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High Temperature Spectroscopy of Alkali Metal Vapors for Solar to Thermal Energy Conversion

Paul S. Erdman
William C. Stwalley

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Interim Report

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NOTICE

FOREWORD

The work reported in this interim report was performed by Paul S. Erdman, University of Iowa, and Professor William C. Stwalley, University of Connecticut under JON: 2308M1R1 with the OLAC PL/RKFE Branch at the Phillips Laboratory, Edwards AFB CA 93524–7680. OLAC PL Project Manager was Dr. C. William Larson.

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C. WILLIAM LARSON
Project Manager

RANNEY G. ADAMS
Public Affairs Director

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Solar Plasma propulsion methods proposed by the Air Force have lead to the study of high temperature optical absorption of metal vapors. The Plasma Spectroscopy Cell in the Phillips Laboratory at Edwards AFB CA has been used to obtain an abundance of absorption spectra at temperatures approaching 2000 K and pressures of one atmosphere for lithium and sodium metal vapors. Tentative assignments of molecular transitions are improved upon by use of modern computational techniques for generating intensities of molecular transitions which possibly have been observed. Identification of contributing molecular transitions to overall absorption of radiant energy assists the efforts to develop propulsion methods which rely on the direct absorption of solar energy.

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INTRODUCTION

It has been suggested that the direct use of solar energy to propel spacecraft from low earth orbit to geosynchronous orbit is best performed by absorbing radiant solar energy directly into the rocket propellant [1]. The absorbed radiant energy would be converted through collisions into thermal energy, heating the propellant to provide a high exhaust velocity. The solar plasma absorber has the advantage that it would be able to reach higher propellant temperatures than the alternately proposed blackbody absorber. Another advantage is the tendency of the plasma to trap reradiated energy, thus reducing loss and increasing efficiency.

The preferred gas for spacecraft propulsion is hydrogen, since as the lightest element, it would provide the highest specific impulse. However, hydrogen is a poor absorber of solar energy because it is transparent in the visible and near infrared region of the spectrum where the solar flux is greatest. To better absorb solar energy, the hydrogen propellant would have to to seeded with lightweight absorbing elements. The alkali metals would be excellent candidates for seedants since it is already known that they absorb well in the visible and near infrared regions of the spectrum [2]. Alkali hydrides would also form and contribute to absorption [3]. In fact, it is likely that previously unobserved species M_xH_x (where M is an alkali metal) may also form and contribute to absorption[3].

EXPERIMENT

In order to study candidate absorbing elements and their hydrides in the high temperature,high pressure conditions that would exist in the solar plasma thruster, the Plasma Spectroscopy Cell (PSC) (Fig. 1) has been constructed at OLAC Phillips Laboratory, Edwards AFB, California. The PSC uses concentric gas flows and resistive elements to create high temperature (potentially 3000 K), high pressure (potentially 100 atmospheres) metal vapors which can be optically studied for their absorptions properties.

The metals are loaded in a crucible surrounded by a rhenium resistive heating ring in a section of the PSC known as the atomizer or evaporator region. A neutral entrainment gas, such as helium or argon, carries the metal vapor through the central tube A into the region known as the hot zone. The hot zone is heated by a molybdenum susceptor which surrounds the concentric tubes A, B, and shroud tube. Tube B carries a gas which can be chosen as neutral or a reactive gas such as hydrogen. The metal vapor jet formed in the central region of the hot zone as it exits Tubes A and B contains the molecules of interest. Optical access to this area is available through four opposing windows on two perpendicular axes.

Absorption experiments carried out with the PSC over the last three years have generally followed the schematic shown in Figure 2. Both xenon and tungsten lamps have been used as sources to pass light through the PSC and into a spectrometer, In several experiments, the extra beam created by the beam splitters has been used with an additional spectrometer to obtain spectra of wider spectroscopic range or higher resolution in a region of particular interest.

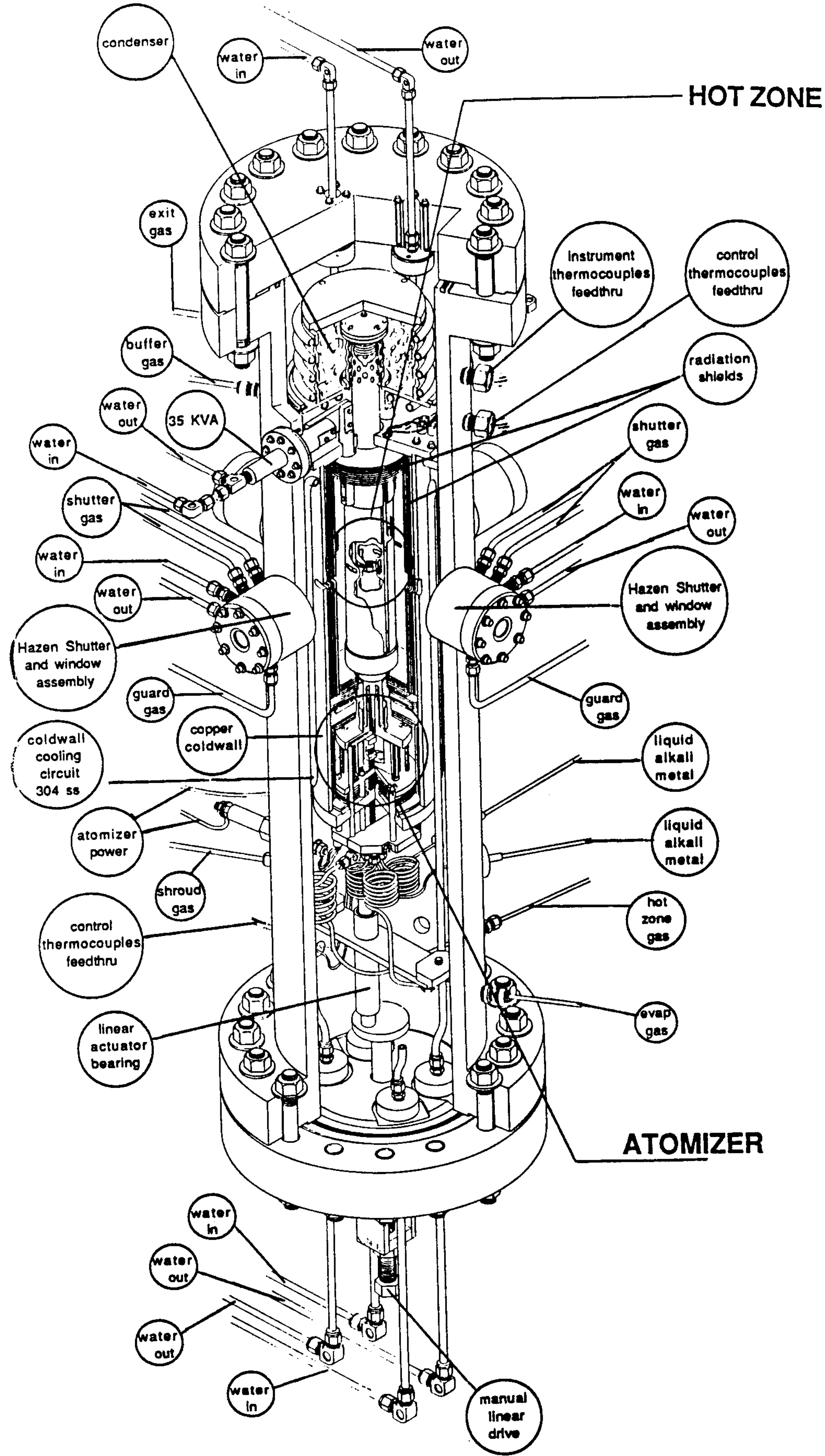

Figure 1.
The Plasma Spectroscopy Cell [3]

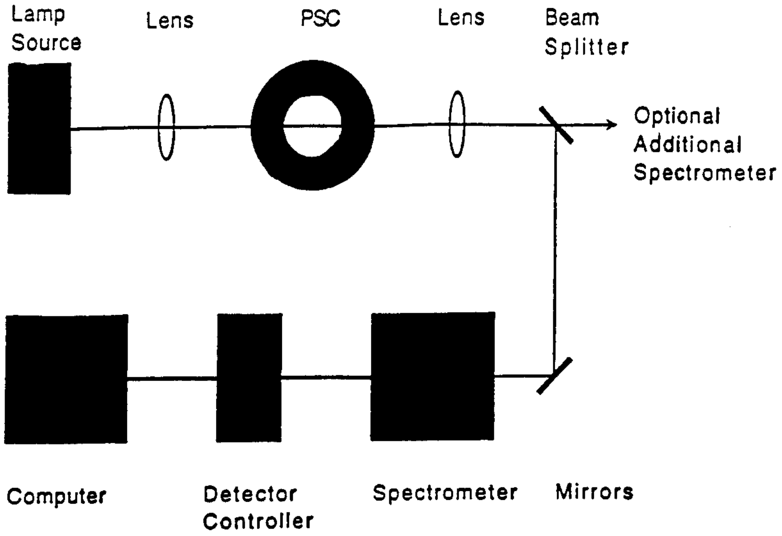

Figure 2.
Schematic of PSC Experiment

DATA

Much of the data obtained in the PSC experiments described above has been in the form of images 384 by 578 pixels. The long dimension corresponds to wavelength, the range of which was 300 to 665 nm. The shorter dimension corresponds to spatial position across the width of the metal vapor jet. Thus, each image file contains 578 cross sections of intensity vs position, and 384 cross sections of intensity vs. wavelength. The image files for the original intensity, I_0, of the source lamp and the transmitted intensity, I, through the metal vapor jet were used to calculate the images of absorbance according to

$$Absorbance = \ln\left(\frac{I_0 - B_0}{I - B}\right)$$

where B_0 and B are the appropriate background intensity images.

It is easier to reproduce and visualize a single absorbance intensity vs. wavelength cross section of an image file rather than the whole image file. An example of such a cross section is shown in Figure 3, which shows absorbance by sodium at 1720 K and a pressure of one atmosphere. Prominent atomic lines are at 330 nm for the 3s-4p transition and the broad, saturated sodium D line at 589 nm for the 3s-3p transition. Centered on 500 nm is absorbance by the $B^1\Pi_u - X^1\Sigma_g^+$ transition of Na_2. Another diatomic sodium absorbance in the ridge between 550 and 560 nm, believed to be attributed to the $1^3\Pi_g - 1^3\Sigma_u^+$ transition.

Experiments performed with a mix of lithium and sodium produced results such as the absorbance plot shown in Figure 4, taken at a temperature of 1600 K and pressure of one atmosphere. Again, the sodium atomic peaks for the 3s-4p and 3s-3p transitions appear, whereas the atomic 2s-2p transition of lithium at 670 nm is off the right edge of the range and only appears as a high ridge of line broadening mixed with the $A^1\Sigma_g^+ - X^1\Sigma_g^+$ transition of Li_2. The ridge centered on 500 nm with more sharply defined bandheads is the $B^1\Pi_u - X^1\Sigma_g^+$ transition of Li_2. Transitions from NaLi and Li triplets may be mixed in with the Li and Na features identified so far.

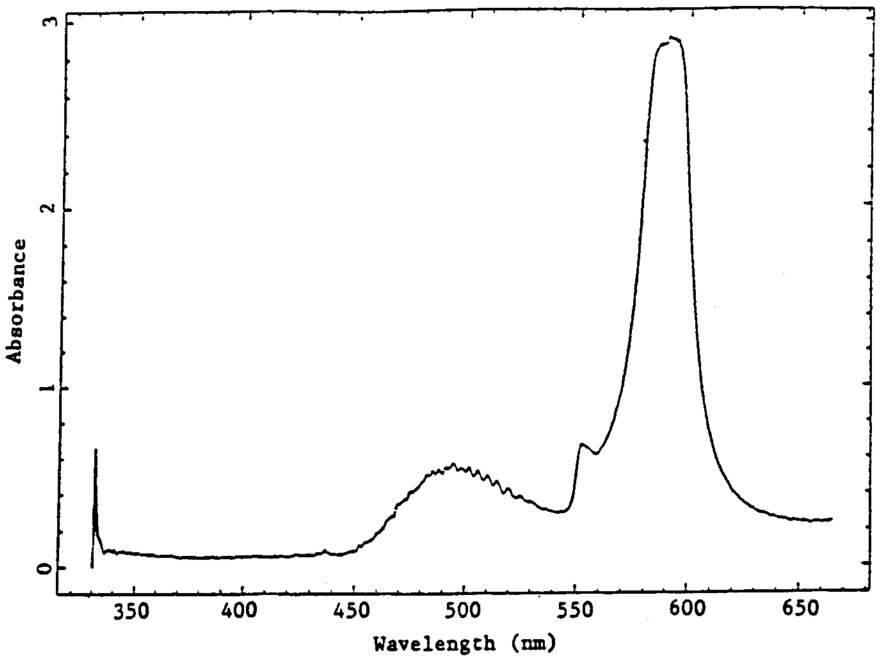

Figure 3.
Absorbance of Na at 1720 K and 1 Atmosphere

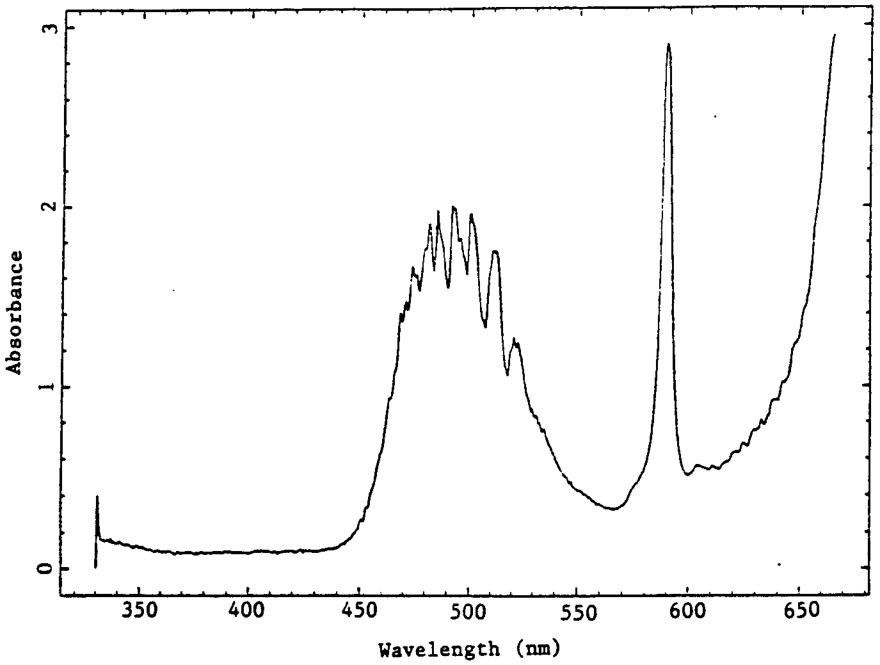

Figure 4.
Absorbance of Na, Li Mixture at 1600 K and 1 Atmosphere

Adding hydrogen as a reactive gas allows the possible formation of hydrides, e.g., LiH and NaH. Figure 5 shows a predominantly lithium absorption spectrum taken at 1900 K and one atmosphere. Residual sodium can still be seen to contribute atomic absorptions at 330 and 589 nm. The molecular transitions of B-X and A-X from Li_2 are seen around 500 nm and above 610 nnm, respectively. The lithium atomic line for the 2p-3d transition can be seen at 610 nm to the right if the ridge believed to belong to the $1^3\Pi_g - 1^3\Sigma_u^+$ transition of Li. The remaining absorption bands from 330 to 430 nm are in the right range for both $C^1\Pi_u - X^1\Sigma_g^+$ absorption of Li_2 and $A^1\Sigma^+ - X^1\Sigma^+$ absorption of LiH.

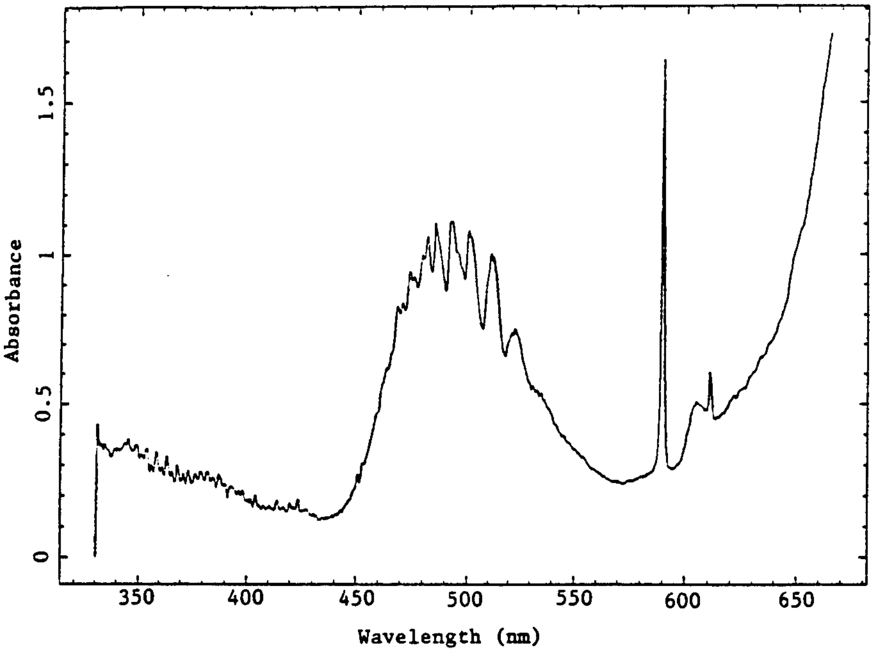

Figure 5.
Absorbance of Na, Li, H Mixture at 1900 K and 1 Atmosphere

ANALYSIS

General references such as Huber and Herzberg's book on Molecular Spectra [4] can be used to give an indication where molecular transitions should occur in the electromagnetic spectrum. However, the absorption spectra obtained in the PSC experiments may have overlapping features contributed by various transitions from the same and different molecules in the chamber. In this mix of transitional spectra, it is more difficult to identify which species are contributing significantly to overall absorption of radiant energy. A more detailed analysis is necessary to identify the contributions potentially useful for the absorption of solar energy in the solar plasma thruster.

To more carefully identify absorption spectra from specific transitions of a diatomic molecule, certain standard techniques of computation, based on molecular theory, have been developed. The method begins with the potential energy curves of the transitions in question. The potential curves are used to generate accurate eigenvalues of the radical Schrôdinger equation. Both the potential curves and the eigenvalues can then be used to calculate the intensities for all rotational-vibrational energy levels of the two electronic states.

To illustrate this, consider the triplet transitions of Li_2 which should appear in the spectra range of the PSC absorption data (330 - 665 nm). Figure 6 shows the potential curves for the $1^3\Sigma_u^+$, $1^3\Pi_g$, $2^3\Sigma_g^+$,and $2^3\Pi_g$ states of Li_2. The lowest state, $1^3\Sigma_u^+$, is an RKR potential curve generated by Zemke and Stwalley [5], which has only eleven bound states.

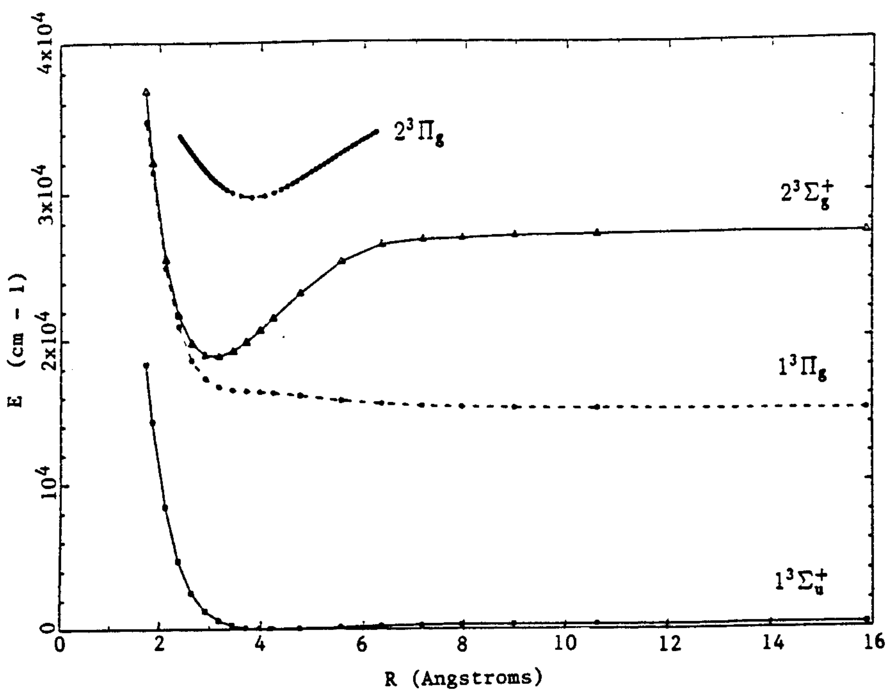

Figure 6.
Potential Curves of Selected Li Triplets [5,6,7]

The $1^3\Pi_g$ and $2^3\Sigma_g^+$ states are from ab initio calculations of Schmidt-Mink, Müller and Meyer [6]. The $1^3\Pi_g$ state is purely repulsive and has no bound states. The $2^3\Sigma_g^+$ state was found to have 54 bound states. The portion of the $2^3\Pi_g$ state shown in Figure 6 is an RKR potential curve generated from molecular constants provided by Xie and Field [7]. It will be necessary to merge the RKR curve with theoretical long range values before eigenvalues can be calculated.

Often when the intensity of molecular transitions are computed, the Franck-Condon Factors (FCFs) are calculated with the assumption that the electronic transition dipole moment can be treated as a constant over the intermolecular distance. For this analysis, the full functions of the electronic transition dipole moments were used to calculate the Franck-Condon Factors, as they depart significantly from a constant at short range. Figures 7 and 8 show the functions used for the $1^3\Sigma_u^+ - 1^3\Pi_g$ and $1^3\Sigma_u^+ - 2^3\Sigma_g^+$ transitions of Li_2, respectively, as calculated by Ratcliff, Fish, and Konowalow [8].

The intensities of the $1^3\Sigma_u^+ - 2^3\Sigma_g^+$ transition of Li_2 are represented by the Franck-Condon factors plotted in Figure 9. Intensities were only calculated for the rotationless transitions from the 11 vibrational states of $1^3\Sigma_u^+$ to the 54 vibrational states of $2^3\Sigma_g^+$. Further calculations will be performed to include rotational energies in the transitions. The intensities can then be binned into small wavelength ranges corresponding to the 578 pixels in the wavelength direction of the PSC image data for comparison with the data.

For bound-free absorption, the intensities are calculated directly in atomic units. Figure 10 shows the computed intensities for the $1^3\Sigma_u^+ - 1^3\Pi_g$ transition at a temperature of 2000 K.

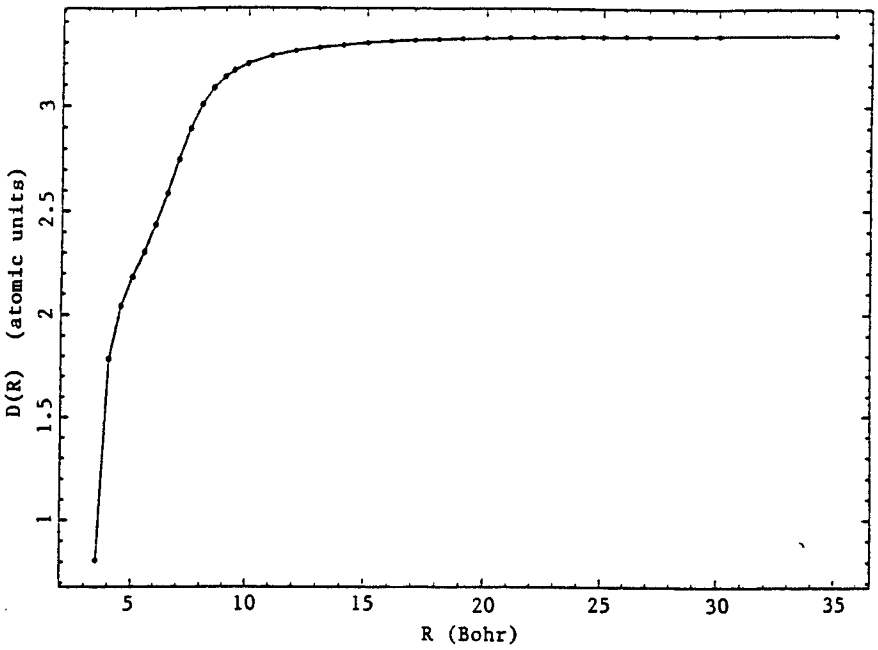

Figure 7.
Electronic Transition Dipole Moment for $1^3\Sigma_u^+ - 1^3\Pi_g$ of Li$_2$ [8]

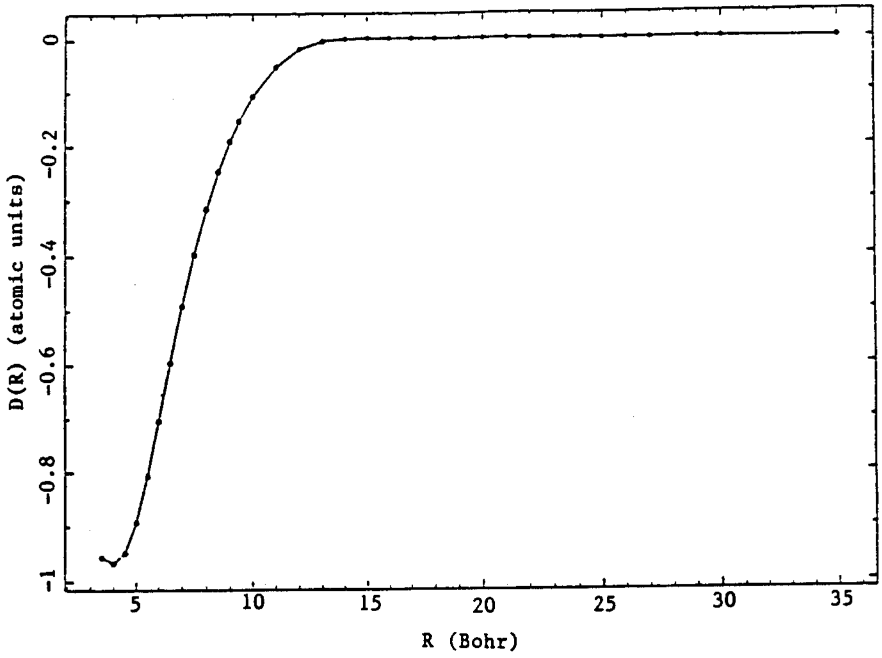

Figure 8.
Electronic Transition Dipole Moment for $1^3\Sigma_u^+ - 2^3\Sigma_g^+$ of Li$_2$ [8]

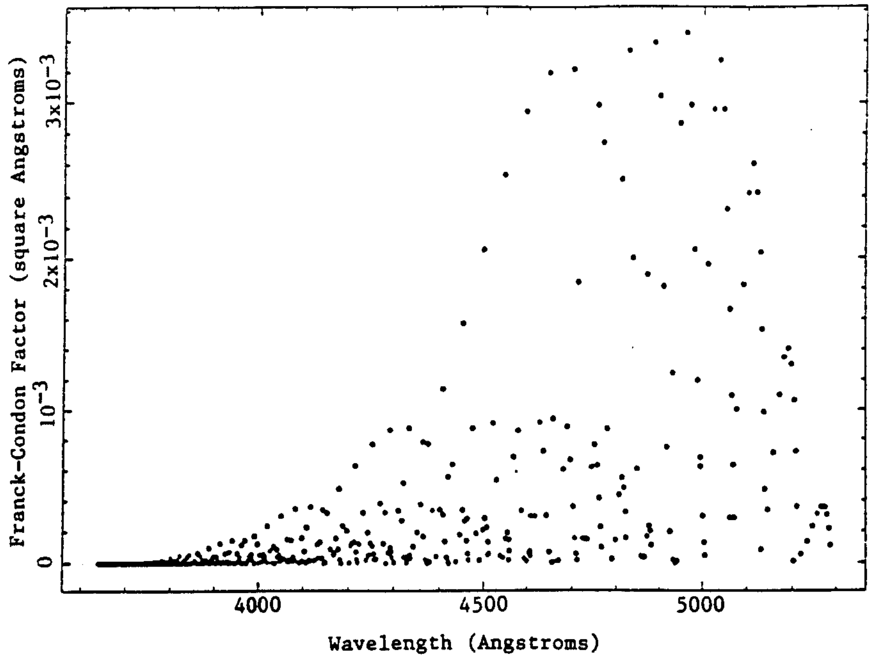

Figure 9.
Rotationless Intensities of the $1^3\Sigma_u^+$ – $2^3\Sigma_g^+$ Transition of Li_2

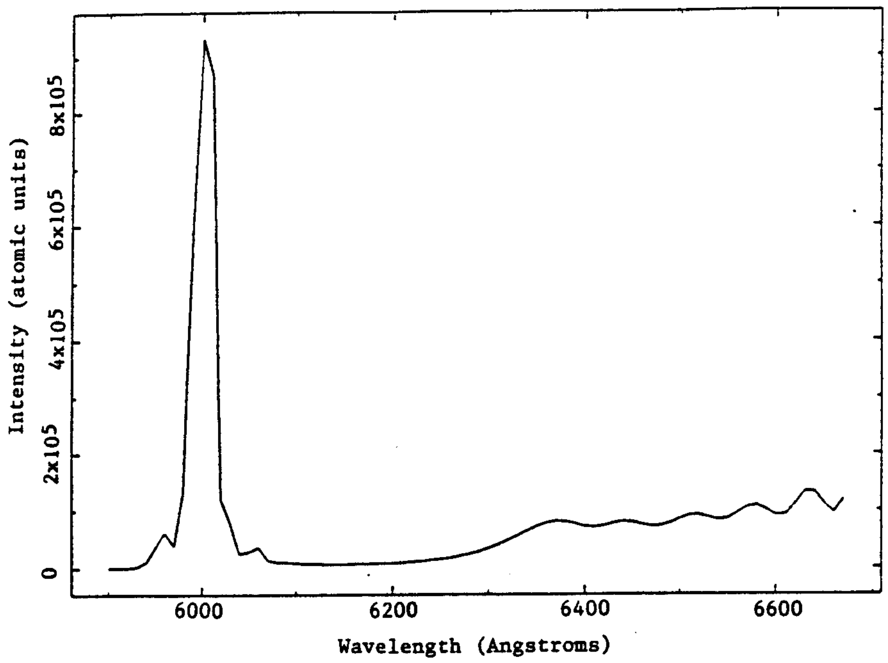

Figure10.
Intensities of the Li_2 $1^3\Sigma_u^+$ – $1^3\Pi_g$ Transition at a Temperature of 2000 K

The jet profiles of absorbance vs. position contained in the PSC image data are not true indicators of the amount of absorbance per unit length occurring in the metal vapor jet. To obtain the radical profile, it is necessary to perform an Abel inversion on the lateral profile. For a measured lateral intensity profile N(x) of a specific wavelength, the inverted profile f(r) is given by

$$f(r) = -\frac{1}{\pi} \int_{r}^{R} \frac{N'(x)dx}{(x^2 - r^2)^{1/2}}$$

where R is the edge of the lateral profile [9]. However, first performing a derivative on the data tends to amplify the effects of noise. A method recommended by Freeman and Katz [10] first rewrites the integral with the derivative on the outside as

$$f(r) = -\frac{1}{\pi r} \frac{d}{dr} \int_{r}^{R} \frac{N(x)xdx}{(x^2 - r^2)^{1/2}}$$

Next, the data is fit to a curve of the form

$$N(x) = \sum_{1=0}^{m} C_1(R^2 - x^2)^i$$

which can be integrated by parts to give the Abel inversion

$$f(r) = \sum_{i} \lambda_i \, C_i \, (R^2 - r^2)^{i-1/2}$$

where

$$\lambda_i = \frac{2^{2i}(i!)^2}{\pi(2i)!}$$

Using the method above, the data in Figure 11 was fit to a curve of eight order. Original lateral data profile represented by small circles was fit to lateral data profile as solid line. Dashed line is Abel inversion multiplied by 100. The resulting Abel inversion has been scaled by a factor of 100 to show the narrower shape of the radical profile as compared with the original data.

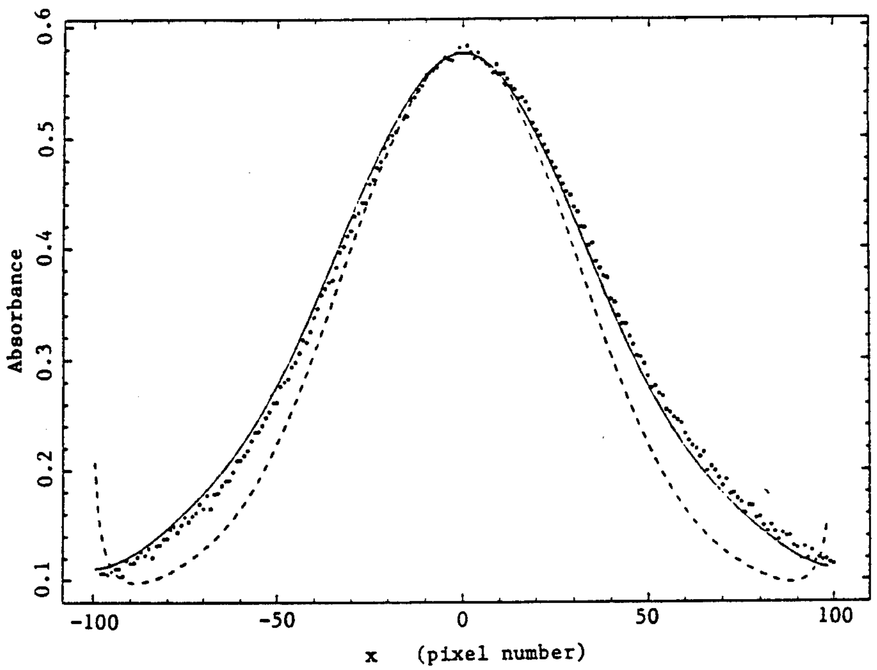

Figure11.
Abel Inversion

CONCLUSIONS

High temperature lithium and sodium experiments in the Plasma Spectroscopy Cell (PSC) have generated a large volume of data which can be analyzed with modern computational techniques. Calculations to date have shown that these techniques can be used to generate intensity profiles that will help to identify the specific molecular transitions observed in the PSC experimental data and thus help to characterize the mix of metal vapors to be used for solar plasma propulsion. Further development of these computational methods will enable the direct comparison of the calculated absorption profiles to the PSC data.

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