TITLE Laser - Based Diagnostics for Density, Temperature, Velocity, and
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Laser - Based Diagnostics for Density, Temperature, Velocity, and Dissociation Fraction in High Temperature Hydrogen Flows

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Abstract

This paper is essentially a review of the current state of the art in hydrogen atom and hydrogen molecule diagnostics. This paper contains some of our own results and ideas along with results from many other laboratories. This is not intended to be an exhaustive review; instead it summarizes some techniques which we believe are ideally suited as diagnostics for high temperature hydrogen flows which are of paramount importance for the Space Exploration Initiative (SEI).

Introduction

Nuclear thermal rocket engines, as typically envisioned, use hot hydrogen as the reactor coolant and propellant. The temperatures which can be achieved in these reactors is high enough that the dissociation fraction of molecular hydrogen is fairly high (perhaps 10%). The ISP of the engine is therefore determined by the temperature (of H_2), as well as the velocity and the number density of the expelled atomic and molecular hydrogen. Therefore diagnostics for hydrogen molecule temperature, velocity, and number density as well as hydrogen atom velocity and number density are invaluable to the characterization of the engine efficiency. One proposed nuclear thermal reactor concept, the "low - pressure" concept, uses a substantially lower pressure of hydrogen (~ 1 atmosphere) to foster dissociation to hydrogen atoms. If the hydrogen atoms can be induced to recombine in the throat of the engine nozzle, a large enhancement in ISP may be realized from the energy given up in the formation of the H_2 bond. For this reason, a viable diagnostic for H_2 dissociation / recombination is of substantial interest for evaluating the efficacy of this concept. This diagnostic requirement can be met by observing the ratio of the H/H_2 number density as a function of distance downstream in a simulated nozzle.

I. Hydrogen Molecule Diagnostics

Hydrogen molecule has been detected previously by a number of techniques including multiphoton ionization (MPI)^{1,2,3,4,5} and laser - induced fluorescence (LIF)^{6,7,8} as well as Raman techniques (e.g. spontaneous Raman and CARS).^{9,10} Rhodes and co-workers first demonstrated two - photon excitation (at cf. 193 nm) of the $E \ ^1\Sigma_g^+ \leftarrow X \ ^1\Sigma_g^+ (2,0)$ transition in H_2 .⁶ Absorption to the E state can be detected either by subsequent ionization and ion or electron detection as implemented by Marinero et al.¹, or by fluorescence from the E state to the B state as demonstrated by Kligler et al.⁶ The laser source used by Kligler et al. was a home built tunable ArF excimer laser; since the time of this work, tunable excimer lasers have become commercially available. Typical operating parameters for one commercially available ArF tunable excimer include a 0.002 nm bandwidth (0.6 cm^{-1}), 100 mJ/pulse, and a tuning range of approximately 192.8 nm - 193.8 nm.¹¹ This tuning range is sufficient to excite the Q (0 - 3) rotational transitions of the $H_2 \ E \ ^1\Sigma_g^+ \leftarrow X \ ^1\Sigma_g^+ (2,0)$ band as well as the Q(2) line of the $v = 4$ level of the F

state.⁵ Marinero et al.¹ detected H₂ via MPI using the E state $v = 0, 1$, and 2 levels as resonant intermediates. The radiation necessary to excite these vibrational levels (193 - 202 nm) was produced by anti-Stokes Raman shifting the output of a frequency doubled YAG - pumped dye laser. In this way they produced 70 - 80 μ J of radiation in the fourth anti-Stokes beam with a bandwidth of 0.9 cm^{-1} . Relatively recent improvements in doubling crystal technology facilitate the production of these wavelengths from the first anti-Stokes Raman shift of a frequency doubled dye laser system which increases conversion efficiency substantially. It is also possible, due to the same advances in crystal technology, to double a dye laser fundamental and mix the residual unconverted light with the doubled output to produce wavelengths down to approximately 197.5 nm.

A. Quantitative Detection of Hydrogen Density, Temperature and Velocity

Quantitative detection of molecular hydrogen is easily accomplished by spontaneous Raman scattering since the cross section is large and has been measured accurately by Bischel, et al.⁹ In addition, rotational temperatures have been measured by MPI for 300 K H₂ by Marinero et al.¹ and Hitchcock et al.³, and therefore LIF measurements of H₂ rotational temperature should be straightforward. However, there are two problems with extending these measurements to higher temperature. First, the tuning range of the ArF excimer allows excitation of only Q(0 - 3). At the temperatures anticipated in the hot hydrogen flows, higher rotational levels will need to be probed for an accurate temperature. Second, Marinero et al.¹ observe systematic discrepancies between the populations deduced from their experimental data and the calculated rotational partition function populations for excitation of the E - X (2,0) and (1,0) bands; the E - X (0,0) band did not exhibit such discrepancies. They attribute this to intramolecular perturbations between the E, F, and C states. Hitchcock et al.³ do not observe this systematic error for the E - X (2,0) band and it is unclear why the experimental results of the two groups do not agree. A reasonable solution to both problems is to utilize the E - X (0,0) band for temperature measurements until it is determined whether the systematic deviations observed by Marinero et al.¹ are real. Excitation of the E - X (0,0) band Q(0 - 7) transitions requires radiation from 201.68 nm to 204.94 nm.¹² These wavelengths can be produced by anti-Stokes Raman shifting (first anti-Stokes) the 222 nm output of a frequency doubled (BBO crystal) excimer pumped dye laser or by doubling and mixing techniques as mentioned above.

Coherent anti-Stokes Raman Spectroscopy (CARS)¹⁰ can yield very accurate rotational temperatures for H₂ as well; however, LIF has the capability of being implemented as a two-dimensional diagnostic⁸, a definite advantage, as explained below. CARS is limited to point measurements. The H₂ velocity can be measured by techniques which monitor the Doppler shift of the LIF features. For instance, a Mach 2 (cf. 3×10^5 cm/sec) hydrogen flow will exhibit a Doppler shift of about 0.7 cm^{-1} using the $E \ ^1\Sigma_g^+ \leftarrow X \ ^1\Sigma_g^+ (2,0)$ band as a resonant state. The one-photon bandwidth of a commercially available tunable excimer¹¹ is 0.6 cm^{-1} which will increase to approximately 1.2 cm^{-1} for the two-photon $E \ ^1\Sigma_g^+ \leftarrow X \ ^1\Sigma_g^+ (2,0)$ transition. A Doppler shift of 0.7 cm^{-1} can be measured with a laser of bandwidth 1.2 cm^{-1} given decent signal to noise; so it is possible, in principle, to measure H₂ velocity by Doppler shift using a tunable ArF excimer. The temperature obtained via LIF excitation scans may be checked by monitoring the linewidth of the LIF features provided that the temperature is high enough to Doppler broaden the lines beyond the laser bandwidth. For H₂ and the commercial excimer described above, this requires a temperature of at least 800 K. Thus, the requirements listed above for the

determination of H_2 temperature and number density can be met by a combination of two - photon excited LIF and spontaneous Raman scattering.

Another technique for the measurement of velocity which has been implemented by Miles et al.¹³ for the measurement of O_2 velocities is velocity tagging. This technique involves tagging a region of the oxygen flow by populating the $v'' = 1$ level of ground state oxygen using stimulated Raman pumping. At some appropriate time delay, a probe laser sheet tuned to detect $v'' = 1$ O_2 is fired and an image of the tagged O_2 is obtained. From the displacement of the tagged line and the time delay between the lasers, a velocity is obtained. This technique is attractive since it provides velocity information along a line; however, it requires a minimum of two lasers which limits its applicability. In addition, vibrational and rotational energy transfer from the tagged level limit the allowable time delay because of loss of population in the probed level. The rates of these transfer processes depend on both the identity and partial pressure of the colliders as well as the temperature. Therefore there is an intrinsic lower limit to the velocities which can be measured using this technique. Another problem is that a substantial thermal population will exist in $v'' = 1$ at the high temperatures in a nuclear rocket engine limiting signal to noise at all time delays. The tagging technique can likely be applied to H_2 molecule as well; however, due to the limitations described above, it is not the technique of choice.

B. Two - Dimensional Hydrogen Molecule Diagnostics

Quite recently, Miles et al.⁸ have demonstrated the ability to image hydrogen molecule in hydrogen / oxygen diffusion flames using a tunable excimer laser and the $E\ ^1\Sigma_g^+ \leftarrow X\ ^1\Sigma_g^+ (2,0)$ $Q(1)$ transition as described above. This technique, Planar Laser - Induced Fluorescence (PLIF), is implemented by forming the rectangular excimer laser output into a very thin sheet of perhaps 2 cm width and 200 - 300 μm thickness using cylindrical lenses. The sheet is passed through the sample, tuned to the proper wavelength for H_2 excitation, and fluorescence on the $E\ ^1\Sigma_g^+ \Rightarrow B\ ^1\Sigma_u^+ (2,1)$ band at 750 nm is captured by a gateable intensified CCD camera.

These images amount to two - dimensional concentration maps of the hydrogen molecule. However, they must be corrected for variations in laser sheet uniformity and temperature variations to yield an image whose intensity is directly proportional to hydrogen concentration. (This was not done in the H_2 imaging experiments of Miles et al.⁸) The former problem is especially severe for two - photon imaging experiments since signal is proportional to the laser power squared in the unsaturated regime. Thus, small variations in the laser sheet intensity can cause large fluctuations in the fluorescence signal. If there is sufficient laser energy to saturate the transition, the signal level will vary with laser power only slightly and the problem of sheet non - uniformity is minimized. If saturation is not possible, one may pass the laser sheet through a cell containing only hydrogen at room temperature. Since the isothermal hydrogen is uniformly distributed throughout the cell and the transition pumped in the two cases is identical, any non - uniformity in the image obtained in the cell experiment must be due to variations in the laser sheet. This image may then be used to correct the image of the actual hot hydrogen flow assuming that the same sheet optics are used.

Correction of the image for temperature variations in the viewing field may be handled in two ways. Typically, this problem has been mitigated by pumping rotational levels in the ground state which have Boltzmann populations that are temperature insensitive over the range anticipated in the experiment. For OH radical imaging experiments in flames, researchers typically excite the $Q_1(7)$ transition of the $A - X (1,0)$ or $(0,0)$ bands whose ground state population varies perhaps 10% from a temperature of 800 to 2000 K (typical flame temperature range).¹⁴ For H_2 , rotational partition function

calculations indicate that the population of $J'' = 4$ varies only 17% from 1000 K to 3000 K. From 2000 K to 3000 K, $J'' = 5$ is a better choice since its population varies by only 2% over this range. Unfortunately, one can only access $J'' = 0 - 3$ with the tunable excimer. In any case, as mentioned above, Marinero et al.¹ suggest that the E - X (2,0) band is inappropriate for temperature measurements due to perturbations. The $J'' = 4$ and 5 rotational levels can be probed by exciting the E - X (0,0) band Q(4) and Q(5) transitions (which are unperturbed). This requires radiation at 202.79 nm and 203.34 nm, respectively.¹² These wavelengths can be produced by anti - Stokes Raman shifting the 222 nm output of a frequency doubled (BBO crystal) excimer pumped dye laser or by doubling and mixing techniques as mentioned previously. These wavelengths can be produced with relative ease using either technique; however, it is unclear whether the laser power obtained will be sufficient for two - photon PLIF imaging.

If sufficient laser power is available in the 202 - 205 nm range for two - photon PLIF imaging, then it is possible to produce a two - dimensional image of the temperature field in the following way. One image is obtained by exciting a transition from a low J'' level and another image is obtained by exciting a transition from a high J'' level. The ratio of these two images is directly related to the temperature. This technique has been used for one - photon OH rotational temperature imaging in reacting flows.¹⁵ It is also possible to obtain a two - dimensional image of the velocity field, although the technique required is much more difficult to implement. Paul et al.¹⁶ have used this technique to obtain velocity field images of NO in an underexpanded free jet flow. This Doppler based technique involves ratioing two images obtained with the K vector of a relatively broadband laser co - and counterpropagating relative to the flow. The signal intensity for each image depends on where its Doppler shifted center frequency occurs relative to the laser spectral output maximum. The ratio of the co - and counterpropagating images turns out to be directly proportional to velocity. This technique is extremely elegant, but it is difficult to implement and has limited accuracy.

II. Hydrogen Atom Density Diagnostics

Atomic hydrogen has been detected via direct one - photon absorption,¹⁷ MPI,^{18,19,20} multiphoton excited LIF,^{18,21,22,23,24,25,26,27,28} laser - excited amplified spontaneous emission,²⁹ and third harmonic generation.³⁰ Bjorklund et al.²⁰ first reported multiphoton excitation of H atom Rydberg levels with n up to 35 by three photon absorption and detection of electrons produced by ionization following absorption of a fourth photon. Subsequently, Goldsmith,^{19,21,23,24} Alden et al.,²² and Lucht et al.²⁵ have devoted a great deal of energy to the development of both MPI and LIF diagnostics for H atom. These techniques typically utilize either two or three photon absorption to populate the $n = 2, 3$, or 4 level of H atom. Detection of the absorption step involves either ionization by absorption of an additional photon, the detection of Balmer series radiation, or the detection of VUV radiation.

Two of these techniques deserve special consideration. First, Lucht et al.²⁵ developed a two - photon excitation scheme in which two 205.14 nm photons excite H atom to the $n = 3$ level followed by subsequent detection of 656 nm Balmer α fluorescence ($n = 3$ to $n = 2$) or collection of the electrons produced by ionization following absorption of a third photon. This wavelength can be produced by direct doubling in a BBO crystal although a special cut would be required as 205 nm is very close to the short wavelength cutoff of the BBO doubling curve. If such a crystal is not available, doubling and mixing of a 615 nm dye laser beam will produce the desired wavelength. The second excitation scheme, developed by Goldsmith et al.,²³ makes use of the unique energy level structure of H atom ($E \propto 1/n^2$). In this method, two 243 nm photons excite H atom to the $n = 2$ level.

A third photon at 486 nm (exactly twice 243 nm) saturates the H atom $n = 3$ to 4 transition. Fluorescence is then detected at 486 nm. This scheme is especially convenient since 243 nm is produced by frequency doubling 486 nm dye laser output. The undoubled light provides the photons for the last step, so that only one laser is required for this technique. The drawback of this technique is that the detection wavelength and the second pump wavelength are identical which can cause problems with scattered laser light.

Laser excited amplified spontaneous emission (LEASE) provides an additional method of monitoring absorption to the $n = 3$ level of H atom. Goldsmith²⁹ has observed LEASE at 656 nm following excitation of H atom with two 205.14 nm photons. The ASE is a bi-directional emission which results from the creation of a population inversion between the $n = 3$ and $n = 2$ levels during every pulse. This gain medium is directional with its long axis along the laser beam focus and therefore 656 nm photons which are spontaneously emitted along the laser beam stimulate more emission than photons spontaneously emitted transverse to the beam axis. Since stimulated emission results in photons which travel in the same direction as the stimulating photon, the ASE emission occurs bi-directionally along the laser axis with a divergence similar to the laser beam divergence. Quantitative detection of H atom using ASE would be difficult due to the fact that the signal depends exponentially on the inversion density. In addition, the competing processes of ionization, fluorescence, and four wave mixing must be taken into account. The relative contributions of these competing processes will depend on the detuning of the laser from resonance, the laser power, and the collision environment. Third harmonic generation, THG, has also been used to monitor H atom in dc H₂ plasmas.³⁰ In this case, three 364.6 nm photons produce a photon which is nearly at the Lyman α wavelength. The wavelength of the created photon is slightly shifted from the Lyman α wavelength due to phase matching considerations and is therefore not absorbed by ground state H atoms. The shift is proportional to H atom concentration and the intensity of the THG signal depends on the square of the H atom density. Therefore THG could be used to make H atom density measurements provided the relevant proportionality constants can be found. This requires calibration of the THG signal shift and intensity in an H atom source of known and variable density which is rather inconvenient but certainly possible.

Hydrogen atom has also been detected via one-photon LIF and absorption using Lyman α radiation.¹⁷ This wavelength is produced by THG of 363.6 nm light in a phase-matched mixture of rare gases. The signal can be detected either by monitoring absorption of the laser beam or by Lyman α fluorescence. The fluorescence is self-absorbed at high H atom concentrations so that absorption is often the better choice. The per cent absorption contains H atom density information and the linewidth contains information about temperature (velocity). Doppler shifts (if they are observable) contain information about bulk flow velocity. Absorption is probably the best choice for quantitative H atom detection since the cross section is accurately known and the technique requires no external calibration. In addition, information about the gas temperature and bulk flow velocity may be obtained from this technique.

Hydrogen Atom Velocity Measurement

Two convenient techniques for the measurement of H atom velocity have been demonstrated by Mertens and Bogen¹⁷ and Liebeskind et al.³¹ The method of Mertens and Bogen, described briefly above, involves measuring the linewidth of the H atom LIF signal on the Lyman α line for measurement of the thermal velocity.¹⁷ The Doppler shift of the resonance is a measure of the bulk flow velocity. (This measurement was not made by Mertens and Bogen because their H atom source was a thermal source with no

directionality.) The Lyman α radiation is produced by frequency tripling of a 364 nm dye laser beam. The linewidth of the Lyman α radiation produced by this source is less than 0.6 cm^{-1} although the exact linewidth was not measured.¹⁷ The Doppler shift for a Mach 2 H atom flow (cf. $4 \times 10^5 \text{ cm/sec}$) on the Lyman α transition is 1.1 cm^{-1} and can therefore easily be detected using this technique. Alternatively, Liebeskind et al.³¹ has measured the H atom velocity in hydrogen arcjet thrusters using a CW argon ion pumped ring dye laser system operating at 656.28 nm to excite fluorescence on the hydrogen atom Balmer α line. A significant population of $n = 2$ will be present in any high temperature hydrogen flow; therefore, LIF or absorption experiments may be performed which cause excitation of the H atom from $n = 2$ to $n = 3$ at 656 nm. The linewidth of the LIF feature is a measure of the gas temperature and the Doppler shift is a measure of the bulk flow velocity as above. The linewidth of the ring dye laser is 0.004 cm^{-1} , and is therefore much narrower than the width of the broadened 656 nm line. Liebeskind et al. measure a Doppler shift of 0.65 cm^{-1} which corresponds to a velocity of 12.8 km/sec or $1.28 \times 10^6 \text{ cm/sec}$. They did not attempt to fit a temperature to the measured halfwidth. In addition, this technique can be used to measure accurately the population of H atoms in $n = 2$. If the temperature is known and the flow is in thermal equilibrium, this information can be used to calculate the ground state H atom density. However, local thermodynamic equilibrium is by no means assured in the type of flows of interest for SEI.

Simultaneous Detection of H Atom and H₂ Molecule with A Single Laser

At Los Alamos, we have been investigating the utility of a technique which allows us to detect simultaneously hydrogen molecule and atom with a single tunable ArF excimer. Simultaneous detection of two flame species (OH and O₂) with a single KrF excimer laser has been demonstrated previously by Arnold et al.³² In this technique, a commercial tunable excimer laser is modified by the addition of a second grating to the oscillator of the laser so that simultaneous two-wavelength operation is achieved. One grating is tuned to the OH A $^2\Pi - X \ ^2\Sigma (3,0) P_1(8)$ line and the other grating to the R(17) of the B $^3\Sigma_u^- - X \ ^3\Sigma_g^- (0,6)$ Schumann - Runge vibrational hot band in O₂. In the hydrogen molecule imaging work of Miles et al.⁸ described earlier, the one - photon wavelength of the Q(1) transition of the E - X (2,0) band in H₂ accidentally coincides with the R(17) line of the (10,2) Schumann - Runge band (one photon transition). Therefore, H₂ and O₂ can be imaged in H₂ / O₂ flames simultaneously with a single laser without the addition of a second grating.

We have investigated the utility of a modified tunable ArF eximer laser for the simultaneous laser-induced fluorescence (LIF) detection of hydrogen atom and molecule. The modification consists of adding a second grating to the laser oscillator as in the work of Arnold et al.³² for operation at 248 nm. One grating is tuned to excite the hydrogen molecule on the Q(1) E $^1\Sigma_g^+ - X \ ^1\Sigma_g^+ (2,0)$ two-photon transition at the one photon wavelength of 193.2608 nm. Fluorescence is detected by either a filtered phototube or a monochromator / phototube combination at approximately 750 and 835 nm on the E $^1\Sigma_g^+ - B \ ^1\Sigma_u^+ (2,1)$ and (2,0) bands. The other grating is tuned to 193.29 nm and is Raman shifted in D₂. The first Stokes output occurs at 205.14 nm and is used to excite H atoms to the $n = 3$ level via a two - photon transition as in the earlier work of Bokor et al.¹⁸ Balmer α fluorescence is detected at 656 nm to monitor the absorption. These LIF signals are proportional to density and can be calibrated for absolute concentration by spontaneous

Raman scattering and direct one - photon laser beam absorption for H_2 and H atom, respectively as described above. Therefore the technique can be used to monitor dissociation fraction and recombination in hot hydrogen flows.

The four panels of Figure 1 demonstrate our ability to detect H_2 and H atom simultaneously. The H atom is produced by photolysis of a small amount of HBr (90 mtorr) seeded in approximately 20 torr of hydrogen. The H_2 molecule signal at 750 nm is displayed in each trace on the left with the H atom signal on the right. In the upper left panel both gratings are blocked causing the excimer to lase broadband. The signals, in this case, are due mostly to scattered light. The upper right panel shows the H atom signal with the grating tuned for excitation of H_2 blocked. The lower left panel shows the H_2 molecule signal with the H atom grating blocked. Finally, the lower right panel shows the H atom and H_2 molecule signal with both gratings unblocked. The increase in the size of the H atom or H_2 signal when lasing at only one wavelength over the signals when lasing at two wavelengths simultaneously is a measure of the gain competition in the laser. Clearly, these traces show that H_2 and H atom may be detected simultaneously by this method.

Several improvements in this technique are expected to increase signal to noise substantially so that single shot two-dimensional images may be obtained of the H atom and H_2 molecule by planar laser induced fluorescence (PLIF). At present, the two wavelengths are not separated before Raman shifting. This causes a large loss in energy for the two wavelengths necessary for excitation since two sets of Raman orders are produced when only one set is needed. Separation is impractical because the two wavelengths are very close and have the same polarization (mostly linear vertical). However, by rotating the polarization of one wavelength by 90° (for instance by rotating one grating by 90°), the output polarizations can be made orthogonal. The two wavelengths may then be easily separated by a Glan laser prism and only the 193.29 nm fundamental is shifted. In addition, rotating the polarization of one color will eliminate gain competition in the laser and reduce shot to shot competition between the two modes. Finally, interference from oxygen absorptions, particularly at the H atom fundamental wavelength (193.29 nm) from the R(19) and P(17) lines of the Schumann - Runge (4,0) band can be mitigated by purging the laser oscillator and amplifier as well as purging the beam path to the cell. This was not done for the data shown in Figure 1. This accidental overlap could be used to advantage for flame imaging of O_2 so that simultaneous detection of H_2 , H, and O_2 is possible using our technique.

Finally, we are investigating the possibility of detecting H_2 and H atom simultaneously using a dual grating tunable XeCl laser at 308 nm. Hydrogen atom has a three-photon resonant excitation at 307.71 nm.²⁰ In flames, this transition is not useful as a result of strong interference from OH radical. However, in a pure hydrogen flow, OH interference will not be a problem. We calculate that the O(6) rotational feature of the $C^1\Pi_u - X^1\Sigma_g^+(0,0)$ band lies at the three photon wavelength of 308.414 nm^{4,12} which is within the locking range of the tunable XeCl excimer. At 2000 K, the population of $v'' = 0$ and $J'' = 6$ is approximately 17%. Also within the XeCl locking range is the $C^1\Pi_u - X^1\Sigma_g^+(1,1)Q(0)$ transition calculated to occur at 308.365 nm.^{4,12} The population of the lower level of the transition is about 5% at 2000 K. Thus it should be possible to detect H atom and H_2 simultaneously via three photon transitions using a dual wavelength tunable XeCl excimer. This eliminates both the need to Raman shift and the O_2 absorption interference. Very high signal to noise detection should be obtainable using this technique and calibration for absolute density and dissociation fraction will proceed as described above for the two-photon transitions.

Conclusion

This paper reviews the current state of the art in hydrogen atom and molecule diagnostics. We conclude that a combination of LIF, laser beam absorption, and spontaneous Raman scattering will be sufficient to measure the absolute density of H_2 and H atom, the temperature, and the flow velocity of hydrogen atom and molecule in high temperature hydrogen flows relevant to the Space Exploration initiative. We also briefly describe some of our own experimental results pertaining to the development of advanced LIF diagnostics for the simultaneous detection of H atom and molecule using a single laser.

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Figure 1