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Chapter

Advanced Optical Diagnostics of Atmospheric Pressure Plasma

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Abstract

Atmospheric-pressure plasma has been employed in various applications including bio-medicine, environmental pollution control, material processing. Diagnostic characterization of plasma sources is critical and indispensable for plasma control and achieving optimized treatment efficiency. In this chapter we will introduce several advanced optical techniques to visualize the detailed physical- and-chemical properties of atmospheric-pressure discharges. Non-invasive approaches of optical emission spectroscopy (OES), schlieren or shadowgraph, invasive methods of active laser spectroscopy including laser-induced fluorescence (LIF), laser or broadband absorption, cavity ring-down spectroscopy (CRDS), and laser scattering are illustrated. Basic plasma parameters of gas temperature, electron density and temperature, electric field strength, and reactive chemical gaseous species (O, H, N, OH, NO, O₃, etc.) are able to be monitored. Comparisons and comments of these approaches are provided depending on diagnostic purposes.

Keywords: advanced optical techniques, plasma parameters, active laser spectroscopy, LIF, absorption spectroscopy

1. Introduction

Atmospheric pressure plasmas attract intensely interests because of non-need of costly vacuum requirement and enabling in-line processing. Prospective novel applications have emerged over recent years, e.g., plasma bio-medicine, material synthesis, pollutant degradation, chemical conversion. However, with increase of gas pressure, plasmas tend to become constricted, unstable, and non-uniform. Miniaturization of discharge volume with non-equilibrium kinetic property are typically characterized by atmospheric pressure plasmas. And in many cases they are of strong gradients in space and in time as well, e.g., the so-called microplasmas. Much higher diagnostic requirements are put forward to atmospheric pressure plasmas with high time-and-space resolution. Not only the traditional optical emission spectroscopy (OES) accessing emitting species, but also advanced active diagnostics particularly the laser-aided techniques probing plasma parameters \((T_g, n_e, T_e)\) and reactive plasma species, are the topics discussed in this chapter.

2. Diagnostics of basic plasma parameters

Plasma parameters mainly are the gas temperature \(T_g\), electron density \(n_e\) and temperature \(T_e\). The three are important physical factors directly influencing the
plasma generation and physical-and-chemical properties. Diagnostics of the three parameters are necessary in plasma field from points of both fundamental research and applications.

2.1 Gas temperature

From points of both fundamental investigation and applications, gas temperature ($T_g$) is one of the important basic plasma parameters strongly affecting the discharge property, especially the plasma chemistry as most chemical reactions are temperature dependent, and thus influences the final outcomes of plasma applications. Standard direct approach by thermocouples is difficult due to induced strong effects on plasma properties. Although thermometric probes based on fiber-optics are developed and applied to plasma diagnostics [1], the use of this technique is still rare and limited to, e.g., microplasmas.

Rotational distributions of molecules, typically from excited molecules are often used to estimate the plasma gas temperature, if the former achieves an equilibrium Boltzmann distribution [2, 3]. In this case the distribution of interested rotational manifold can be estimated from corresponding emissions in UV to visible range and easy to be detected by a spectrometer. Excited species OH (A$^2\Sigma^+$) and $N_2$ (C$^3\Pi_u$) are often used for the purpose of $T_g$ estimation, by using programs of Lifbase or SpecAir [4, 5]. However, it needs to keep in mind that, on one hand this method is strongly affected by the production process of excited molecular state. Its rotational population distribution may highly deviate from thermal equilibrium state. This is typically characterized by atmospheric pressure plasmas, in which fast collisions significantly reduce the lifetime of rotational states and if the rotational energy transfer (RET) process is not fast enough to thermalized all rotational levels, a non-thermalized distribution is resulted. In this case $T_g$ estimation will be not precise and overestimated due to over-populated high rotational states. This situation is often existent in water-contacting discharges if OH (A$^2\Sigma^+$), or argon discharges if $N_2$ (C$^3\Pi_u$), are applied for $T_g$ determination [6–9]. In this case, method of Boltzmann plotting may help by using the part of rotational states with small rotational number, as these levels with low rotational energy potential are easily thermalized by RET process [2].

On the other hand, it should mention that the emitting region usually characterizes only a part but not the whole discharge space. Commonly, it corresponds to the hot core of the discharge [10]. Other advanced approaches are desired if the full-space distribution of $T_g$ is needed, for instance to estimate the heat flux of discharge to treated object. Laser scattering techniques such as Rayleigh scattering and Raman scattering, and calibrated schlieren photography are proposed and will be illustrated in this chapter. All these methods depend on the neutral density which directly relates to $T_g$ if the ideal gas principle is valid.

Rayleigh scattering is elastic scattering on heavy species and its signal has the same wavelength as the laser. Its intensity depends proportionally on the scattering cross section, laser intensity, and amount of neutral particles probed in the scatter volume [11–14]. By comparing the scattering signals of plasma off $I_{R\text{off}}$ and plasma on $I_{R\text{on}}$, the gas temperature is obtained if the gas composition does not vary significantly in the probed volume:

$$T_g = T_{\text{ref}} \frac{I_{R\text{off}}}{I_{R\text{on}}} \quad \text{(1)}$$
where $T_{\text{ref}}$ is the known room temperature when plasma is off. An example of a Rayleigh scattering measurement in a pin-to-pin micro-glow air discharge is shown in Figure 1. This technique is favored for capturing the $T_g$ spatial distribution of atmospheric pressure plasmas directly, but still following issues needs to be considered if it is applied:

- Laser-induced breakdown needs to be avoided by using appropriate laser energy. UV laser wavelength is suggested for this purpose, even laser energy is low it still able to produce intense scattering signal as the cross section has a strong wavelength dependence ($\sigma \propto \lambda^{-4}$) [12].
- Mie scattering on dust particles and stray scattering light from electrodes needs to be avoided. Therefore, this technique is quite difficult for probing discharge regions close to electrodes.
- The scattering signal will be weak for helium discharge due to the low Rayleigh cross section of helium atoms.
- Deviation will increase for temperature level above 2000 K as intensity of $I_{\text{on}}^R$ will be very low in above equation.

Schlieren photography also is applied to measure the gas density gradients and correspondingly, to estimate the gas temperature [15, 16]. The advantage of this approach is achievable of the whole $T_g$ distribution by only one schlieren image, if after calibration. A schlieren image visualizes the deflection of light rays along the optical path. The signal intensity of each pixel on the schlieren image is an integration result of bent light ray which strongly depends on the density distribution of gas species. If the gas composition is known and its spatial gradient is induced by thermal motion, then $T_g$ map is able to be calculated through Abel inverse integral transformation. Symmetric assumption is usually made for the $T_g$ map in non-uniform discharges such as pin-to-pin microplasma. For asymmetric discharges, it

![Figure 1.](image)

*Figure 1.* Radial profiles of Rayleigh scattering intensities when the discharge was off and on, and the estimated gas temperature profile in the middle of discharge column with current of 8 mA [10].
is difficult but still possible by a computed tomographic reconstruction technique and multi-directional calibrated Schlieren imaging [16, 17]. Figure 2 shows an example of full $T_g$ map estimated by calibrated schlieren photography [10]. It needs to point out that this technique suffers the optical diffraction effect on the object boundary, which usually induces an overestimation of temperature. However, compared to laser scattering approach, calibrated schlieren is a low-cost way for full-mapping gas temperature in discharges. Its drawback is the calibrated calculation process and need extra calibration by a long-focus lens.

Other methods including Raman scattering also allows one to measure the gas temperature [13]. It is the inelastic scattering of light on molecules such as N$_2$ or O$_2$ and its signal depends on neutral density, similar to the Rayleigh scattering. However, this technique requires expensive laser equipment and filter system for removing strong interference of Rayleigh scattering. Doppler broadening and Van der Waals broadening are analyzed for line profiles to estimate $T_g$ as well if the Stark broadening is not dominant [18, 19]. However, the broadening routines require high spectral resolution to reduce the effect from instrumental broadening. Compared to emission lines, fine structure of atomic absorption line is achievable by tunable diode laser absorption measurement [8]. Compared to Doppler broadening, Van der Waals broadening is preferred for atmospheric-pressure plasmas with low gas temperature as the latter depends strongly on the neutral density. It should mention that the both broadening routines are line-integrated measurements and Abel inversion is required if radial profile of $T_g$ is desired. Table 1 concludes and compares all these methods for $T_g$ diagnostics described above. Two or more techniques are suggested if diagnosing non-uniform high-pressure plasmas.

### 2.2 Electric-field strength

Electric-field strength $E$ determination is always a tough issue for high-pressure plasmas. Compared to emission spectroscopic methods based on Stark effect of atomic lines, coherent Raman scattering (CRS) technique is favored for both static and fast transient discharges at elevated pressures [22, 23]. Its basic principle is vibrational excitation of Raman-active molecular which produces an infrared (IR)
coherent beam under the effects of two extra nanosecond pulsed laser beams and an electric field. The IR light can be considered as an anti-Stokes wave produced by the electric fields of two laser beams and a third field at zero frequency, i.e., the probed dc electric field [22, 24, 25]. At the same time the laser beams also produce conventional coherent anti-Stokes Raman scattering (CARS) regardless of the presence of the dc electric field. And $E^2$ is able to be determined from the detected intensities of the two coherent Raman scattering beam, according to:

$$I_{IR} = C_1(N_g - N_{ex})^2 I_1 I_2 E^2$$

(2)

$$I_{CARS} = C_2(N_g - N_{ex})^2 I_1 I_2$$

(3)

$$E^2 = \frac{C_0 I_{IR}}{C_1 I_{CARS}} = \frac{C_0 I_{IR}}{C_{IR}}$$

(4)

$N_g$ and $N_{ex}$ are the number densities of scattering molecules at the ground and excited levels involved in the vibrational transition. Since the incident laser intensity $I_1$ is known and can be treated as a constant with two other constants $C_1$ and $C_2$. The value of parameter $C_0$ is almost independent of the gas density or temperature which significantly simplifies the analysis of this technique for $E$ measurement in discharges.

Molecules including $N_2$ and $H_2$ have been used as the probe species, particularly the latter due to its large Raman cross section [22, 25]. However, compared to $H_2$ nitrogen gas has significant potentials for diagnosing atmospheric-pressure discharges especially discharges mixing with nitrogen gas. Based on the four-wave mixing principle of CRS technique by two laser beams, recently a novel and simpler CRS scheme was developed by I. Adamovich’s group in Ohio State University by using only one laser beam [26–29]. A high-pressure gas cell filled with $N_2$ and He
with 1:1 mixture ratio was used and pumped by the same laser beam to produce the 607 nm first order Stokes signal of N\textsubscript{2}. The 607 nm Stokes beam was generated to replace the need of another nanosecond laser system used in traditional CRS technique. Then the pump and Stokes beams are focused in the discharge region to produce the IR anti-Stokes beam under the presence of probed dc electric field [28]. They applied a picosecond laser at 532 nm especially for probing the transient electric field in nanosecond discharges.

A further simpler approach based on the second harmonic generation (SHG) was developed by the same group for diagnosing the time-resolved evolution of the electric field vector in a nanosecond atmospheric-pressure surface plasma [29]. A single picosecond laser was used without Stokes gas cell. The pump laser wavelength is 1064 nm and focused to the discharge region and under the presence of an external electric field, SHG at 532 nm is generated with intensity proportional to the probed \( E \) of discharge [29]. Compared to CRS measurements, this SHG technique involves only one nonlinear optical process which enables better shot-to-shot signal reproducibility and signal/noise level. By using a polarizer in front of the SHG detector the vertical and horizontal components of \( E \) in discharge are able to be measured separately. Absolute calibration is required for above all approaches by measuring a known Laplacian electric field between two parallel metal plate electrodes. It should be mentioned that low-frequency nanosecond lasers, such as 10 Hz Nd:YAG pumping laser, is also suitable for \( E \) measurement in atmospheric-pressure discharges if ns time-resolution is not required.

### 2.3 Electron density and temperature

Electron density \( n_e \) and temperature \( T_e \) are two important fundamental plasma parameters since plasma property is mostly drove by electrons. Stark broadening of atomic line profile is often applied for estimating electron density if \( n_e \) typically exceeds \( 10^{14} \text{ cm}^{-3} \) in atmospheric-pressure plasmas. The H\( _\beta \) line is most frequently used for the diagnostic purpose of \( n_e \) due to its strong Stark broadening but less self-absorption and weak effect from ion dynamics in discharges [30, 31]. Other hydrogen Balmer lines including H\( _\alpha \) and H\( _\gamma \) are also studied and used for \( n_e \) determination. The H\( _\alpha \) line is more intense of emission but easily suffered self-absorption effects. The Stark broadening of hydrogen Balmer lines has been studied extensively in [32] by group of M. Gigosos. They calculated the line widths of H\( _\beta \) Stark broadening for wide ranges of electron density, temperature and emitter-perturber reduced mass. An equation is derived for \( n_e \) based on the full-width at half-maximum (FWHM) of H\( _\beta \) Stark broadening profile [32].

\[
\text{w}_s = 4.8 \text{ nm} \left( \frac{n_e}{10^{17} \text{ cm}^{-3}} \right)^{0.68116} \tag{5}
\]

The Stark broadening of H\( _\beta \) line facilitates the \( n_e \) determination in atmospheric-pressure plasmas. High-spectrum resolution (e.g., 10 pm) is recommended for capturing a clear shape of the H\( _\beta \) line profile since other broadenings including Doppler, van der Waals, and instrumental broadenings contribute also to the detected line profile. The effects of these broadenings need to be separated to obtain the Stark part and accurate deconvolution procedures normally are required for this purpose [33]. Other atomic lines are also possible for \( n_e \) measurement based on their Stark broadening if hydrogen gas is absent, for example, He (447.1 nm) or Ar (415.9 nm) lines [34, 35].

Microwave interferometry and CO\textsubscript{2}-laser heterodyne interferometry have been applied as well to \( n_e \) measurement in plasmas based on the principle of change in
refractive index of electromagnetic radiation passing through the discharge region [36, 37]. The main advantage of this technique is that it is able to measure electron densities at order of \(10^{13} \text{cm}^{-3}\) lower than that by the Hβ Stark line broadening. However, since it is a line-integrated method and thermal effect may contribute also to the detected phase shift of probed electromagnetic radiation. This issue can be solved by using two laser sources with different wavelength [36]. Abel inversion is necessary to obtain spatially resolved electron density.

Compared to above two line-integrated techniques, Thomson scattering is a more advanced optical approach allows one probe directly information of both \(n_e\) and \(T_e\) [13]. This technique is based on the elastic scattering of light on free electrons, and its signal is Doppler broadened due to the velocity of electrons if the electron energy distribution function (EEDF) is a Maxwell-Boltzmann distribution. Therefore, \(n_e\) is able to be determined from the measured scattered power per unit of wavelength \(S_\lambda\) [38]:

\[
S_\lambda = C n_e \frac{d\sigma}{d\Omega} G_\lambda(\lambda) \tag{6}
\]

where \(C = f l I l \Delta\Omega\) is a constant factor depending on the optics efficiency \(f\), length of detection volume \(l\), laser power \(I_l\), and detection solid angle \(\Delta\Omega\). Absolute calibration needs to be done to determine the \(C\) value normally by means of Raman scattering on ambient air at atmospheric-pressure and room temperature [13]. \(d\sigma/d\Omega\) is the differential cross section and \(G_\lambda(\lambda)\) is the function of spectral distribution and normalized normally that \(\int G_\lambda(\lambda)d\lambda = 1\). \(T_e\) can be obtained by the measured Gaussian profile of Thomson scattering signal according to [13, 39]:

\[
T_e = \frac{m_e c^2}{4k_B} \left( \frac{\Delta\lambda}{\Delta\lambda} \right)^2 \tag{7}
\]

\(\Delta\lambda\) is the 1/e width of the Gaussian profile. Although these advantages of this advanced diagnostic technique, its implementation is not straightforward in general due to the weak scattered signal typically orders of magnitude lower than that of Rayleigh scattering in addition to stray light. A notch filter or a triple grating spectrometer, or an atomic absorption cell, are necessary to capture the weak scattered light [40–42]. And, laser-induced optical effects such as photo-detachment, photon-ionization, or electron heating may occur if high laser power is used in measurements, and need to be checked by measuring the signal as a function of laser power. More details about the Thomson scattering approach can be found in [13, 39, 41, 43–48].

3. Diagnostics of plasma chemistry (reactive species)

Plasma chemistry covers broad ranges of chemical properties of discharge plasmas, and rapidly grows to an important research area of scientific endeavor holding great promise for many novel plasma applications. Reactive species, including neutrals, metastable or excited species, ions consist the dominant active agents of discharges and play critical roles in plasma treatments, e.g., in fields of medicine, material, energy, etc. Various diagnostic techniques have been developed and applied for probing different reactive species quantitatively. And in this chapter three important techniques based on principles of laser-induced fluorescence (LIF) and absorption spectroscopy, are included.
3.1 Laser-induced fluorescence spectroscopy

Laser-induced fluorescence (LIF) is an in situ sensitive technique monitoring transient species with high temporal and spatial resolution [49]. This approach is based on a two-step process, where atoms or molecules in the initial electronic state \( i \) are firstly pumped to an upper electronic state \( j \) by absorbing laser photons with energy \( \Delta E = h\nu_{ij} \) same to the transition gap between states \( i \) and \( j \). Secondly, the excited state \( j \) undergoes spontaneous transition to a lower state \( k \) and emits photons with energy \( h\nu_{jk} \) called the fluorescence signal. As an example, a conceptual LIF scheme of OH radicals, one typical reactive molecular species studied frequently by this technique, is depicted in Figure 3. For molecules fast vibrational energy transfer (VET) and rotational energy transfer (RET) processes are occurring after laser excitation, as well as the pre-dissociation process.

For atomic species these ro-vibrational processes are not existent. Although LIF is a direct technique allows us detect the spatial distributions of interested species, absolute calibration and analysis model are required for quantitative measurements [50–54]. For the case of single-photon excitation the fluorescence calibration is relative simple with the aid of Rayleigh scattering. It is based on a comparison under identical conditions of laser irradiation in Rayleigh scattering and fluorescence detection in LIF. A reference gas with known density is usually used for Rayleigh calibration, for instance air gas under room temperature. Typical laser excitations and fluorescence transitions of various species are listed in Table 2 together with suggested calibration.

Analysis of fluorescence signal for absolutely determining probed species density can be very complicated under high gas pressure due to the fast collisional processes [67]. In this case the excited state after laser pumping may redistribute because of fast collisions at same timescale or even faster and these processes have to be considered in the analysis model. This could be more complicated for molecular species, for instance OH, NO, etc. in addition to the fast processes of VET and RET.
Assumptions are often made for simplifying the LIF model, e.g., RET is fast enough to redistribute the rotational manifold of excited vibrational state and in this case the lifetime of the vibrational band can be considered only depending on quenching and emission coefficients. Effective lifetime of excited vibrational band instead of single rotational level, is used in the LIF model. And this is normally correct if RET process is fast, but still need to check if concentrations of quenching species such as H2O to OH is very high [54, 68–70]. Furthermore, the laser power needs to be kept low and linear LIF is achieved to avoid stimulated emission and large depletion of initial pumped state density.

In many cases the excitation radiations locate range of deep UV (e.g., <100 nm) and are strongly absorbed by ambient gaseous medium (e.g., air or water molecules), then two-photon excitation in the UV spectral range (>200 nm) can be applied for the same diagnostic purpose, namely the so-called two-photon absorption LIF (TA-LIF) [49]. Compared to single-photon LIF, TA-LIF is considerably less efficient and the excitation rate scales with the square of laser power. Normally higher laser power is required to produce detectable fluorescence intensity, but laser stimulated effects including photon-ionization, induced breakdown, stimulated emission, etc. needs to be avoided [71, 72]. Table 3 lists excitation schemes of TA-LIF for various active atomic species in plasmas. An example of two-dimensional distribution of atomic oxygen in an atmospheric-pressure plasma jet-source by TA-LIF is presented in Figure 4.

### 3.2 Absorption spectroscopy

Another important diagnostic technique for atmospheric-pressure plasmas is absorption spectroscopy (AS) [77]. Compared to LIF or OES approaches, AS is an in
situ and non-invasive technique probing absolute densities of interested species without need of extra calibration and independent on collisional quenching process. It relies on the Beer-Lambert law:

\[
A(\lambda) = -\ln\left(\frac{I_s}{I_0}\right) = N\sigma(\lambda)L
\]  

where \(I_s\) is the light intensity passing through sample, \(I_0\) is the incident radiation, \(N\) is species density, \(\sigma(\lambda)\) is the wavelength dependent absorption cross-section, and \(L\) is the absorption path-length. If probed species density is low, the absorption length is normally increased by using a multi-pass spectroscopic absorption cell where light reflects between two mirrors, e.g., the Herriott cell [78]. However, if for micro-plasmas this technique maybe not sensitive enough if species density is not high to obtain a distinct absorbance signal.

The sensitivity of absorption measurements is strongly dependent on the stability of used light source. Various types of light sources, narrow-band or broadband with wavelength range from VUV to mid-infrared, are applied together with high spectral resolution detection system such as spectrometer or FTIR. AS by laser light sources, particularly tunable diode-lasers or quantum cascade lasers are attractive light sources have been applied to measure species densities in micro-plasmas [8, 79, 80]. These laser sources output specific wavelengths of large absorption cross-sections and enable fine scan of wavelength to obtain a clear absorption line profile, and from which species density and even gas temperature are able to be derived.

Wavelength selectivity is important in the implementation of AS technique as absorption may overlap by multi-species. And, it should be mentioned that absorption measurements yield line-integrated densities and spatial distribution is achievable by Abel inversion. Special efforts are required for non-uniform micro-plasmas by AS approach, since gas temperature and species density are spatially dependent. In this case broadband absorption can provide more details for deriving both the gas
An example of OH density determination by broadband UV absorption in an atmospheric-pressure pin-to-water discharge is depicted in Figure 5 [83].

Another quite sensitive approach by using a cavity of two highly reflective mirrors is the cavity ring-down spectroscopy (CRDS) [84]. The laser pulse goes-and-back in the cavity and that effectively enhances the absorption path length in the probed gas sample by several orders of magnitude. The time-decay of light intensity leaking from the cavity depends on the reflectivity of mirrors and species density in the cavity. Based on that the species density is able to be obtained with the known mirror reflectivity. In addition to the high sensitivity, compared to absorption spectroscopy, CRDS is independent on fluctuations of light intensity since a time constant rather than an absolute absorbance is measured. More details of CRDS technique are included in Refs. [84-90].

4. Summary

High-end diagnostic techniques have been applied to atmospheric-pressure plasmas. Even for highly transient non-uniform micro-plasmas, reliable insights of discharge properties are able to be achieved. This chapter includes several important advanced diagnostic approaches specifically for plasma parameters and reactive plasma species. Two approaches are suggested for a same diagnostic purpose, for example, the determination of gas temperature or electron density, and compared to ensure and increase the measurement accuracy, particularly for atmospheric-pressure plasmas. Other important plasma properties, such as densities of ion species and ion flux, surface charges, have been investigated as well and related diagnostic techniques can be found in above (review) references.
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