THEORETICAL STUDIES OF KINETIC MECHANISMS OF NEGATIVE ION FORMATION IN PL. (U) UNITED TECHNOLOGIES RESEARCH CENTER EAST HARTFORD CT. H H MICHELS ET AL. JUL 84
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Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas

Annual Technical Report
Theoretical Studies of Kinetic Mechanisms of Negative Ion Formation in Plasmas
Annual Technical Report

Contract No. F49620-83-C-0094
Project Task 2301/A7

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DATE July 1984
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 \( \text{H}^+ \) source devices, primarily of the Belchenko-Dinov-Dudnikov (BDD) type. The primary goal of this research program was to identify the most important reactions leading to \( \text{H}^+ \) production or destruction and to estimate these reaction rates as a function of system conditions.
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.
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 F49620-83-C-0094, Project-Task No. 2301/A7. The performance period for the technical program was from 1 June 1983 through 1 June 1984. The project monitor was Captain Henry L. Pugh, Jr., USAF.
ACKNOWLEDGEMENTS

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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\(^-\)\(\text{(D}^-\text{)}\), source devices, primarily of the Belchenko-Dimov-Dudnikov (BDD) type. The primary goal of this research program was to identify the most important reactions leading to \(\text{H}^-\text{(D}^-\text{)}\) 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 \textit{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. As a new task, 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 LASL and IRT 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 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 potential energy hypersurfaces describing the following reactions:

\[
e + \text{H}_3^+ + \text{H} + \text{H}_2
\]

\[
e + \text{H}_3^+ + \text{H}^- + \text{H}_2^+
\]

\[
\text{H}^- + \text{H}_2^+ + \text{H} + \text{H}_2
\]

\[
\text{H}^- + \text{H}_2^+ + \text{H} + \text{H}^*
\]

b. Quantum mechanical calculations of the cross-sections and kinetic rates for the reactions specified in (a) above, including predictions of product states and branching ratios.

c. A survey of current experimental studies on negative ion source devices and comparisons of available gas phase kinetic data with the results obtained from this theoretical study.

Other gas phase reactions than those specified in (a) above may be substituted for detailed study if experimental and particle beam program directions indicate more optimum choices.
d. Quantum mechanical calculations of the potential energy curves for Li/Li$_2^-$ and an analysis of the probability of Li$^-$ formation via dissociative-attachment of e + Li$_3^+$ and of e + Li$_2$.

e. Theoretical studies of the electronic structure and surface density of states for base metal (Cr, Mo, W)/alkali (Cs, Rb)/H interactions on representative base metal clusters or prototype base metal surfaces.
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 was to explore new chemical sources for the production of light negative atomic ions, in particular H\(^-\) and Li\(^-\). Studies included 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\(_2\).
RESEARCH PROGRESS DURING THE CONTRACT YEAR

In contrast to surface catalyzed reactions, the mechanisms of most of the known volume-dependent gas phase reactions involving H⁻ are relatively simple to analyze, although much remains to be done to identify the state distributions for the products. A major problem, which has been addressed during the past year, has been to identify the most likely reaction kinetics leading to the formation of H⁻ atoms.

Hiskes (Ref. 10) has proposed a mechanism for the production of vibrationally excited H₂ and the subsequent production of H⁻ via dissociative-attachment of electrons. The initial step proposed by Hiskes involves electron excitation of ground state H₂ to an electronically excited state:

\[ e \text{ (fast)} + H_2 \rightarrow H_2^* \quad (1) \]

Both of these states have allowed radiative transitions to the ground state of H₂ but the displaced equilibrium separations of these excited states yield vibrationally excited H₂ upon radiative decay according to the most favorable Franck-Condon transitions:

\[ H_2^* \rightarrow H_2 \quad (2) \]

Vibrationally excited H₂ has been shown (Refs. 8, 9) to have a greatly enhanced cross-section for electron dissociative-attachment:

\[ e \text{ (slow)} + H_2^* \rightarrow H \quad (3) \]

This proposed mechanism is critically dependent on the magnitude of the overall cross-section for reactions (1) and (2). Hiskes (Ref. 10) has estimated this cross section to be \( \sim 10^{-18} \) cm², a rather low value for a volume-dependent route for the production of H⁻.
As an alternative mechanism for producing vibrationally excited H₂, we have undertaken an analysis of the branching and product distribution for dissociative-recombination of e + H₃⁺. The reaction scheme is as follows:

\[
e + H₃⁺ [1A₁'] + H₃ [2A₁ + 2B₂] + H₂ [X 1Σ⁺] + H
\]

\[
+ H₂⁺ [X 2Γ⁺] + H⁻
\]

Detailed quantum mechanical calculations of these reaction surfaces have been carried out. The H₃ correlation diagram and possible low-lying dissociative-recombination reaction paths are indicated in Figs. 1 and 2, respectively. Dissociative recombination of e + H₃⁺, as shown in Reaction (4), is exothermic by 9.3 eV to form H₂ + H and endothermic by 5.4 eV to form the ion pair, H₂⁺ + H⁻. However, the detailed branching of Reaction (4) depends critically on the shape of the \(2A₁\) and \(2B₂\) hypersurfaces for H₃ for interatomic separations in the vicinity of 2-3 Å since the Coulomb attraction of the ion pair gives rise to a degeneracy in the hypersurfaces of H₃ in this region. During the past year, we have undertaken a series of ab initio calculations of the potential energy surfaces for H₃ in both \(C₂v\) and \(D₆h\) symmetries to ascertain the character of the low-lying states. These calculations were carried out using optimized Slater-type orbital (STO) basis functions and a full CI within each symmetry group. The resultant potential energy surfaces are shown in Fig. 3. Based on these results, we find a reaction path for dissociative recombination which involves the electron attachment of e + H₃ to form a symmetric \(2A₁\) state of H₃ which is nearly energy resonant for recombination of H₃⁺ ions with three of four quanta of vibrational energy:

\[
e + H₃⁺ (v = 3,4) + H₃ [2A₁] \Delta E = 0
\]

This state of H₃ correlates diabatically with the ion pair, H₂⁺ + H⁻, but exhibits many curve-crossings of the lower-lying Rydberg states of H₃. In particular, the lowest-lying recombination pathway yields vibrationally excited H₂ molecules and electronically excited H with \(n = 2\):

\[
H₃ [2A₁] \text{ curve crossing } H₂ [X 1Σ⁺] + H⁺ (n = 2)
\]
The overall recombination pathway is illustrated in Fig. 4. We find that the overall cross-section for this route to \( H_3^+ \) is \( \sim 10^{-15} \) cm\(^2\), and thus the rate of reaction (3) alone becomes rate determining. This study indicates that dissociative-recombination of vibrationally excited \( H_3^+ \) is a kinetically important volume dependent reaction for production of vibrationally excited \( H_2 \). In high density hydrogen plasmas, relaxation of \( H_3^+ \) through collision lessens the contribution of this process in forming \( H_3^+ \).

In addition to these studies of dissociative-recombination \( e + H_3^+ \), we have undertaken a series of calculations of \( Li_2^- \) in order to assess the energetics of this anion. McGeoch (Ref. 11) 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:

\[
e \text{(fast)} + Li_2 [X 1\Sigma^+] + Li_2^* [A 1\Sigma^+_u, B 1\Pi_u] + e \tag{7}
\]

or

\[
Li_2 [X 1\Sigma^+] + h\nu + Li_2^* [A 1\Sigma^+_u, B 1\Pi_u] \tag{8}
\]

The \( A 1\Sigma^+_u \) and \( B 1\Pi_u \) state both exhibit fast radiative decay back to the ground \( X 1\Sigma^+_g \) state but the most favorable Franck-Condon transitions favor population of \( Li_2 \) with \( \nu = 5 \) greater:

\[
Li_2^* [A 1\Sigma^+_u, B 1\Pi_u] + Li_2^* [X 1\Sigma^+ (\nu > 5)] + h\nu \tag{9}
\]

Our present understanding of the energetics of the \( Li_2/Li_2^- \) system are shown in Figs. 5 and 6. The dashed curves in Fig. 5 were estimates based on \( H_2^- \) and the known molecular orbital structure of \( Li_2^- \). Our most recent \textit{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. 6. This suggests that electron dissociation-attachment is possible for this system for vibrationally excited Li$_2$ molecules:

$$e \text{ (slow)} + \text{Li}_2 [X \, \Sigma^+_g] \rightarrow \text{Li} \, \Sigma^+_g + \text{Li}^- \, \Sigma^-_g$$

(10)

The final potential energy curves governing reaction (10) are shown in Fig. 6. There is still considerable uncertainty in the location of the excited resonant states of Li$_2^-$, especially in the auto-ionizing region above Li$_2^+$ e. The ground [X $\Sigma^+_g$] state is well characterized theoretically (Refs. 12, 13) but little is known about the location of the low-lying excited electronic states which connect to Li$^2P$ + Li$^-\Sigma^-_g$. In addition, by analogy with H$_2^-$, low-lying electronic states of Li$_2^-$ with MO configuration (1$\sigma^2$ 1$\sigma^2$ 2$\sigma^2$ 1$\sigma^2$) $^{2,4}\Sigma^+_g$ may, in fact, actually lie lower than some of the states shown in Fig. 5. Such states dissociate to very high atom-ion limits and their general characteristics are uncertain. The curves shown in Fig. 6 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 $^{2}\Sigma^+$ state of Li$_2^-$ has the molecular orbital configuration [1$\sigma^2$ 1$\sigma^2$ 2$\sigma^2$ 2$\sigma^2$] $^{2}_g$ for large separations and was the focus of our studies of this system during the past year. At short internuclear separations, this state mixes with a second bound $^{2}\Sigma^+$ state arising from Li$^2P$ + Li$^-\Sigma^-_g$ with a molecular orbital configuration [1$\sigma^2$ 1$\sigma^2$ 2$\sigma^2$ 3$\sigma^2$] $^{2}_g$. This mixing at intermediate separations results in a lowering of the interaction potential for the lowest $^{2}\Sigma^+$ state. Our preliminary calculations, as shown in Fig. 5, indicate that this mixing is stronger than expected from MO considerations and lower the $^{2}\Sigma^+$ potential curve into a feasible region for dissociative-attachment to occur. A preliminary analysis of the imaginary part of the $^{2}\Sigma^+$ potential has been carried out. We find $\Gamma(R) \sim 0.01 \, \text{k}(R)$ indicating that this state is mainly Feshbach in character and has a long lifetime against autoionization.

Further theoretical studies of these interactions potentials are required to define the overall reactive kinetics leading to Li$^-$ production. A study parallel to that reported by Hiskes (Ref. 10) for H$_2$ has been carried out to estimate the overall cross sections for production of vibrationally excited Li$_2$. In addition, theoretical studies are in progress in collaboration with Professor J. Wadehra, to estimate the low-energy electron dissociative attachment cross-section for e + Li$_2^*$ + Li + Li$. The results of these studies would be of value to the experimental program of McGeoch (Ref. 11) to define the overall utility of this volume-dependent source of Li$^-$ ions.

Eleven technical papers and presentations have resulted from the research efforts conducted under this contract.
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


5. "Vibrational Excitation of \( Li_2 (X \, ^1Σ_u^+ ) \) via Electron or Photon Excitation of the \( A \, ^3Σ_u^+ \) or \( B \, ^1Π_u \) State." J. M. Wadehra and H. H. Michels, to be published in Chemical Physics Letters, 1984.

B. Technical Paper and Lecture Presentations


2. Attended the Dynamics of Molecular Collisions Symposium, Kaiserlautern, Germany, August 2-5, 1983.

3. Attended the 8th International Seminar on Ion-Atom Collisions, Utrecht, Netherlands, August 1983.


REFERENCES


11. McGeoch, M. W.: A Dissociative Attachment \(Li^-\) Source. AVCO/Everett Research Laboratory, work in progress.


# H₃ CORRELATION DIAGRAM

<table>
<thead>
<tr>
<th>STATES OF SEPARATED ATOMS</th>
<th>ENERGY (eV)</th>
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<tr>
<td>H(n = 1) + H⁺ + H⁻ (¹S)</td>
<td>17.3223</td>
</tr>
<tr>
<td>H₂⁺ (Χ²Σ⁺₉) + H(n = 1) + e</td>
<td>15.4258</td>
</tr>
<tr>
<td>H⁺(n = 2) + H(n = 1) + H(n = 1)</td>
<td>14.6826</td>
</tr>
<tr>
<td>H₂⁺ (Χ²Σ⁺₉) + H⁻ (¹S)</td>
<td>14.6716</td>
</tr>
<tr>
<td>H₂(Χ¹Σ⁺₉) + H⁺ + e</td>
<td>13.6058</td>
</tr>
<tr>
<td>H₂(Χ¹Σ⁺₉) + H⁺(n = 4)</td>
<td></td>
</tr>
<tr>
<td>H₂⁺(C₁⁺Π₉) + H(n = 1)</td>
<td>12.7556</td>
</tr>
<tr>
<td>H₂⁺(Χ¹Σ⁺₉) + H⁺(n = 3)</td>
<td>12.2966</td>
</tr>
<tr>
<td>H₂⁺(a³Σ⁺₉) + H(n = 1)</td>
<td>12.0942</td>
</tr>
<tr>
<td>H₂⁺(c³Π₉) + H(n = 1)</td>
<td>11.7950</td>
</tr>
<tr>
<td>H₂⁺(B¹Σ⁺₉) + H(n = 1)</td>
<td>11.7709</td>
</tr>
<tr>
<td>H₂⁺(Χ¹Σ⁺₉) + H⁺(n = 2)</td>
<td>10.2045</td>
</tr>
</tbody>
</table>

\[ \text{e + H₃}^{\dagger} (¹A_i) + \text{H}^{\dagger} (¹A_i) \]

\[
\begin{align*}
\text{H}_2^+(\chi^2\Sigma^+_g) + H^- (¹S) & : 9.2950 \\
\odot R = 5.061 \text{ BOHRS} & \\
\text{H}(n = 1) + \text{H}(n = 1) + \text{H}(n = 1) & : 4.4781 \\
\text{H}_2(\chi^1\Sigma^+_g) + \text{H}(n = 1) & : 0.0000
\end{align*}
\]
DISSOCIATIVE — RECOMBINATION REACTION PATHS

\[ \text{e} + \text{H}_2[^1\text{A}_1] \rightarrow \text{H}_3[^2\text{A}_1] \]

\[ \text{H}_3[^2\text{A}_1] \rightarrow \text{H}_2[^1\Sigma^+_\text{g}] + \text{H}^* (n = 2) \quad \Delta E (\text{eV}) = +0.91 \]

\[ \rightarrow \quad \text{H}_2[^3\Sigma^+_\text{u}] + \text{H} (n = 1) \quad +1.89 \]

\[ \rightarrow \quad \text{H}_2[^a^3\Pi_u] + \text{H}(n = 1) \quad +2.48 \]

\[ \rightarrow \quad \text{H}_2[^a^3\Sigma^+_\text{g}] + \text{H}(n = 1) \quad +2.50 \]

\[ \rightarrow \quad \text{H}_2[^1\Sigma^+_\text{g}] + \text{H}^* (n = 3) \quad +2.80 \]

\[ \rightarrow \quad \text{H}_2[^1\Sigma^+_\text{g}] + \text{H}^* + \text{e} \quad +4.31 \]

\[ \rightarrow \quad \text{H}_2[^2\Sigma^+_\text{g}] + \text{H}^- \quad +5.38 \]
POTENTIAL ENERGY CURVES FOR H₃

Energy (Hartrees)

R (Bohrs)

-1.7 -1.6 -1.5 -1.4 -1.3 -1.2 -1.1 -1.0

-1.7 -1.6 -1.5 -1.4 -1.3 -1.2 -1.1 -1.0

H₂ [²Σ⁺₁] + H⁻ [¹S]  
H₂ [¹Σ⁺₁] + H⁺(n = 3)  
H₂ [¹Σ⁺₁] + H⁺(n = 1)  
H₂ [²Σ⁺₁] + H(n = 1)  
H + H + H (h = ∞)

2A₁  
2B₂  
1A₁ (H₃⁺)  
RESONANT STATE

H₂ [¹Σ⁺₁] + H(n = 1)

FIG. 3
### e + H$_3^+$ RECOMBINATION ENERGETICS

<table>
<thead>
<tr>
<th>( e + H_3^+ (\nu) \rightarrow H_3 \rightarrow H_2 \left[ X^1\Sigma_g^+ (\nu) \right] + H^* (n = 2) )</th>
<th>( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+0.91</td>
</tr>
<tr>
<td>1</td>
<td>+0.52</td>
</tr>
<tr>
<td>2</td>
<td>+0.13</td>
</tr>
<tr>
<td>3</td>
<td>-0.26</td>
</tr>
<tr>
<td>4</td>
<td>-0.64</td>
</tr>
<tr>
<td>4</td>
<td>-0.12</td>
</tr>
</tbody>
</table>

\[
H_2^+ + H_2 \rightarrow H_3^+ (\nu = 0) + H \quad \Delta E = -1.73 \text{ eV}
\]

\[
\rightarrow H_3^+ (\nu = 4) + H \quad \Delta E = -0.17 \text{ eV}
\]

### RECOMBINATION PATHWAY

\[
e + H_3^+ (\nu = 4) \rightarrow H_3 \left[ ^2A_1' \right] \text{ Resonance} \quad \Delta E \approx 0
\]

\[
H_3 \left[ ^2A_1' \right] \rightarrow H_2 (\nu = 1) + H^* (n = 2) \quad \Delta E = -0.12 \text{ eV}
\]
Potential energy curves of Li$_2^-$

- $B^1\Pi_u$
- $A^1\Sigma^+_u$
- $2\Sigma_u^+$
- $2\Pi_g$
- $X^1\Sigma^+_g$
- $X^2\Sigma^+_u$

Reactions:
- $e + Li (2S_g) + Li (2P_u)$
- $2\Sigma_g^+$
- $2\Pi_u$
- $2\Pi_g$
- $2\Gamma_g$
- $2\Gamma_u$
- $e + Li (2S_g) + Li (2S_g)$
- $Li (2S_g) + Li (1S_g) 2s^2$
- $Li (2P_u) + Li (1S_g) 2p^2$

Notations:
- $2\Sigma_g^+$
- $2\Pi_u$
- $2\Pi_g$
- Current calculations ($2\Sigma_g^+$)
- $Li_2$
- $Li_2^-$

Labels:
- $E (\text{eV})$
- $R (\text{Å})$

Sources:
- Calculations (24+)

Graphical representation of potential energy curves for lithium dimers.
LOW- LYING POTENTIAL ENERGY CURVES OF Li$_2^-$
APPENDIX A

LOW TEMPERATURE DISSOCIATIVE RECOMBINATION OF e + H_3^+

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ABSTRACT

Accurate ab initio calculations of the ground and excited H_3 potential energy surfaces have been carried out. These surfaces have been examined at geometries appropriate for an analysis of the reaction products of e + H_3 dissociative recombination. Direct recombination occurs through the 2A_1 resonance state which correlates diabatically to H_2^+ + H-. For low collisional energies, this resonance state is accessible only to H_2^+ ions with at least three quanta of vibrational energy. Indirect dissociative recombination of e + H_3^+, via capture into vibrationally excited Rydberg states of H_3, also has a very low probability since there are no effective curve crossings with the lower valence states dissociating to H + H + H or H + H_2. We estimate that the currently accepted values of the e + H_3^+ recombination coefficient for interstellar conditions are two orders-of-magnitude too large.

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APPENDIX B

DISSOCIATIVE-RECOMBINATION OF e + H₃⁺. AN ANALYSIS OF REACTION PRODUCT CHANNELS

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ABSTRACT

Accurate ab initio calculations of the ground and excited H₃ hypersurfaces have been carried out within a configuration-interaction framework. These surfaces have been examined for geometries appropriate for an analysis of the reaction products of dissociative recombination of e + H₃⁺. Direct recombination occurs through the ²A₁ resonance state which connects diabatically to H₂⁺ + H⁻. This resonance state is accessible for low-energy electron attachment to H₃⁺ ions carrying three or more quanta of vibrational energy. Under these conditions the predicted products are H⁺(n=2) + H₂(1Σ₉⁺), where any excess vibrational energy in the H₃⁺ ions is transferred to the product H₂ molecule. Direct dissociative recombination of H₃⁺ ions in their ground vibrational state is unlikely for low collisional energies (< 6 eV) and indirect capture processes must be examined for this case.

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APPENDIX C

ELECTRONIC STRUCTURE OF THE HELIUM MOLECULAR ANION, He$_2^-$

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ABSTRACT

The recently discovered He$_2^-$ ion is examined using configuration-interaction wavefunctions constructed from an extended STO basis. We find that the $^4\Pi_g$ state of He$_2^-$ is bound relative to the $^3\Sigma_u^+$ state of He$_2$. The calculated electron affinity is 0.233 eV compared to 0.077 eV for the He$^-$ [4p$^0$] atomic ion. This anion decays through the long-lived 5/2g component with $\tau \sim 350$ $\mu$sec and the much shorter-lived 3/2g, 1/2g components with $\tau \sim 10$ $\mu$sec.

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APPENDIX D

ELECTRONIC STRUCTURE OF THE LITHIUM MOLECULAR ANION, \( \text{Li}_2^- \)

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ABSTRACT

The electronic structure of the ground and excited states of the \( \text{Li}_2^- \) anion has been studied using optimized CI wavefunctions. The low-lying \( 2\Sigma^+ \) state is of the Feshbach type and exhibits a near-degeneracy between \( 2\Sigma^+ (v'=0) \) of \( \text{Li}_2^- \) and \( 1\Pi_g^+ (v''=6) \) of \( \text{Li}_2 \). In contrast with the \( \text{H}_2 \) system, we find a rich spectrum of low-lying resonant states for \( \text{Li}_2^- \).

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APPENDIX E

VIBRATIONAL EXCITATION OF Li₂(X 1Σ⁺) VIA ELECTRON OR PHOTON EXCITATION OF THE A 1Σ⁺, B 1Π State

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ABSTRACT

Cross sections for vibrational excitation (VE) of the X 1Σ state of Li₂ via formation of the excited A 1Σ⁺ or B 1Π electronic states are reported. For VE through the A 1Σ⁺ state, the cross sections are nearly constant for forming 3 ≤ ν'' ≤ 9 via electron collisional excitation. For photon pumping (670 nm ≤ λ ≤ 700 nm) of the A 1Σ⁺ state, levels ν'' ≤ 9 are predominantly formed. VE via the B 1Π state has a lower probability.

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