the experimental spectrum was finally obtained by assuming a rotational temperature of ~ 15000 K, with significant contributions from higher vibrational levels of He_2^-. This collaborative experimental and theoretical effort solved a formidable problem but introduced new questions concerning our understanding of electron autodetachment processes. Our conclusion that vibrational autodetachment must be slow in the He_2^- system runs counter to previous ideas and suggests that several electron coupling mechanisms must be reexamined theoretically.

H_3^-

There have been numerous thermochemical and kinetics studies of weakly bound ionic clusters during the past decade (Refs. 76 and 77). 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. 78). 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. 79 and 80) have measured the stability of the odd-membered hydrogen clusters that are formed by the association reaction:

$$H_n^+ + H_2 \rightarrow H_{n+2}^+ \quad ; \quad n = 3,5,7,... \qquad (11)$$

These clusters exhibit stabilization energies of approximately 3-6 kcal/mol, in good agreement with theoretical calculations (Refs. 81 and 82). 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. 83). A very recent study of the even-membered clusters (Ref. 84) 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. 85). There have been several theoretical studies (Refs. 86 and 87) which support the existence of stable H_3^-, and higher clusters, but more accurate ab initio calculations (Ref. 88) 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. 87 and 88), and by the recent experimental study of Bae, Coggiola, and Peterson (Ref. 85).

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

$$H_n^- + H \rightarrow H_{n+1}^- \tag{12}$$

$$H_n^- + H_2 \rightarrow H_{n+2}^- \tag{13}$$

Although previous studies by Hirao and Yamabe (Ref. 88) 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 (12) or (13). 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 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. "Electronic Structure of He_2^-." H. H. Michels, Chemical Physics Letters, 126, 1986, pp. 537-540.

2. "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.

3. "The Electronic Structure and Stability of the H_3^- Anion," H. H. Michels and J. A. Montgomery, Jr., Chemical Physics Letters, 139, 1987, pp. 535-539.

4. "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.

5. "Electronic Structure and Stability of Small Cation and Anion Hydrogen Clusters," J. A. Montgomery, Jr. and H. H. Michels, Published in the Proceedings of the 1987 Cooling, Condensation and Storage of Hydrogen Cluster Ions Workshop, J. T. Bahns, ed., 1988, p. 83.

6. He_2^- $[{}^4\Pi_g] \rightarrow He_2$ $[X^1\Sigma_g^+]$ Autodetachment Energy Spectrum: "Assessment of the He_2^- and He_2 Ground State Potentials," Y. K. Bae, J. R. Peterson, H. H. Michels and R. H. Hobbs, Physical Review A, 37, 1988, pp. 2778-2784.

B. Technical Paper and Lecture Presentations

1. "Low-Lying Resonances in Electron-Lithium Molecule Scattering." Presented at XIV ICPEAC Collisions Conference, Palo Alto, California, July 23-27, 1985.

2. "Analysis of Quintet He_2^* Formation Through Collisions of Triplet Metastable Helium Atoms." Presented at Gaseous Electronics Conference, Monterrey, California, October 14-17, 1985.

3. "Overview of Dissociative Attachment Reactions to form Li^-." Presented at Neutral Particle Beam Technical Interchange Meeting, Los Alamos, New Mexico, February 4-7, 1986.

4. "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.

5. "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.

6. "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.

7. "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.

8. "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.

9. "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.

10. "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.

11. "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, Stanford Research Institute, Menlo Park, California, January 8-10, 1987.

12. "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, Massachusetts, May 18-20, 1987.

13. "Ion-Molecule Association Reactions for H_n^+ and H_n^- Clusters." Presented at the XV ICPEAC, Brighton, England, July 21-25, 1987.

14. "Ab Initio Studies of the Stability of H_3^-." Presented at the National American Chemical Society Meeting, New Orleans, Louisiana, August 30 - September 4, 1987.

15. "Ion-Pair Production in Excited Rydberg Atom Collisions." Presented at the Neutral Particle Beam Program Annual Review, Los Alamos, New Mexico, October 6-8, 1987.

16. "Electronic Structure and Photabsorption Characteristics of Ar_3^+." Presented at the 40th Annual Gaseous Electronics Conference, Atlanta, Georgia, October 13-16, 1987.

17. "Electronic Structure and Stability of the Ar_3^+ Cluster Ion." Presented at the 1988 Sanibel Symposia, Florida, March 12-19, 1988.

18. "Ionization and Electron Attachment Processes for Lithium Rydberg Atom Collisions." Presented at the 19th Annual Meeting of the Division of Atomic, Molecular and Optical Physics of the American Physical Society, Baltimore, Maryland, April 18-20, 1988.

19. "Energetics of Dissociative Recombination of $e + HeH^+$." Presented at the International Symposium on Dissociaative Recombination, Lake Louise, Alberta, Canada, May 28, 1988.

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TABLE I

LOW-LYING MOLECULAR STATES OF Li_2 AND THEIR DISSOCIATION LIMITS

Separated atoms	$E(cm^{-1})$*	Molecular states
Li + Li		
$^2S_g(2s) + {}^2S_g(2s)$	0.0	$^1\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$
$^2S_g(2s) + {}^2P_u(2p)$	14903.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$ $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$
$^2S_g(2s) + {}^2S_g(3s)$	27206.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$
$^2P_u(2p) + {}^2P_u(2p)$	29807.0	$^1\Sigma_g^+(2)$, $^1\Sigma_u^-(1)$, $^3\Sigma_u^+(2)$, $^3\Sigma_g^-(1)$ $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$ $^1\Delta_g(1)$, $^3\Delta_u(1)$,
$^2S_g(2s) + {}^2P_u(3p)$	30925.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$
$^2S_g(2s) + {}^2D_g(3d)$	31283.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$, $^1\Delta_g(1)$, $^1\Delta_u(1)$, $^3\Delta_g(1)$, $^3\Delta_u(1)$
$Li_2^+[{}^2\Sigma_u^+]$ + e	33200.0	
$^2S_g(2s) + {}^2S_g(4s)$	35012.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$
$^2S_g(2s) + {}^2P_u(4p)$	36469.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$

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* C. E. Moore, Atomic Energy Levels, 1, 9 (1949).

TABLE I (Continued)

$^2S_g(2s) + {}^2D_g(4d)$	36623.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$, $^1\Delta_g(1)$, $^1\Delta_u(1)$, $^3\Delta_g(1)$, $^3\Delta_u(1)$
$^2S_g(2s) + {}^2F_u(4f)$	36630.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$, $^1\Delta_g(1)$, $^1\Delta_u(1)$, $^3\Delta_g(1)$, $^3\Delta_u(1)$, $^1\Phi_g(1)$, $^1\Phi_u(1)$, $^3\Phi_g(1)$, $^3\Phi_u(1)$
$^2S_g(2s) + {}^2S_g(5s)$	38299.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$
$Li^+ [{}^1S_g(1s^2)]$ + $Li^- [{}^1S_g(2s^2)]$	38474.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$
$^2S_g(2s) + {}^2P_u(5p)$	39015.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$
$^2S_g(2s) + {}^2D_g(5d)$	39094.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$, $^1\Delta_g(1)$, $^1\Delta_u(1)$, $^3\Delta_g(1)$, $^3\Delta_u(1)$
$^2S_g(2s) + {}^2F_u(5f)$	39104.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$, $^1\Delta_g(1)$, $^1\Delta_u(1)$, $^3\Delta_g(1)$, $^3\Delta_u(1)$, $^1\Phi_g(1)$, $^1\Phi_u(1)$, $^3\Phi_g(1)$, $^3\Phi_u(1)$
$^2S_g(2s)$ + Doublets $(5<n\lesssim 9)$	39987.0 → 42003.0	Singlet, triplet Σ, Π, Δ, (g,u)

TABLE I (Concluded)

$^2P_u(2p) + {}^2S_g(3s)$	42110.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^3\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$, $^3\Pi_g(1)$, $^3\Pi_u(1)$
$^2S_g(2s)$ + Doublet ($9 \leq n \leq \infty$)	42118.0 →	Singlet, triplet Σ, Π, Δ (g,u)
$Li^+ [{}^1S_g(1s^2)]$ + $Li [{}^2S_g(2s)]$	43482.0	$^2\Sigma_g^+(1)$, $^2\Sigma_u^+(1)$
$^2P_u(2p) + {}^2P_u(3p)$	45829.0	$^1\Sigma_g^+(2)$, $^1\Sigma_u^+(2)$, $^3\Sigma_g^+(2)$, $^3\Sigma_u^+(2)$, $^1\Sigma_g^-(1)$, $^1\Sigma_u^-(1)$, $^3\Sigma_g^-(1)$, $^3\Sigma_u^-(1)$, $^1\Pi_g(2)$, $^1\Pi_u(2)$, $^3\Pi_g(2)$, $^3\Pi_u(2)$, $^1\Delta_g(1)$, $^1\Delta_u(1)$, $^3\Delta_g(1)$, $^3\Delta_u(1)$
$^2P_u(2p) + {}^2D_g(3d)$	46187.0	$^1\Sigma_g^+(2)$, $^1\Sigma_u^+(2)$, $^1\Sigma_g^-(1)$, $^1\Sigma_u^-(1)$, $^3\Sigma_g^+(2)$, $^3\Sigma_u^+(2)$, $^3\Sigma_g^-(1)$, $^3\Sigma_u^-(1)$, $^1\Pi_g(3)$, $^1\Pi_u(3)$, $^3\Pi_g(3)$, $^3\Pi_u(3)$, $^1\Delta_g(2)$, $^1\Delta_u(2)$, $^3\Delta_g(2)$, $^3\Delta_u(2)$ $^1\Phi_g(1)$, $^1\Phi_u(1)$, $^3\Phi_g(1)$, $^3\Phi_u(1)$
$^2P_u(2p)$ + Doublet (n=4, 5)	51088.0 → 53782.0	Singlet, triplet Σ, Π, Δ, Φ, Γ (g,u)
$^2S_g(3s) + {}^2S_g(3s)$	54412.0	$^1\Sigma_g^+(1)$, $^3\Sigma_u^+(1)$
$Li^+ [{}^1S_g(1s^2)]$ + $Li^- [{}^1P_u(2s2p)]$	57920.0	$^1\Sigma_g^+(1)$, $^1\Sigma_u^+(1)$, $^1\Pi_g(1)$, $^1\Pi_u(1)$

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^-.

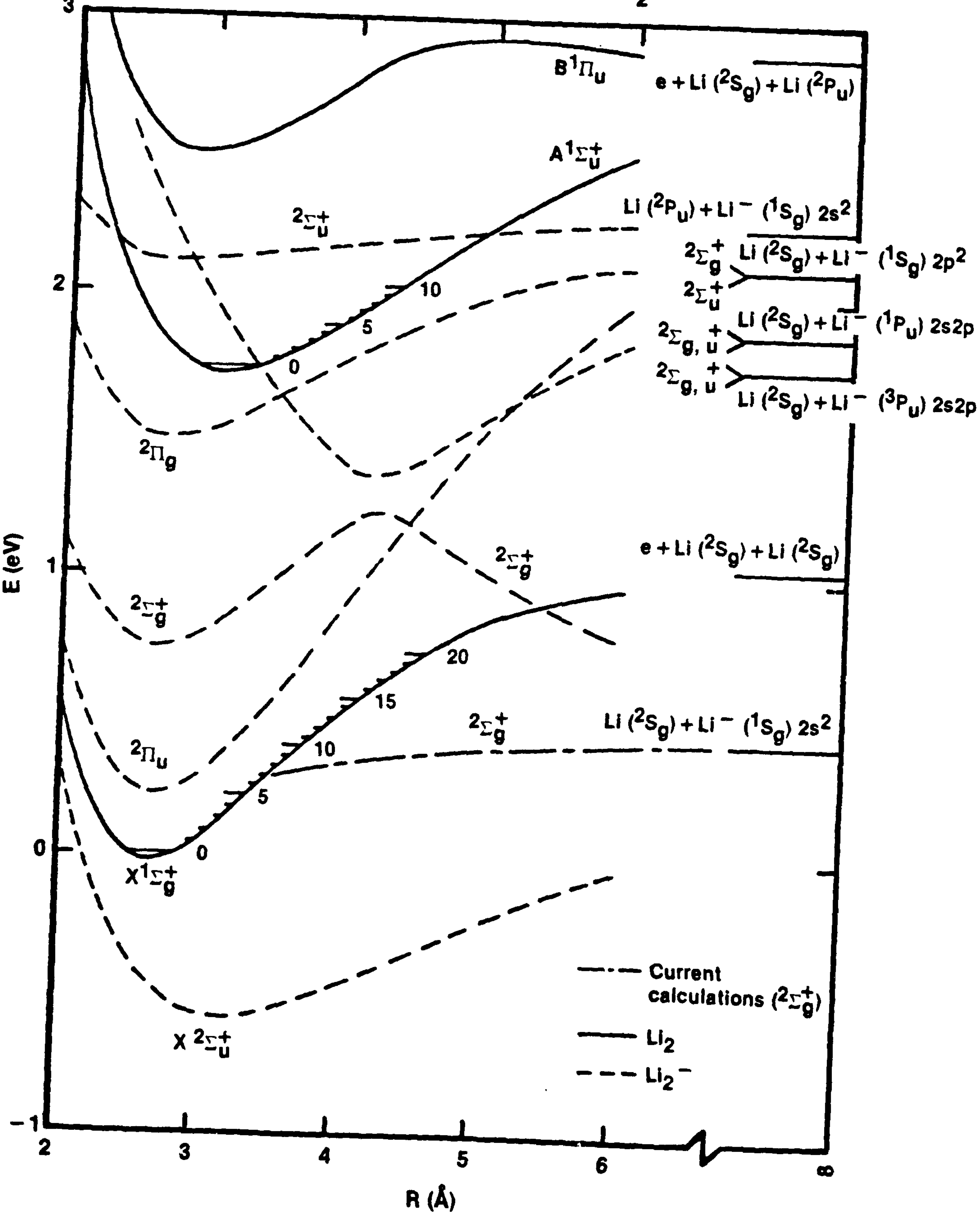
Level	R1	R2	H_3^- electronic energy	H_3^- zero-pt. energy	H^- electronic energy	H_2 electronic energy	H_2 zero-pt. energy	D_e	D_o
SCF/small	0.7340	3.2120	-1.621341	0.01250	-0.487640	-1.132408	0.01046	1.29	-0.75
MP2/small	0.7451	2.8977	-1.668994	0.01277	-0.507128	-1.160181	0.01030	1.68	-0.79
MP4/small	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

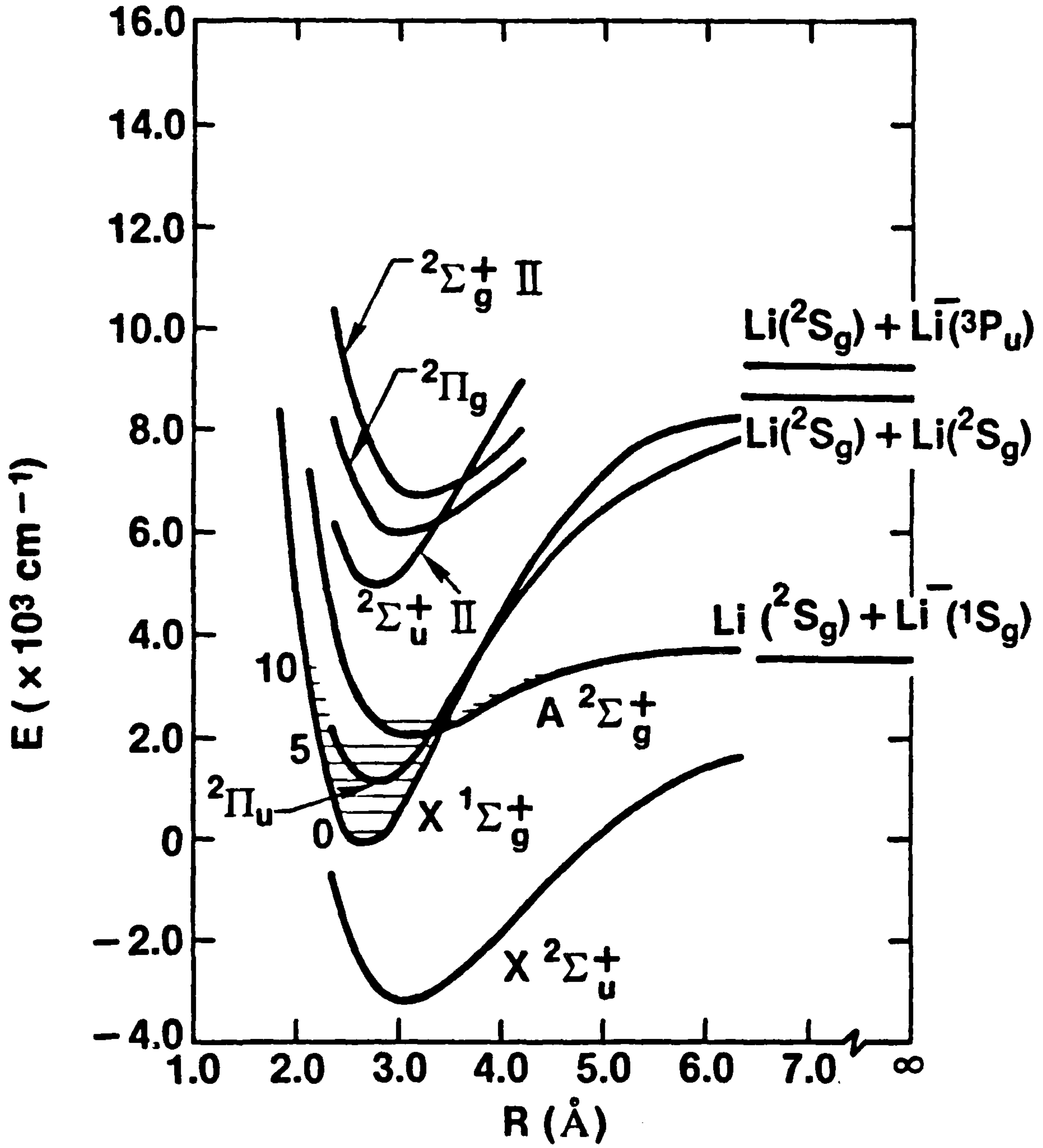
Potential energy curves of Li_2^-



82-3-121-1

FIG. 2

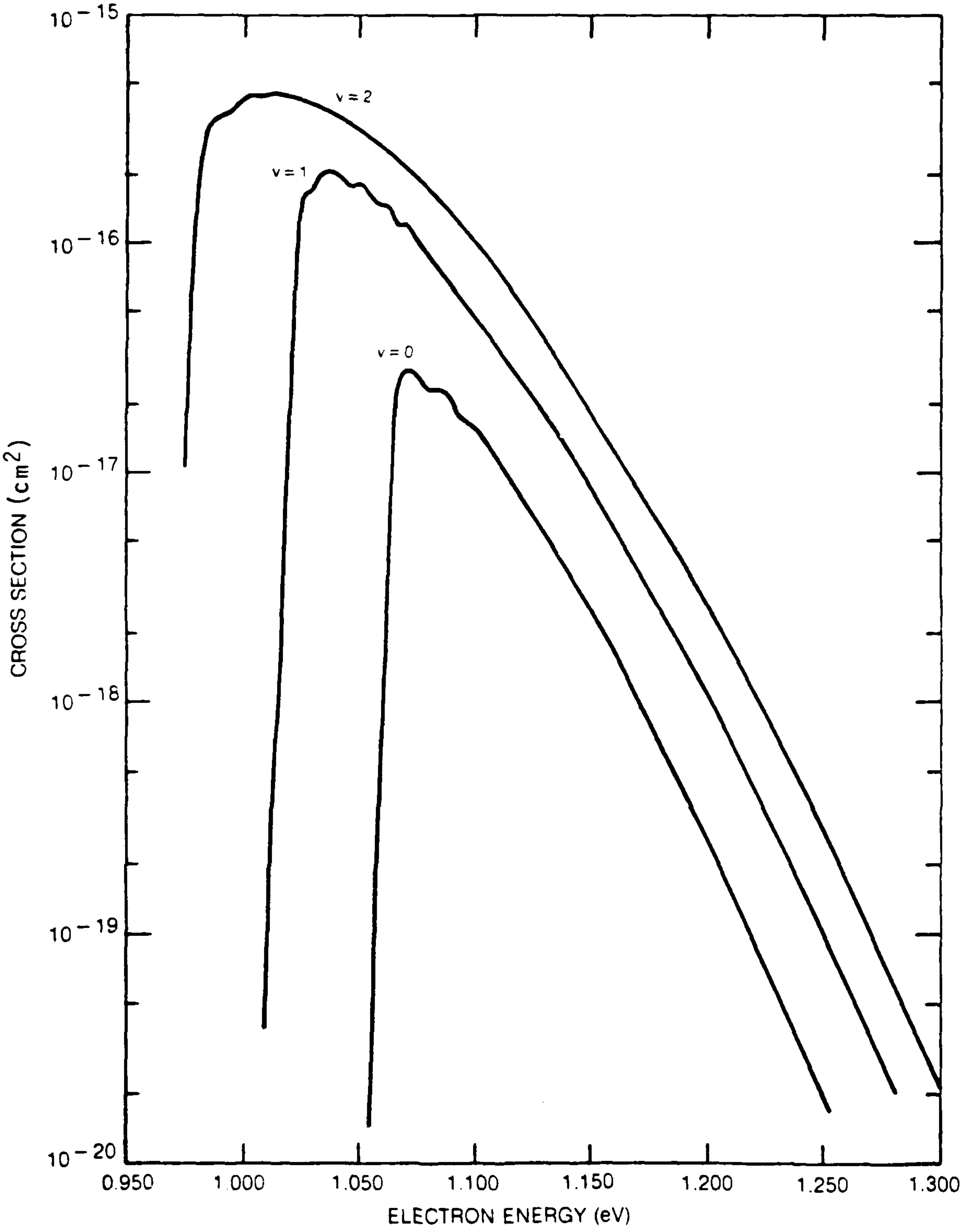
Low-Lying Potential Energy Curves of Li_2^-



86-2-76-3

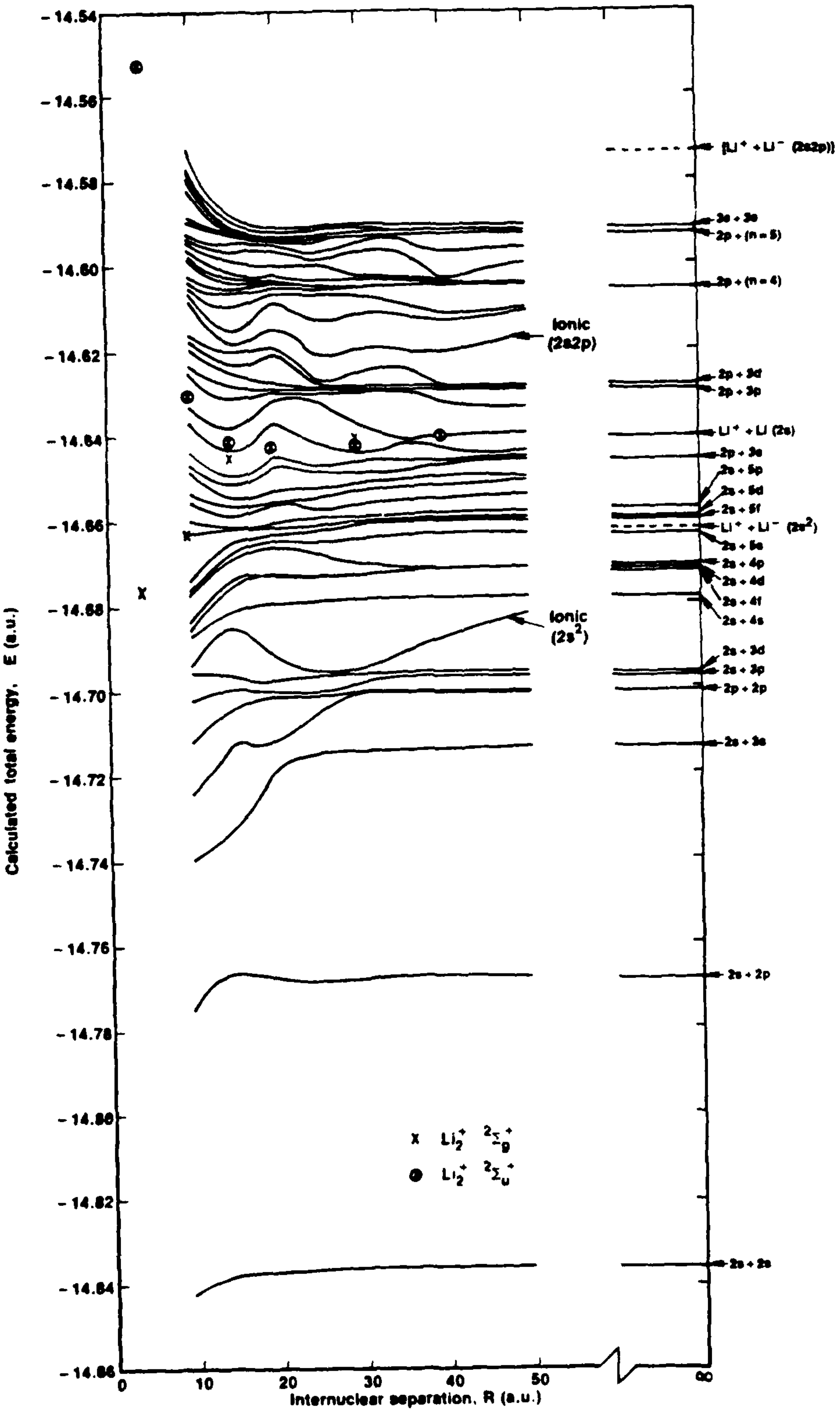
FIG. 3

DISSOCIATIVE ELECTRON ATTACHMENT CROSS SECTION FOR $e + Li_2\ [X\ ^1\Sigma_g^+]$



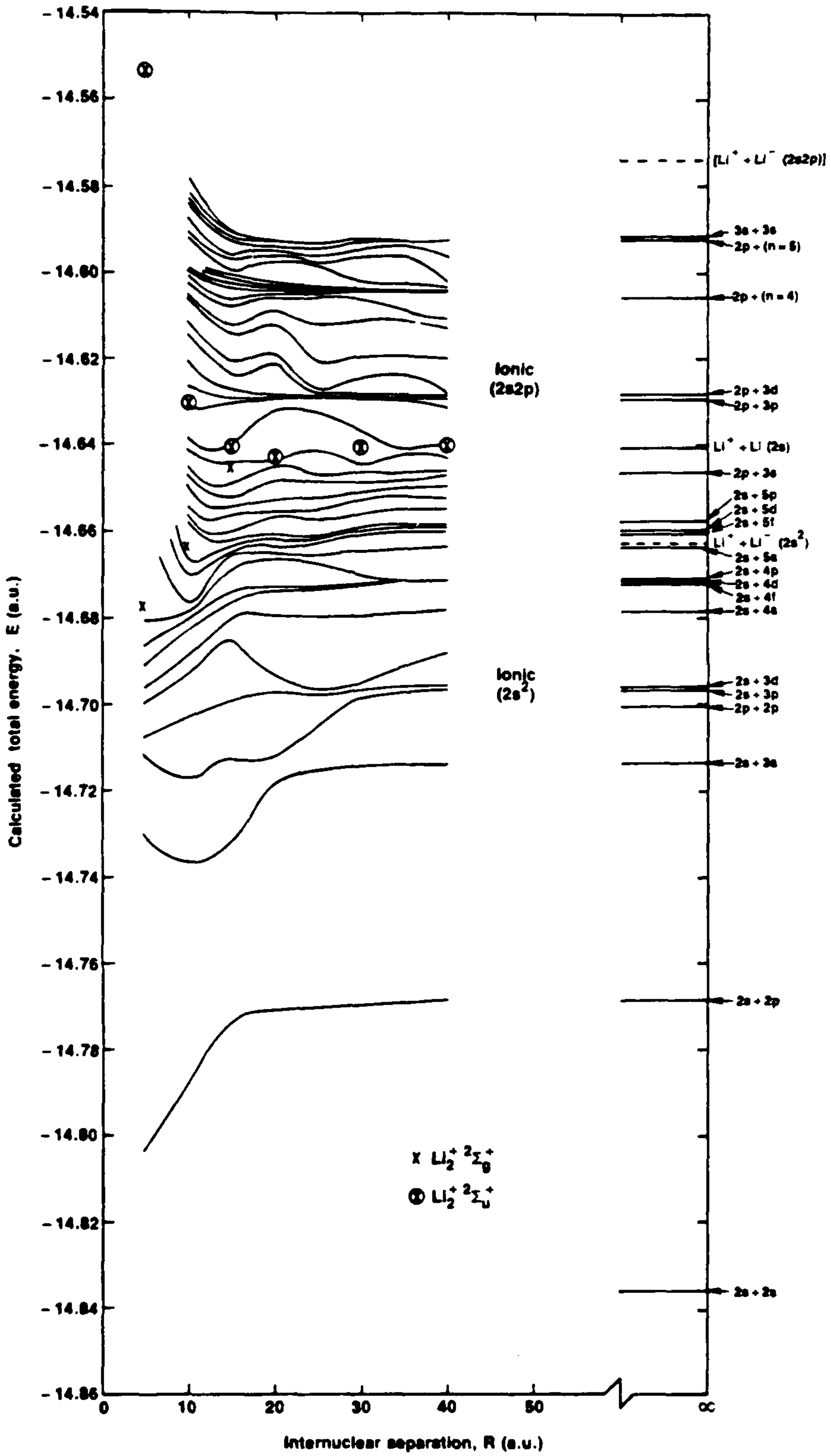
85-7-91-1

FIG. 4



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

FIG. 5



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

FIG. 6

POTENTIAL ENERGY CURVES FOR He_2 AND He_2^-

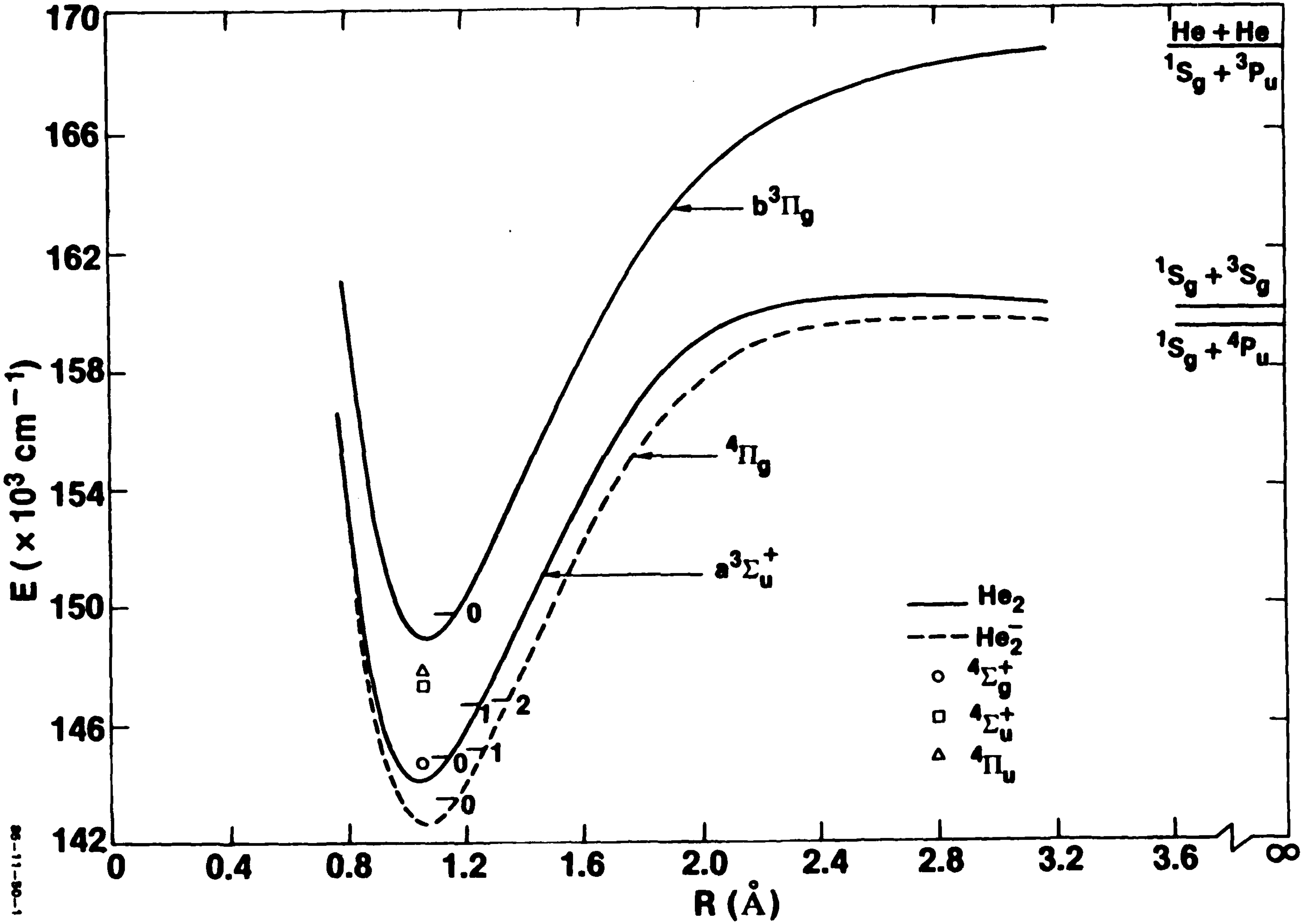
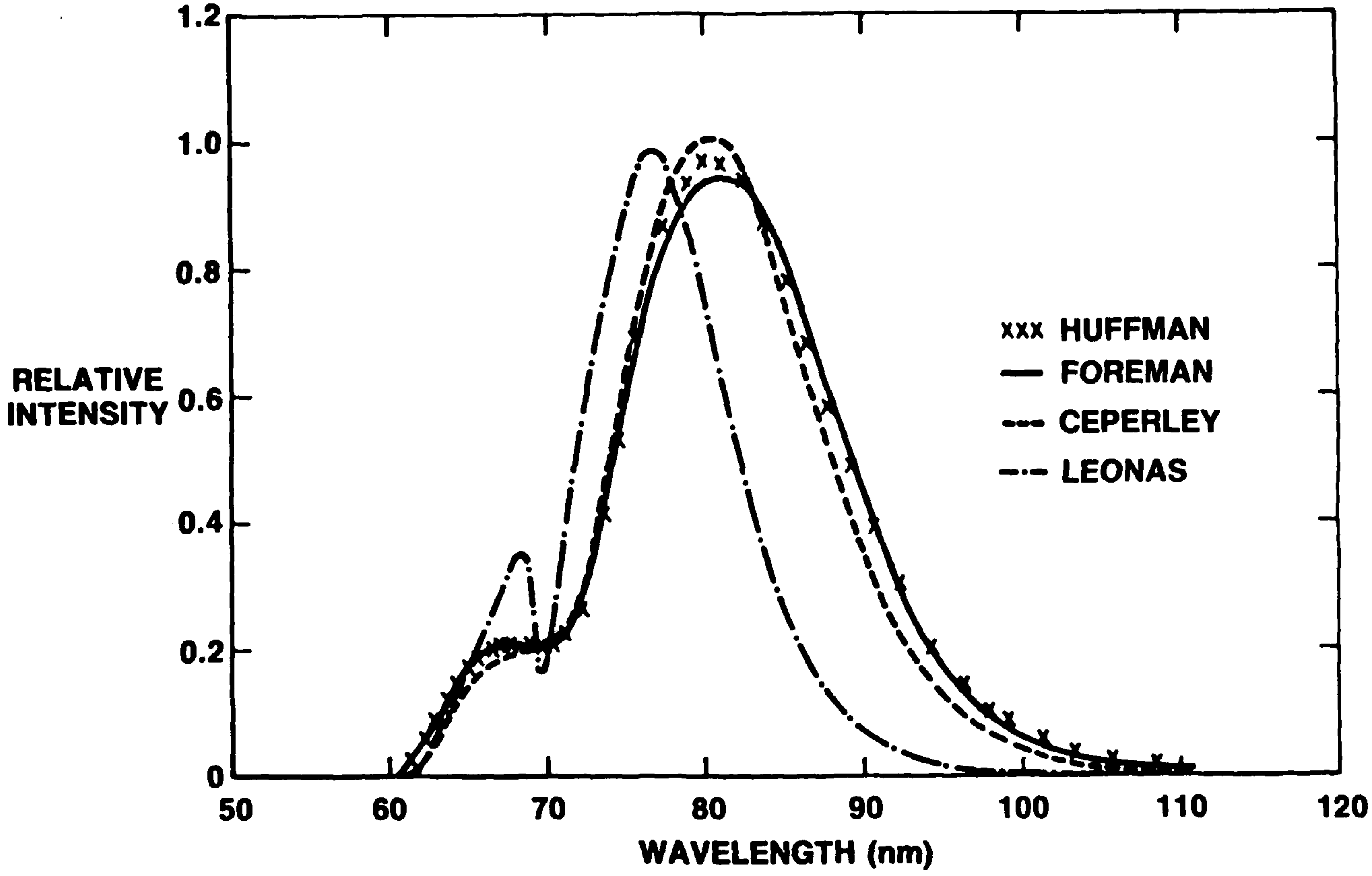


FIG. 7



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

86-6-63-1

APPENDIX A

ELECTRONIC STRUCTURE OF He_2^- *

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ABSTRACT

The electronic structure of the He_2^- anion has been studied using optimized CI wavefunctions. We find that the $^4\Pi_g$ state of He_2^- is bound relative to the $a^3\Sigma_u^+$ state of He_2, with a calculated electron affinity of 0.182 eV. Only the lowest vibrational level of this anion is stable relative to the He_2 $[a^3\Sigma_u^+]$ + e continuum.

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APPENDIX B

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 C

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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APPENDIX D

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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APPENDIX E

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.

---

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APPENDIX F

He_2^- $[^4\Pi_g]$ → He_2 $[X^1\Sigma_g^+]$ Autodetachment Energy Spectrum: Assessment of the He_2^- and He_2 Ground State Potentials

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ABSTRACT

The energy spectrum from the spin-forbidden electronic autodetachment from the metastable He_2^- $[^4\Pi_g]$ ion has been measured. The single-peaked continuum, resulting from a vertical transition to the repulsive wall of the He_2 $[X^1\Sigma_g^+]$ ground state, has a maximum at 15.70 ± 0.15 eV. For a rotationally cool beam, the spectrum is inconsistent with the existing potentials of He_2^- and He_2 $[X^1\Sigma_g^+]$. A suitable fit, neglecting rotational effects, would require an increase of 0.06 Å in the calculated R_e of He_2^-. However, a very good fit can also be obtained from the existing potentials by assuming a rotationally hot (15000 K) distribution. Surprisingly, both fits require contributions from levels $v > 0$, which are known to undergo vibrational autodetachment to $He_2[a^3\Sigma_u^+]$. For such contributions, the latter process must be exceptionally slow ($<10^6$/s).

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