MASTER

THE DISTRIBUTION OF ENERGY IN BIMOLECULAR
CHEMILUMINESCENT REACTIONS INVOLVING HYDROGEN ATOMS

Final Report

William C. Stwalley
Department of Chemistry
University of Iowa
Iowa City, Iowa 52242

May 1, 1978 - April 30, 1979

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared for the United States Department of Energy under Contract EY-76-S-02-2326.*002

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EB

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

FINAL TECHNICAL REPORT

MAILED

ABSTRACT OF FINAL REPORT

Analysis of spectroscopic observations of the production of visible and ultraviolet photons from the collision of ~5 eV H atoms with a Li/Li₂ crossed beam and with O₂ and H₂O crossed beams is described. Complementary theoretical and non-beam spectroscopic work related to the Li₂H system is also noted.

LEGAL NOTICE

"This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Department of Energy, nor any person acting on behalf of the Department:

- A. makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained, in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, 'person acting on behalf of the Department' includes any employee or contractor of the Department, or employee of such contractor, to the extent that such employee or contractor of the Department, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Department or his employment with such contractor."

INTRODUCTION

Bimolecular chemiluminescent reactions of the form

have been 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 has been crossed with relatively slow Li/Li₂, O₂ or H₂O beams of low internal energy or has been impacted upon Li-coated surfaces. The photons and ions produced were then analyzed and counted. This provided information on the final distribution of energy into translational, electronic, vibrational and rotational degrees of freedom in a variety of reactive and non-reactive processes.

The Li₂H system is the simplest experimentally feasible system for which ab initio potential energy surfaces can be (and have been) accurately calculated. These experiments could ultimately provide definitive examples of simple chemical collisions where the complete final distribution of energy can be determined and begin to answer the fundamental question: How is energy redistributed in chemical collisions? Moreover, this high information content would in turn provide a much greater challenge to theories seeking to explain the microscopic dynamics of chemical collisions. Unfortunately, the cross section for photon production was only on the order of 10⁻¹⁹ cm², and thus its determination experimentally difficult. Also the observed spectra in the case of the Li₂H system included previously unobserved spectra which may be due to Li₂⁺. Until the Li₂⁺ spectrum is analyzed in other experiments, it is likely the promise of detailed dynamic information will remain unfulfilled.

However, to quickly demonstrate the power of the present approach

despite the difficulties for Li_2H , we have also recently examined the reactions:

These experiments are relatively much easier; they have reasonable cross sections ($\sim 10^{-17} \text{ cm}^2$) and their emission is localized in a very small portion of the visible spectrum.

For convenience, this report is divided into four sections dealing with 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. Theoretical and Non-Beam Spectroscopic Results Relevant to the Li_2H System.
- D. The Photon Detection Experiments and Analysis ($\text{H} + \text{O}_2, \text{H}_2\text{O}$).

A. The Present State of the Apparatus

The supersonic plasma-arc H atom source has previously 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 O₂ and H₂O sources are simple constricted copper tubes.

The secondary apparatus for analysis of the Li cross beam sources is also operational. The E-H balance has been constructed 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 have been using Xe-arc and laser-induced fluorescence detection. For Li₂(¹ Σ_g^+), this allowed determination of the internal temperature of the Li₂ beam ($T_{\text{vib}} = 195$ °K, $T_{\text{rot}} = 70$ °K; C00-2326-27). We hope to carry out a determination of the Li₂⁺ spectrum in future work on a different contract using the same Li/Li₂ source.

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

Previously (C00-2326-21 and 34), we reported 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^* ($C^1\Pi_u$), LiH ($B^1\Pi$) 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. Further work is needed before we can determine conclusively whether LiH^* ($A^1\Sigma^+$) is present although we strongly 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, 35, 36) 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.

Extensive A-X emission spectra ($\sim 3000\text{-}5000\text{ \AA}$) of all four isotopic variants of LiH have previously been reported (C00-2326-28). Additional A-X emission spectra ($\sim 5000\text{-}9000\text{ \AA}$) for ^7LiH have been analyzed by our collaborator here at Iowa, Dr. F. Orth (J. Mol. Spectrosc. 76, 17 (1979); C00-2326-36). 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. In addition Dr. Verma has recently seen HeNe and Kr^+ laser excited fluorescence in A-X Li_2 up to very high vibrational levels. 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 by examining the Li_2^+ spectrum. We note in passing that much of this lithium spectroscopy is potentially applicable to diagnostics of "lithium fall" and similar concepts for inertial confinement fusion reactors.

D. Photon Detection and Analysis for $H + O_2$ and $H + H_2O$.

In the final year of the contract, we studied the reactions (COO-2326-37):

by observing the uv fluorescence. Figure 1 shows the O-O band of the readily observable $A^2\Sigma^+ - X^2\Pi$ bands from $H + O_2$ and $H + H_2O$ collisions. Such data can be easily analyzed to obtain rotational temperatures as shown in Figure 2 for O_2 and summarized in Table I. Note the relationship between increased average kinetic energy and rotational and also vibrational temperatures. Figure 3 shows that OH^* formation is in fact quite reasonable for 5 eV H atoms.

Rotational distributions for $H + H_2O$ relative to O_2 are given in Figure 4. Note that the distribution is anomalous, i.e. not fit by a rotational temperature. This is not surprising since photodissociation, electron impact, and metastable atom impact on H_2O also yield anomalous OH^* rotational distributions (see COO-2326-37 for references). The $H + H_2O$ energetics, shown in Figure 5, indicate OH^* production is favorable at ~5 eV only if H_2 is formed simultaneously. This constraint plus details of the excited H_2O potential surfaces may ultimately explain this rotational anomaly.

Figure 1.

Spectra of OH molecule (O-O band) from the source chamber in Hydrogen Beam Experiment:

- (a) from standard arc close to nozzle (without water)
- (b) from pencil arc close to skimmer (without water)
- (c) from cross beam of hydrogen and water (close to skimmer)

Figure 2.

8-G79-365

Table I.

CONDITION	$\overline{\text{KE}}_{\text{H}}$ (eV)	T_{VIB} (K)	T_{ROT} (K)
STANDARD ARC	~2	4000	6500
PENCIL ARC	~5	8000	10000

Figure 3.

Figure 4.

Figure 5.

PERSONNEL

1. William C. Stwalley, Principal Investigator and Professor of Chemistry and Physics, University of Iowa. Supervised all aspects of the project.
2. Warren T. Zemke, Associate Professor at Wartburg College and Research Associate during summer. Worked principally on theoretical computations of spectra.
3. K. K. Verma, Postdoctoral Associate. Worked on primary apparatus principally photon and ion detection experiments with Li/Li₂ beam and with O₂ and H₂O beams.

FINAL LIST OF PUBLICATIONS FOR EY-76-S-02-2326.*002, April 30, 1979.

- 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. 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 Non-Scattering 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", Rev. Sci. Instrum. 47, 1049 (1976).
- C00-2326-13. W. C. Stwalley, "The Dissociation Energy of $^7\text{Li}_2$ ", J. Chem. Phys. 65, 2038 (1976).
- C00-2326-14. K. C. Li and W. C. Stwalley, "New RKR Potential Curves from Emission Spectra of Lithium Hydride", presented at the 31st Annual Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1976.

FINAL LIST OF PUBLICATIONS (cont.)

- C00-2326-15. W. C. Stwalley, Progress Report for AT(11-1)-2326 for the period May 1, 1975 - April 30, 1976.
- C00-2326-16. W. T. Zemke, W. C. Stwalley, K. C. Li, K. R. Way and T. R. Proctor, "The Potential Energy Curves of the $X^1\Sigma^+$ and $A^1\Sigma^+$ States of LiH", J. Chem. Phys. 66, 5412 (1977).
- C00-2326-17. K. C. Li, "Lines in the Spectrum of ^6LiH (2985 - 5158 Å)".
- C00-2326-18. K. C. Li, "Lines in the Spectrum of ^6LiD (3086 - 5156 Å)".
- C00-2326-19. K. C. Li, "Lines in the Spectrum of ^7LiH (4728 - 5298 Å)".
- C00-2326-20. K. C. Li and W. C. Stwalley, "Assigned Lines of the $A^1\Sigma^+$ - $X^1\Sigma^+$ Bands of ^6LiH , ^6LiD , ^7LiH and ^7LiD ".
- C00-2326-21. W. C. Stwalley, Progress Report for EY-76-S-02-2326.*000 for the period May 1, 1976 - April 30, 1977.
- C00-2326-22. W. T. Zemke and W. C. Stwalley, "Radiative Transition Probabilities for the $A^1\Sigma^+$ - $X^1\Sigma^+$ Bands of ^7LiH ", J. Chem. Phys. 68, 4619 (1978).
- C00-2326-23. W. T. Zemke, J. B. Crooks and W. C. Stwalley, "Radiative and Nonradiative Lifetimes for Vibrational Levels of the $A^1\Sigma^+$ State of ^7LiH ", J. Chem. Phys. 68, 4628 (1978).
- C00-2326-24. W. T. Zemke and W. C. Stwalley, "Tabulated Radiative Transition Probabilities for the $A^1\Sigma^+$ - $X^1\Sigma^+$, $B^1\Pi$ - $X^1\Sigma^+$, and $B^1\Pi$ - $A^1\Sigma^+$ Bands of ^7LiH ".
- C00-2326-25. W. T. Zemke and W. C. Stwalley, "Transition Probabilities for the $A^1\Sigma^+$ - $X^1\Sigma^+$ Bands of LiH", Abstracts of the Tenth Midwest Theoretical Chemistry Conference, Argonne National Laboratory, May 27-28, 1977, p. 42.
- C00-2326-26. W. C. Stwalley, K. R. Way, S. C. Yang, J. B. Crooks, and C. Y. R. Wu, "Atomic Beam Collisions in the Superthermal (1-10 eV) Range", in H. J. Ache, editor, Abstracts of the Ninth International Hot Atom Chemistry Symposium, Blacksburg, Virginia, September 18-23, 1977, p. 8.
- C00-2326-27. C. Y. R. Wu, J. B. Crooks, S. C. Yang, K. R. Way and W. C. Stwalley, "A Li/Li₂ Supersonic Nozzle Beam", Rev. Sci. Instrum. 49, 380 (1978).
- C00-2326-28. K. C. Li and W. C. Stwalley, "The $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ Bands of the Isotopic Lithium Hydrides", J. Mol. Spectrosc. 69, 294 (1978).
- C00-2326-29. W. T. Zemke, K. R. Way and W. C. Stwalley, "Radiative Transition Probabilities for the $B^1\Pi$ - $X^1\Sigma^+$ and $B^1\Pi$ - $A^1\Sigma^+$ Bands of ^7LiH ", J. Chem. Phys. 69, 402 (1978).

FINAL LIST OF PUBLICATIONS (cont.)

- COO-2326-30. W. C. Stwalley, W. T. Zemke, K. R. Way, K. C. Li and T. R. Proctor, "Erratum: The Potential Energy Curves of the $X^1\Sigma^+$ and $A^1\Sigma^+$ State of LiH [J. Chem. Phys. 66, 5412 (1977)]", J. Chem. Phys. 67, 4785 (1977).
- COO-2326-31. K. C. Li and W. C. Stwalley, "Mass-Reduced Quantum Numbers: Application to the $X^1\Sigma^+$ State of the Isotopic Lithium Hydrides", J. Chem. Phys. 70, 1736 (1979).
- COO-2326-32. W. T. Zemke and W. C. Stwalley, "Radiative Lifetimes for Vibrational Levels of the $B^1\Pi$ State of ^7LiH ", J. Chem. Phys. 69, 409 (1978).
- COO-2326-33. J. B. Crooks, K. R. Way, S. C. Yang, C. Y. R. Wu and W. C. Stwalley, "Photon and Positive Ion Production from Collisions of Superthermal Hydrogen Atoms with Lithium Atoms and Molecules", J. Chem. Phys. 69, 490 (1978).
- COO-2326-34. W. C. Stwalley, Progress Report for EY-76-S-02-2326.*001 for the period May 1, 1977-April 30, 1978.
- COO-2326-35. W. T. Zemke and W. C. Stwalley, "Lithium Hydride Revisited", Abstracts of Papers of the 90th Session of the Iowa Academy of Sciences, Cedar Falls, Iowa, April 21-22, 1978.
- COO-2326-36. F. B. Orth and W. C. Stwalley, "Lines in the Spectrum of ^7LiH (5177-8643 Å)".
- COO-2326-37. K. K. Verma and W. C. Stwalley, "The Production of OH ($A^2\Sigma^+$) from Collisions of Superthermal Hydrogen Atoms with H_2O and O_2 ", Abstracts of the VIIth International Symposium on Molecular Beams, Riva del Garda, Trento, Italy, May 28-June 1, 1979.
- COO-2326-38. W. C. Stwalley, Final Report for EY-76-S-02-2326.*002 (this report).