THE DISTRIBUTION OF ENERGY IN BIMOLECULAR
CHEMILUMINESCENT REACTIONS INVOLVING HYDROGEN ATOMS

Progress Report

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TECHNICAL PROGRESS REPORT

ABSTRACT OF PROGRESS REPORT

Analysis of spectroscopic observations of the production of photons throughout the visible region from the collision of ~ 5 eV H atoms with a Li/Li₂ crossed beam is described. The present state and future plans for the photon-detection experiments are discussed. Complementary theoretical and non-beam spectroscopic work related to the Li₂H system is also noted.

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INTRODUCTION

Bimolecular chemiluminescent reactions of the form

are being studied in a molecular beam apparatus; * indicates electronic excitation, A and B are atoms or simple groups or a surface. A high-intensity, high-energy (~5 eV) source of H atoms has been developed and characterized. This H atom beam is crossed with relatively slow Li/Li₂ beams of low internal energy or impacts upon Li-coated surfaces. The photons and ions produced are then analyzed and counted. This provides information on the final distribution of energy into translation, electronic, vibrational and rotational degrees of freedom in a variety of reactive and non-reactive processes. This Li₂H system is the simplest experimentally feasible system for which ab initio potential energy surfaces can be (and have been) accurately calculated. These experiments provide definitive examples of simple chemical collisions where the complete final distribution of energy can be determined and will begin to answer the fundamental question: How is energy redistributed in chemical collisions? Moreover, this high information content will in turn provide a much greater challenge to theories seeking to explain the microscopic dynamics of chemical collisions.

For convenience, this progress report will be divided into three sections dealing with progress in the following areas:

- A. The Present State of the Apparatus.
- B. The Photon and Ion Detection Experiments (H + Li/Li₂).
- C. Theoretical and Non-Beam Spectroscopic Results Relevant to the Li₂H System.

A. The Present State of the Apparatus

The supersonic plasma-arc H atom source has now been characterized (C00-2326-9, 11, 12) and operates routinely at total flow rates (~1 millimole/sec) slightly lower and kinetic energies (~5 eV) somewhat higher than estimated in the original proposal for this contract. The (Li/Li₂) supersonic cross beam sources also work about as originally expected (C00-2326-27).

The secondary apparatus for analysis of the Li cross beam sources is now operational. The E-H balance has been constructed to separate the species Li, Li₂(¹Σ_g⁺), Li₂(³Σ_u⁺), Li₃,..., by their different spins, masses and polarizabilities. In addition to mass spectrometric detection already used for this source, we have been using Xe-arc and laser-induced fluorescence detection. For Li₂(³Σ_g⁺), this allowed determination of the internal temperature of the Li₂ beam (T_{vib} = 195°K, T_{rot} = 70°K; C00-2326-27).

B. Photon and Ion Detection Experiments ($H + Li/Li_2$)

In the previous progress report (C00-2326-21), we reported preliminary experiments with the "close" oven configuration in which a small Li/Li_2 oven is located between the skimmer and the velocity-selection magnet. We have continued these experiments, demonstrated that the photon signals are not the result of a number of conceivable spurious causes, begun analysis of the fascinating visible spectra observed and written reports (C00-2326-26 and 33) of our observations.

In summary, we have seen collisional production of Li^* , $Li_2^*(B\ ^1\Pi_u$ and $A\ ^1\Sigma_u^+)$, Li^+ , Li_2^+ , and have not seen $Li_2^*(C\ ^1\Sigma_u^+)$, $LiH(B\ ^1\Pi)$, Li_2^+ or LiH^+ . Moreover, most of the molecular bands are apparently not assignable to any spectrum known to us. Our current feeling is that the most likely candidate for some or all of this unassigned spectrum is $Li_2^+({}^2\Pi_u)$, which is thought (on the basis of theory) to have an intense visible emission in the 4000 - 6700 Å region and we hope to do Li_2^+ spectroscopy in the future. Further work is needed before we can determine conclusively whether $LiH^+(A\ ^1\Sigma^+)$ is present although we suspect it is. It should be noted that our spectroscopic efforts on this contract (see e.g. C00-2326-16, 20, 22, 23, 28, 29, 32) have been invaluable in assigning these spectra and in precisely determining the energetics.

C. Complementary Non-Beam Results (Theoretical and Spectroscopic) Relevant to the Li_2H System.

The ab initio calculations by our collaborators at Argonne (W. England and N. Sabelli) are continuing (see C00-2326-21). The molecule Li_2H has also been observed by Ihle and Wu infrared-spectrometrically, in good agreement with theory.

Extensive A-X emission spectra ($\sim 3000 - 5000 \text{ \AA}$) of all four isotopic variants of LiH have now been reported (C00-2326-28). Additional A-X emission spectra ($\sim 5000 - 9000 \text{ \AA}$) for ^7LiH have been analyzed by our collaborator here at Iowa, Dr. F. Orth. Dr. Lynn Melton (University of Texas - Dallas) has been studying LiH resonance fluorescence spectra under medium resolution, which is helpful in our assignments also. $^7\text{Li}_2$ spectra are available (C-X, B-X and A-X) from the work of Drs. D. Hsu, M. Hessel, P. Kusch and C. R. Vidal. Hence assignment of LiH and Li_2 emission lines in our collision spectra is now straightforward. In addition, total potential curves (and even transition moments) are now available for the relevant LiH states (C00-2326-16, 22, 23, 24, 29, 32) and Li_2 states (C00-2326-13; D Konowalow, private communication; D. Hsu, M. Hessel and C. R. Vidal, private communication; D. Watson, private communication). Thus calculation with reasonable accuracy of previously unobserved lines and their intensities is also now possible; the ^7LiH lifetimes we have calculated are in excellent agreement with experiment (C00-2326-23). Good ab initio calculations also exist for Li_2^+ , but they are not of spectroscopic accuracy (say $< 10 \text{ cm}^{-1}$) at the present time. In these regards, the Li_2H system is now almost unique as to the wealth and quality of the experimental and theoretical information available. Hence we intend to continue with the system despite the difficulties imposed by the small cross sections.

PERSONNEL

1. William C. Stwalley, Principal Investigator and Professor of Chemistry and Physics, University of Iowa. Supervised all aspects of the project. Will continue.
2. Warren T. Zemke, Associate Professor at Wartburg College and Research Associate during summer. Worked principally on theoretical computations of spectra. Will continue summers only.
3. Sze C. Yang, Assistant Professor at National Taiwan University and Research Associate during summer. Worked principally on secondary beam apparatus in summer 1977. Will continue summers only.
4. Kwong C. Li, postdoctoral assistant. Worked briefly in summer 1977 to complete analyses and manuscript of LiH spectra. Will not continue.
5. K. K. Verma, postdoctoral assistant. Worked on primary apparatus principally photon and ion detection experiments with Li/Li₂ beam. Will continue.

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