DOE/ER/13332--T5

A Spectroscopic Study of Hydrogen Atom and Molecule Collisions

Progress Report for 1994-1997

John F. Kielkopf
Department of Physics
University of Louisville

January 15, 1997

DISCLAIMER

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

Contents

1 Introduction

In this project the fundamental processes which occur in low energy collisions of excited states of atomic hydrogen with other atoms and ions are being studied with optical, vacuum ultraviolet, and laser spectroscopy. This report covers the period from 1994 to early 1997. We begin here with a brief description of the status of the work at the beginning of this project period, then discuss the goals for this period, our results, and the work in progress now.

As the accompanying renewal proposal describes in more detail, the purpose of our work is to understand low energy atom-atom collisions during which light is emitted or absorbed. Because of their fundamental character, such collisions of atomic hydrogen could play a central role if experimental data could be compared with *a priori* theory. Some interactions involving atomic hydrogen can be calculated very accurately, namely those of H_2, H_2^+, H_3, and H_3^+, and simpler diatomic radicals including OH, CH, and NH. The primary difficulty from the experimental side has been the development of techniques to observe neutral atomic hydrogen interactions at densities high enough for spectral line broadening effects to be observable.

When this project began, the highest densities which were feasible were those produced by continuous sources such as a Wood's tube, in which the H_2 molecule was dissociated in a discharge from which atomic H could be extracted. When R. W. Wood discovered this source, he noted its "fiery purple" color because of the dominance of atomic emission over molecular emission under restrictive source conditions. Typically such a source operates at a few Torr (*e.g.* $\approx 10^{16}$ atoms cm^{-3}). With wet H_2 and treated discharge tube walls to inihibit atom-atom recombination, the dissociation can be alomost total, but this density is low compared to what is typically needed for line broadening experiments. As improved theories of the far wing profile of the resonance line of atomic H were developed, it became apparent that densities of the order of $\approx 10^{18}$ atoms cm^{-3} would be needed for some of the more interesting regimes, and various methods were explored experimentally to see what would be practical for line shape measurements. At the beginning of this project period, we had identified the laser-produced plasma in H_2 as a very promising source. It was bright, permitting emission spectroscopy, but could be observed with time resolution and offered the possibility of laser fluorescence studies in the"post-plasma" phase before atom-atom recombination occured. The theory of line broadening had been applied to some of the possible contributing quasimolecular states of colliding H atoms. We had also identified what seemed to be line broadening effects in an astrophysical laboratory – the atmospheres of those white dwarf stars that are rich in atomic H.

We were working on the formation and dissociation of OH, in particular to detect the structured continua which would be emitted following selective excitation of bound excited electronic states. We had found that OH could be produced by photodissociation of H_2O with a pulse from an ArF laser at 1930 Å, and laser-induced fluorescence from the $A \rightarrow X$ band had been was used to characterize the rotation-vibration state of the dissociation products. Experiments with H_2O added to a laser-produced plasma were being conducted to see when and in what state OH appeared.

Following our discovery that Al could be stimulated to emit laser radiation in a resonance line when a solid Al surface in the presence of H_2 is illuminated with light from an ArF laser, we were also investigating excitation processes in H_2 which followed from its interaction with 1930 Å light. One result was that it appeared that the H^- ion might be important, interacting with Al^+ through a charge neutralization collision to produce an excited state of atomic Al.

Some of the goals of the project during this period were to develop the experimental work on the laser-produced plasmas as a source of atomic H and OH, to make a definitive measurement of the Lyman α wing above 1215 Å for comparison with a theoretical model, to develop the theory of the Lyman α line to include all possible contributing molecular states, and to study H^- formation in H_2 illuminated by 1930 Å light. Other work is now underway on the detection of OH continua, a search for H_3^+ emission from the laser-produced plasmas, a study of Lyman α for initial densities above 10^{19} atoms cm^{-3}, and the measurement of the broadening of the resonance lines of atomic Na by H. The progress which has been made is described in the following sections.

2 Laser-Produced Plasmas in H_2, $H_2 + H_2O$, and $H_2 + Na$

The source of atomic H for these experiments is the plasma produced when an energetic laser is focused into H_2. An immediate goal was to confirm a model with diagnostics of the plasma and the post-plasma gas. Much work has been done on laser-produced plasmas with higher energy pulses than ours, both for x-ray laser generation and for laser fusion experiments. Recently, there has also been interest in phenomena on a picosecond time scale. However, our system is optimized for the production of neutral and ionized hydrogen atoms at low temperature, and falls in a range of laser intensities and gas pressures for which there is little data. Although theories of blast shock wave generation are appropriate to explain the formation of the plasma, their application is made difficult because the shock speed attenuates rapidly, and molecular dissociation is a factor. During the time the laser is on, the role of self-focusing is on a microscopic spatial scale that is not easily observed.

The new experiments produced high quality images of the plasma with a spatial resolution of 9 μm, time-resolved schlieren images of the shock front for the first few μs after breakdown, and shadowgraphic images of the cooling gas for up to several hundred μs. We also obtained spectra of Lyman α and its extended wing in the vacuum ultraviolet, and of the Balmer series and bremsstrahlung in the visible with a time resolution of a few ns. The Balmer β profiles were spatially resolved as well, which led to the detection of emission from the expanding cylindrical shell of excited atomic H that was predicted by shock wave theory and Saha ionization-equilibrium.

This work demonstrates that it is possible to model the initial luminous phase of the plasma with a simple blast wave theory, at least when the shock front speed is several times the ambient sound speed in H_2. At later times, as the shock front slows, the theory remains valid but numerical methods of solving the problem will require development. Complicating factors include the change from cylindrical to spherical symmetry as the front expands beyond the length of the breakdown region, and, as noted, the role of dissociation of H_2 in dissipating shock energy. The character of the post-shock gas can be measured experimentally with spectroscopic diagnostics of temperature and electron density, and with schlieren diagnostics of refractive index. An example of that is an analysis of the emission in the vacuum ultraviolet during an early phase of the plasma, 20 to 100 ns after breakdown. At that time, for an initial H_2 density of 2×10^{19} cm^{-3}, the densities of H^+ and H are both greater than 10^{18} cm^{-3} in the shell surrounding the optical axis where $n = 2$ states of H, the upper states of the Lyman-α line, are most populated.

Experiments were carried out to understand how the source might be used for work on systems other than H-H collisions. For example, we introduced H_2O as the vapor off of ice in controlled fractions of a static fill with He, and then measured the emission spectrum and laser-induced fluorescence from

OH as a function of time after the laser shot which produced the plasma. The fluorescence was compared with observations of OH produced by photodissociation of H_2O in the 1930 Å ArF laser pulse to probe the vibrational and rotational population distribution. OH appeared 10 μs following breakdown. The experiments were very promising in that OH could be detected through its emission in the $A \rightarrow X$ bands for more than 60 μs following the production of the plasma. Even against the emission background it was possible to use $A \rightarrow X$ laser fluorescence spectroscopy to measure the ground state rotational temperature. A spatial scan of the probe dye laser across the volume surrounding the laser-produced plasma indicated qualitatively that the OH was localized off-axis. Followup experiments with H_2 and a quantitative measurement of the radial distribution are planned.

In another experiment we measured the spatial distribution of excited states of Na in H_2 created by a laser-produced plasma in front of a solid Na target. The residual defocused light at 1064 nm from the breakdown Nd:YAG laser vaporized a small amount of Na from the target. The vapor diffused through the chamber to provide a background of Na in the H_2 fill gas, and the H-Na plasma was observed by spectroscopic imaging. As expected, the yellow D-lines appeared in the heated region (about 1 cm in diameter) near the laser axis, excited by the passage of the shock front. The laser ablation technique was too efficient in this trial, and the D-lines were self-reversed because the Na density in the chamber was too high. This will be reduced by using a separate Na reservoir heated just sufficiently to seed low density Na in to the cell. Experiments of this type in which the Na spectrum is measured in emission or fluorescence are expected to yield line profiles for Na transitions broadened by atomic H.

In summary, experimental work on the laser-plasma atomic H source has yielded

- a schlieren measurement of shock propagation
- confirmation of cylindrical blast wave theory for the plasma model
- detection of very unusual self-focusing phenomena at the onset of the plasma
- observation of the evolution of the plasma long after it is self-luminous, including a change from spheroidal to toroidal symmetry with flow back toward the excitation laser

- observation of emission and absorption by OH and Na intentionally added to the post-plasma gas

3 Lyman α Wing

We have expected for many years that the resonance line of atomic H would have a complex wing due to collisions with other H atoms or with H^+ ions, although the theory was incomplete and experimental confirmation was illusive. Gradually, improvements to the unified theory of spectral line profiles applied to the Lyman α line produced theoretical spectra that were remarkably similar to the spectra of selected white dwarf stars. The success of that comparison led to the development of techniques to determine temperatures of white dwarf atmospheres, and encouraged a search in the laboratory for supporting observations. During this project period we repeated previous observations of the emission spectra of the laser-produced plasmas in the vacuum ultraviolet with better time resolution and improved signal-to-noise ratio. In the meantime, in collaboration with Dr. Nicole Allard (CNRS Institut d'Astrophysique) we completed a thorough review of the theory, and calculated complete profiles over a density range for N_H and N_{H^+} appropriate for the plasmas, based on the improved models and diagnostics. The comparison of experiment and theory in the long-wavelength wing of Lyman α for densities of the order of 10^{18} atoms or ions cm^{-3} confirmed the identification of the white dwarf spectral features, and the basic character of the theoretical spectra.

Work continued in collaboration with Dr. Allard on the development of a more complete theory which would include the effect of the variation of the radiative dipole moment during collision. With this, the influence of otherwise forbidden components on the transition profile could be included. Fairly dramatic effects were anticipated because even for the allowed transitions the variation of the dipole moment with R may change the transition probability by a factor of 2 or more. Furthermore, in the case of broadening of excited H by other neutral H atoms, there are many molecular states which may contribute to the profile in emission, some of which are asymptotically forbidden. A complete calculation of Lyman α with many of these states included has now been made.

The result of the combined experimental and theoretical efforts is the identification of several features in the Lyman-α spectrum as due to free-free transitions of $H(n = 2) + H$ and $H(n = 2) + H^+$. Calculations are underway on other transitions and higher densities of perturbers.

In summary, the work on Lyman α led to

- the development of the theory and practical methods of computing the Lyman-α profile for simultaneous broadening by H and H^+
- development of theoretical and computational methods to include the variation of the transition probability with interatomic separation
- successful comparisons of theory to the observations in the laboratory and to spectra of hydrogen-rich white dwarf stars

4 Line Shape Theory

In support of experimental measurements of the broadening of spectral lines by atomic H collisions, notably Na as described above, we have been working on improved calculations of the width, shift and asymmetry of spectral lines in non-resonant cases. In collaboration with Dr. Warren Kreye (Wright State University) we have used pseudopotential methods to compute long range excited state interactions as would be needed in line core calculations. The case of K-Ar was chosen to test some of the methods since accurate width and shift measurements are available for several temperatures. Our work uses a quantum theory of spectral line broadening and realistic potentials to compute line shifts and widths with non-adiabatic theory, including the effects of state degeneracies and inelastic collisions. The theory is based on the fundamental work of Baranger, and the elegant developments of Mies and Julienne. For the case of the 7s state of K colliding with Ar, we were able to demonstrate that while inelastic effects on line width were small, they were not negligible, and they increased with relative velocity of the colliding atoms. Both non-adiabatic contributions to the shift, and inelastic and non-adiabatic contributions to the width, were large enough to be detectable in precision measurements. A variation of potential parameters in the context of the quantum lineshape calculation reproduced the experiments in this instance. The success of this theoretical work suggests that a comparison of an exact line core calculation with a quantum theory of line broadening for a case in which the potential is well known *a priori* would be warranted.

5 ArF Laser Interaction with H_2

In an effort to understand how the ArF laser light at 1930 Å interacts with H_2, a collaborative experimental study was undertaken with the Dr. Lal Pinnaduwage and Dr. Panos Datskos (Oak Ridge National Laboratory). Detailed electron attachment and spectroscopic measurements were made of ArF excimer laser-irradiated H_2. Two-photon excitation of the EF state is well-known, but electron attachment studies showed the presence of H^-, e^- and positive charge carriers with lifetimes greater than 40 ns. The spectroscopic studies revealed fluorescence from the $B^1\Sigma_u^+$ state of H_2, and from the atomic $H(n = 2)$ state, with lifetimes that depended on pressure, but could be longer than 100 ns. Solutions of coupled equations modeling the rates of the expected collisional processes indicate that a likely source for $H(n = 2)$ is attachment to Rydberg states of H_2. Models of the emission spectrum based on our H_2 spectrum simulation code show very clearly that the observed molecular emission arises in $B \to X$ transitions in which the upper B state is populated by cascades from states other than the E, F state, the one which is pumped directly by the two-photon absorption. Collisional processes in highly excited H_2 appear to be responsible for some of the observed effects.

H^- is of interest because of the role it may play in creating population inversion in H-metal plasmas, as we have studied for Al and In. The mechanisms by which H^- is made are not yet unambiguously identified, but these experiments indicate that additional state-selective experiments would be useful.

6 Work in Progress

The experiments and theoretical work underway now will be described briefly here. For the most part, this work would continue next year, and more information about it is in the accompanying renewal proposal.

We are interested in measuring the broadening of higher members of the Lyman series because recent space-based far ultraviolet observations of white dwarf stars has shown what appears to be collisional far wing structure on Lyman β. Theoretical work on this profile is underway now, and a paper on broadening by H^+ is in preparation. Experimental work at this wavelength is a problem because all window materials absorb in this spectral region, and techniques have to be developed to do the experiments with a windowless source. One possibility is the use of a pulsed valve, timed to produce a gas jet in which a plasma is produced. Although this technology is not new, the need to obtain high density at the breakdown region does place constraints on nozzle design. Schlieren measurements of H_2 gas density near the pulsed valve nozzle are being made in preparation for the spectroscopic experiments.

An experiment to observe Lyman α at an order of magnitude higher density is underway. A source which will work safely at 10 atmospheres pf H_2 has been constructed and is ready for testing. The goal of the experiments is to detect multiple perturber effects in the line wing, where more than one perturber interacts with the radiating atom simultaneously. Ultimately, densities of the order of 100 atmospheres will be needed, so the present experiments are a first step to that region. A new data acquisition technique was developed last year for this and similar experiments where time-resolved spectroscopic data are acquired. A fast multichannel scaler counts photons in 1024 channels with 5 ns resolution, and accumulates data for a large number of laser shots. With dispersive spectroscopy, the analyzing spectrometer is tuned to one wavelength as counts are accumulated for all times simultaneously. The data for this wavelength are downloaded and the spectrometer is then set to another wavelength for an equal number of laser shots. The resulting "data cube" has photon counts for each time and spectral element. It may be visualized as a two-dimensional image which permits a rapid selection of regions of interest. Cuts may be made to yield spectra at fixed delay times, or lifetimes at fixed wavelengths. The method was first used to study fluoresence from two-photon excited H_2 in the the H^- production experiment described above. It replaces a boxcar type of detection method, and increases data acquisition efficiencies by up to 1024 times.

In collaboration with Dr. Allard, we are continuing work on Lyman β to calculate the effects of neutral interactions on the profile. As noted above, a low density calculation for H^+ interactions has been made which includes the effects of variation of the dipole moment. The neutral problem involves more states, but there are now sufficiently reliable H_2 potentials to make a line shape calculation. The intention is to compare this calculation with a measurement using the pulsed valve source.

Work on OH has been waiting for the completion of a new spectrometer for the Lyman α region. The instrument which we are building is based on the conventional normal-incidence vacuum ultraviolet spectrometer design, but it makes use of computer-control of grating motion rather than mechanical linkages to reduce cost and increase flexibility. The system is being fabricated in our shops, essentially for the cost of vacuum hardware and optics. At the present time the vacuum chamber and a prototype grating mount have been constructed. By providing rapid high resolution vacuum ultraviolet scans under computer control, this instrument will yield improved spectral resolution and signal-to-noise ratio near Lyman α for studies of its profile. The instrument could also be used to search for $D \rightarrow X$ band emission from OH in the presence of background from H, H_2, and H_2O. When this new spectrometer is completed, we will be able to use our other, lower resolution, monochromator to filter the output of the four-wave sum-frequency mixing laser source. It is that laser system that will be used for vacuum ultraviolet work on OH.

7 Publications

Recent Journal Articles

Lasing in Al following photoionization and neutralization in the presence of H_2: The role of H^-, J. F. Kielkopf, L. A. Pinnaduwage, and L. G. Christophorou, Phys. Rev. A **49**, 2675-2680 (1994)

Spectroscopic study of laser produced plasmas in hydrogen, J. F. Kielkopf, Phys. Rev. E. **52**, 2013-2024 (1995)

Satellites on Lyman alpha due to H–H and H–H^+ collisions, J. F. Kielkopf and N. F. Allard, Ap. J. **450**, L75-L78 (1995).

Submitted for Publication

Non-adiabatic effects in the broadening and shift of the K 7s-4p transition by Ar, W. C. Kreye and J. F. Kielkopf, J. Phys. B: Atom. Molec. Opt. Phys., submitted

Photophysical and electron attachment properties of ArF excimer laser irradiated H_2, P. G. Datskos, L. A. Pinnaduwage and J. F. Kielkopf, Phys. Rev. A, submitted

Satellites on the Lyman β line of atomic hydrogen due to H–H^+ collisions, N. F. Allard, J. F. Kielkopf, and N. Feautrier, Astron. Astrophysics, to be submitted January 1997

In Preparation for Submission, Spring 1997

J. F. Kielkopf, Observation of Self-Focusing and Filamentation in Plasmas in Hydrogen Produced by a Q-Switched Laser

J. F. Kielkopf and F. Coupere, Torus Formation in the Post-Plasma Gas of a Laser-Produced Plasma in Hydrogen

N. F. Allard, J. F. Kielkopf, A. Royer, and N. Feautrier, The Effect of the Variation of the Radiative Dipole Moment in the Unified Theory of Spectral Line Broadening

Presented Papers

Production of the 4*s* $^2S_{1/2}$ state of Al and stimulated emission at 3962 Å by $Al^+ + H^-$ charge neutralization collisions, J. Kielkopf, L. A. Pinnaduwage, and L. G. Christophorou , Annual Meeting of the Division of Atomic, Molecular, and Optical Physics of the American Physical Society, Washington, D.C., April 18-21, 1994 Bull. Am. Phys. Soc. **39**, 1219 (1994).

Non-adiabatic effects in the broadening and shift of the K $7s\ ^2S_{1/2} - 4p\ ^2P_{3/2}$ transition perturbed by Ar, W. C. Kreye and J. F. Kielkopf, 11^{th} International Conference on Spectral Line Shapes, Toronto, Canada, June 1994, *Spectral Line Shapes* Volume 8, AIP Conference Proceedings 328, edited by A. David May and J.R. Drummond (AIP, New York, 1995), pp. 384-385.

Neutral atom collision broadening in the spectra of laser-produced plasmas, Tenth Topical Conference on Atomic Processes in Plasmas, San Francisco, California, January 14-18, 1996, unpublished.

Quantum broadening and shift of spectral lines in the non-imapct regime, W. C. Kreye and J. F. Kielkopf, 12^{th} International Conference on Spectral Line Shapes, Florence, Italy, June 1996, *Spectral Line Shapes*, Volume 9.

8 Students

Fang Huang, M.S., 1994, Research on Laser Produced Hydrogen Plasmas by Quantitative Shadowgraphy

Zhonghing Hu, M.S., 1996, Real Time Data Acquisition for Laser Spectroscopy under Linux

Florence Coupere, 1996 (visiting student from the University of Paris), worked on schlieren, shadowgraph, and streak camera measurements of laser-produced plasmas; production of a video showing the post-plasma dynamics.

Kim Edmondson, M.S., 1997 (pending), Continuous Spectra of H_2

Jianming Xu, M.S., 1997 (pending), Schlieren Analysis of a Pulsed Hydrogen Jet for Laser Produced Plasmas

Shi Huang, M.S., 1997 (in progress)

Ji-Tzuoh Lin, M.S., 1997 (in progress)

Pam Graham, M.S., 1997 (in progress)

Aaron Sparks, M.S., 1997 (in progress)

Taka Tsuchiya, Ph.D., (in progress)