THE DISTRIBUTION OF ENERGY IN
BIMOLECULAR CHEMILUMINESCENT REACTIONS
- INVOLVING HYDROGEN ATOMS

Progress Report

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TECHNICAL PROGRESS REPORT

ABSTRACT OF PROGRESS REPORT

Preliminary observations of photon and ion production from the collision of ~ 5 eV H atoms with Li and Li₂ and also with a Li-coated surface are described. The present state and future plans for the primary and secondary molecular beam apparatuses are discussed. 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 a relatively slow Li_2 beam of low internal energy and with a Li-coated surface. The photons emitted are then analyzed and counted. This will provide the final distribution of energy into translation, electronic, vibrational and rotational degrees of freedom in a variety of reactive and nonreactive processes. This Li_2H 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 four sections dealing with progress in the following areas:

- A. The Present State of the Apparatus.
- B. The Photon and Ion Detection Experiments ($\text{H} + \text{Li}, \text{Li}_2$).
- C. The Photon and Ion Detection Experiments ($\text{H} + \text{Li-coated surface}$).
- D. Theoretical and Non-Beam Spectroscopic Results Relevant to the Li_2H System.

A. The Present State of the Apparatus

The supersonic plasma-arc H atom source has now been characterized (COO-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 also works about as originally expected.

The photon counting system and 0.5M spectrometer have recently been used by Dr. Robert Wu for low noise, medium resolution observation of the visible spectrum of the "pencil" arc to supplement earlier such observations of the "standard" arc, including 18 lines in the Balmer series of H, and electronic emission bands of H₂, CH, NH, OH, and C₂ with rotational resolution for the hydrides. No Cu (from nozzle erosion) was observed. A variety of temperatures (electronic, vibrational, rotational) may be estimated from the relative linestrengths, but their interpretation in this highly nonequilibrium system is not yet fully understood.

While it is clear that most of the hydrogen in our "pencil" arc beam is in fact atomic hydrogen, it is possible that some fraction of the photon and ion signals reported below may be due to very energetic H₂ molecules, and we are now working to estimate this fraction. It has been shown in several cases, however, that photons and H(2²S) atoms do not contribute.

The secondary apparatus for analysis of the Li cross beam source is nearly operational (power installation is nearly complete). The E-H balance has been constructed and will soon be installed to separate the species Li, Li₂ (¹ Σ_g^+), Li₂ (³ Σ_u^+), Li₃, ..., by their different spins, masses and polarizabilities. In addition to mass spectrometric detection already used for this source, we plan to use laser-induced fluorescence

detection for $\text{Li}_2(X^1\Sigma_g^+)$ at least. This should allow determination of the internal temperature of the Li_2 beam.

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

Using a pencil H arc (~ 5 eV kinetic energy) and a (Li, Li_2) supersonic beam, Dr. Jon Crooks (with assistance at various times from Drs. Kermit Way, Sze Yang, and Robert Wu) has observed a signal of $\sim 10^2 \frac{\text{counts}}{\text{sec}}$, corresponding to a total photon production of $\sim 10^6$ photons/second (normalized to 4π and corrected for detection efficiency). This corresponds to a total photon production cross section of $\sim 10^{-18} \text{ cm}^2$, where it is assumed that only $(H + Li_2)$ contributes (see D. for a discussion of why the $(H + Li)$ photon production cross section should be $\sim 10^{-22} \text{ cm}^2$). Of these photons, $75 \pm 6\%$ arise from $Li(2^2P)$ emission at $6707 \text{ \AA}$ and the $3000 - 4000 \text{ \AA}$ region, where $LiH(A-X)$ emission for ordinary spectral sources is intense, is almost devoid of chemiluminescent photons. It is also strange that more highly excited states of Li are apparently not produced in significant quantity (each such emission is $< 1\%$ of the total). A total of $90 \pm 6\%$ of the signal is in the $6200 - 6900 \text{ \AA}$ range, presumably due to the $Li_2(A-X)$ bands plus the $Li(2^2P \rightarrow 2^2S)$ line mentioned above.

Two construction projects have been undertaken to shed further light on these experiments: 1) a small Li oven for the source chamber has been designed and is now being machined; and 2) a heat pipe scattering chamber for the collision chamber has been designed and is now being machined. Both of these will produce more intense photon emission than is possible with the present Li, Li_2 cross beam. The source chamber oven will operate under non-single collision, non-velocity-selected conditions, but should produce $\sim 10^3 - 10^4$ times more photons and should allow observation with a monochromator of some LiH emission. The collision chamber heat pipe scattering chamber should produce $\sim 10 - 10^2$ times more photons than

the crossed beam under single-collision, velocity-selectable conditions by more fully attenuating the H atom beam. The Li oven itself cannot be used to produce a significantly more intense beam because the rate of nozzle erosion quickly becomes a problem when higher temperatures and pressures are attempted.

We also plan some quick survey experiments of other metals (e.g. Na, K, Mg, Hg) or compounds (e.g. $(CO)_2$, $(NO)_2$) using the source chamber oven idea; indeed it may also be used as a source of useful or new hydride spectra (H_2 , CH, NH and OH spectra have been observed in the pencil arc--presumably due to reaction with background gases, e. g. diffusion pump oil).

The studies of energy-dependence of the photon production at specific wavelengths will be carried out after most promising wavelengths have been clearly identified in the above studies.

Under the same conditions, Dr. Crooks also observed Li^+ and Li_2^+ production (some production of H_2^+ , OH^+ , H_2O^+ and N_2^+ was also observed, presumably from the collision of H atoms in the high energy tail of the velocity distribution with background gas). The Li_2^+ signal was $\sim 5-8\%$ of the Li^+ signal of $\sim 10^5$ ions/second (corresponding to $\sim 10^{-19}$ cm² cross section, assuming production only from Li_2 (see D. below)). No LiH^+ was observed and the upper limit of $\sim 0.02\%$ of the Li^+ signal was determined; this is to be expected since the basically repulsive potential for LiH^+ is only very weakly attractive because of the $Li^+ - H$ long-range polarization and dispersion.

Ab initio calculations (see D. below) suggest $H + Li_2 \rightarrow Li^+ + LiH^-$ may be important, so we hope to search for LiH^- (as well as Li^- , etc.) which might be produced.

C. Photon and Ion Detection Experiments (H + Li-Coated Surface)

The same "pencil" H arc and Li cross beam were employed to carry out surface experiments with photon and ion detection. A tilted roughly room temperature iron or tantalum surface was broadly and continuously coated with Li ($\sim 10^{15} - 10^{17}$ Li atoms/cm²-sec depending on conditions). When the H beam was then directed upon the surface, $\sim 10^6$ additional photons/second were emitted. Since all the H atoms hit the surface, while only $\sim 0.1\%$ of the H atoms hit Li₂ molecules in the cross beam experiments, this indicates that photon-production in H + Li-surface collisions is several orders of magnitude less probable than in H + Li₂ collisions. Observed ion production rates of $\sim 10^6$ additional ions/second imply a similarly lowered probability. In addition, however, the photon emission spectrum was drastically different than for H + Li, Li₂. In particular, the peak emission was in the 4000 - 5000 Å region and was not particularly strong in the 6600 - 6800 Å region where Li(2²P) emission occurs.

D. Theoretical and Non-Beam Spectroscopic Work

The initial theoretical work by our collaborators at Argonne (A. C. Wahl, W. England, and N. Sabelli) has now been published (J. Chem. Phys., 63, 4596 (1975)), although further work, especially on other geometries, is in progress. These calculations indicate that it is likely that a majority of reactive collisions of $H + Li_2$ should lead adiabatically to $Li + LiH(X^1\Sigma^+)$, especially at low energies (in agreement with the observations of Lee, Gordon and Herschbach for $H + M_2$, where M is a heavier alkali than Li and consistent with our observations of small photon production cross sections). A nitrogen-pumped tunable dye laser has been recently purchased from departmental funds and we are now considering the feasibility of direct observation of $LiH(X^1\Sigma^+)$ using laser-induced fluorescence. A second process (but of much lower probability) suggested by these calculations is $H + Li_2 \rightarrow Li^+ + LiH^-$ and we plan to look for LiH^- to see if this process is indeed responsible for the observed Li^+ . Estimates of photon and ion production cross sections involving nonadiabatic interactions are planned following the $H + Li$ calculations mentioned below and the provision of surface geometries other than C_{2v} and $C_{\infty v}$.

Extensive emission spectra of all four isotopic variants of LiH have been observed and assigned (C00-2326-14). Potential energy curves for the X and A states have been obtained by a combination of experimental and theoretical techniques to complement the earlier determination of the B state potential curve. These curves have been used to calculate the transition probabilities for the A-X bands of LiH which we hope to observe in our chemiluminescent beam experiments. The accuracy of these calculations is felt to be $\sim 10\%$ and this estimate is confirmed by the essentially perfect agreement between our lifetime

calculations based on these transition probabilities and the recent experiments of Dagdigan (J. Chem. Phys., 64, 2609 (1976)) and Melton (J. Chem. Phys., 64, 2692 (1976)). The agreement between our calculated radiative lifetime and these experimental lifetimes implies predissociation of the A state is very slow ($> 10^{-7}$ sec) and thus the cross section for the reverse process (A state Feshbach resonances in $H + Li$ collisions) must be very small. Dr. Jon Crooks has considered this in detail and obtained an upper bound of 10^{-22} cm^2 for this process. This in turn implies other cross sections such as for $H + Li \rightarrow H^- + Li^+$ or $H + Li(2^2P)$, which both depend on the nonadiabatic interaction of the X and A states, should be very small. More quantitative coupled channel quantum scattering calculations are now beginning.

Finally, an improved potential energy curve and dissociation energy for $Li_2(X^1\Sigma_g^+)$ has been obtained (COO-2326-13).

Personnel*

1. William C. Stwalley, Principal Investigator and Professor of Chemistry, University of Iowa (on leave 8/1/75 - 7/31/76). Supervised all aspects of the project - formally until 8/1/75, informally afterward. Will continue and resume formal supervision 8/1/76.
2. H. Bruce Friedrich, Acting Principal Investigator (8/1/75 - 7/31/76) and Professor of Chemistry, University of Iowa. Supervised all aspects of the project while Stwalley was on leave. Will not continue after 8/1/76.
3. Sze Yang, Assistant Professor at National Taiwan University and Research Associate during summer. Worked principally on secondary beam apparatus in summer 1975. Will continue summers only.
4. Kermit Way, Assistant Professor at Drake University and Research Associate during summer. Worked principally on primary apparatus, especially hydrogen atom beam source and photon detection. Will continue summers only.
5. Jon Crooks, postdoctoral assistant. Worked on primary apparatus, principally photon and ion detection experiments with Li beam and Li-coated surface. Will continue.
6. Robert Wu, postdoctoral assistant. Worked principally on spectrum of hydrogen arc, assembly of secondary apparatus, and assembly of tunable dye laser for Li beam analysis. Will continue.
- * Dr. Warren T. Zemke and Mr. Kwong C. Li, supported in earlier years, are no longer doing research related to this project. They are, however, still contributing to the preparation of manuscripts including portions of their former research. In addition collaborative efforts with Dr. R. Velasco (Institute of Optics, Madrid) on LiH spectra and with Drs. A. C. Wahl, N. Sabelli, and W. England (Argonne National Lab) on the LiH potential surfaces should also be noted, although they were not directly supported by this contract.

Running List of Publications for AT(11-1)-2326, April 1976.

- C00-2326-1. W. C. Stwalley, Initial Summary for AT(11-1)-2326.
- C00-2326-2. W. C. Stwalley, K. R. Way and R. Velasco, "The Dissociation Energies of ^7LiD ", J. Chem. Phys., 60, 3611 (1974).
- C00-2326-3. W. C. Stwalley, Progress Report for AT(11-1)-2326 for the period May 1, 1973 - April 30, 1974.
- C00-2326-4. W. C. Stwalley, K. R. Way, K. C. Li and W. T. Zemke, "The Potential Energy Curves for the $X\ ^1\Sigma^+$, $A\ ^1\Sigma^+$ and $B\ ^1\Pi$ States of LiH ", presented at the 29th Annual Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1974.
- C00-2326-5. W. C. Stwalley, First Renewal Summary for AT(11-1)-2326.
- C00-2326-6. W. C. Stwalley and W. T. Zemke, "Selected Bibliography on Ground and Excited State Potential Curves of H_2 , LiH and Li_2 ".
- C00-2326-7. K. R. Way, S. C. Yang and W. C. Stwalley, "Progress Report on Development of a Superthermal High-Intensity Source of Hydrogen Atoms", presented at the Conference on the Dynamics of Molecular Collisions, Santa Cruz, California, July 1974.
- C00-2326-8. W. C. Stwalley, Progress Report for AT(11-1)-2326 for the period May 1, 1974 - April 30, 1975.
- C00-2326-9. K. R. Way, S. C. Yang and W. C. Stwalley, "A High Intensity Superthermal Source of Hydrogen Atoms", Proc. Ninth Intl. Conf. on Physics of Electronic and Atomic Collisions (Univ. Wash. Press, Seattle, 1975), p. 957.
- C00-2326-10. W. C. Stwalley, J. B. Togeas, K. R. Way, K. C. Li and T. R. Proctor, "Total Scattering Cross Sections Calculated from Nonscattering Information", Proc. Ninth Intl. Conf. on Physics of Electronic and Atomic Collisions (Univ. Washington Press, Seattle, 1975), p. 1005.
- C00-2326-11. K. R. Way, S. C. Yang and W. C. Stwalley, "Documentation of the Operation of an Arc-Heated Hydrogen Source".
- C00-2326-12. K. R. Way, S. C. Yang and W. C. Stwalley, "An Arc-Heated, High Intensity Source of Hydrogen Atoms", submitted to Rev. Sci. Instrum.
- C00-2326-13. W. C. Stwalley, "The Dissociation Energy of $^7\text{Li}_2$ ", J. Chem. Phys., in press.

Running List of Publications (cont'd)

- C00-2326-14. K. C. Li and W. C. Stwalley, "New RKR Potential Curves from Emission Spectra of Lithium Hydride", to be presented at the 31st Annual Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1976.

Annual List of Publications for AT(11-1)-2326, April, 1976.

- C00-2326-8. W. C. Stwalley, Progress Report for AT(11-1)-2326 for the period May 1, 1974 - April 30, 1975.
- C00-2326-9. K. R. Way, S. C. Yang and W. C. Stwalley, "A High Intensity Superthermal Source of Hydrogen Atoms", Proc. Ninth Intl. Conf. on Physics of Electronic and Atomic Collisions (Univ. Washington Press, Seattle, 1975), p. 957.
- C00-2326-10. W. C. Stwalley, J. B. Togeas, K. R. Way, K. C. Li and T. R. Proctor, "Total Scattering Cross Sections Calculated from Nonscattering Information", Proc. Ninth Intl. Conf. on Physics of Electronic and Atomic Collisions (Univ. Washington Press, Seattle, 1975), p. 1005.
- C00-2326-11. K. R. Way, S. C. Yang and W. C. Stwalley, "Documentation of the Operation of an Arc-Heated Hydrogen Atom Source".
- C00-2326-12. K. R. Way, S. C. Yang and W. C. Stwalley, "An Arc-Heated, High Intensity Source of Hydrogen Atoms", submitted to Rev. Sci. Instrum.
- C00-2326-13. W. C. Stwalley, "The Dissociation Energy of $^7\text{Li}_2$ ", J. Chem. Phys., in press.
- C00-2326-14. K. C. Li and W. C. Stwalley, "New RKR Potential Curves from Emission Spectra of Lithium Hydride", to be presented at the 31st Annual Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1976.