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Nonequilibrium effects in thermal plasmas

Charles H. Kruger, Tom Owano, Matt Gordon, and Christophe Laux

Mechanical Engineering Department, High Temperature Gasdynamics
Laboratory, Stanford University, Stanford, California 94305, USA

Abstract - An assessment is made of the occurrence, nature, and effects of nonequilibrium in "thermal" plasmas at atmospheric pressure, ranging from high-temperature highly ionized plasmas to lower-temperature molecular gases. Particular attention is directed to recombining plasmas, which occur in many plasma-chemistry applications, where the electron density significantly exceeds its equilibrium value with respect to the ground state. For an atomic argon plasma, experiments with a 50kW inductively coupled plasma and optical diagnostics support a partial-equilibrium hypothesis where the bound and free electrons are mutually equilibrated, but elevated with respect to the ground state, for a range of moderate-temperature conditions of interest. Under those circumstances, radiation from the plasma can be substantially enhanced from its equilibrium value and spectroscopic diagnostics must be interpreted with considerable care. When a molecular diluent (N_2,H_2) is added to the recombining argon plasma, excited state populations are observed to be "quenched", the partial-equilibrium approximation breaks down, and the Boltzmann temperature based on ratios of excited state number densities is no longer useful. However, elevated electron densities and enhanced radiation can still be present. This quenching is interpreted in terms of a two-species collisional/radiative model which allows for near-resonant transfer of bound electronic energy between the species. Under such circumstances, which are of considerable practical importance, direct temperature measurements are recommended. To this end, the wavelength dependence of two-body recombination radiation in the UV is used as a direct measurement of the electron temperature.

INTRODUCTION

Partially ionized plasmas at atmospheric or near atmospheric pressure are typically described as "thermal" plasmas. This terminology implies local thermodynamic equilibrium, such that for a given pressure a single temperature is adequate to describe the plasma. The assumption of LTE is often used in the modeling and diagnostics of atmospheric-pressure plasmas. For relatively high electron densities, at temperatures above approximately 10,000 K, rapid collisions between charged and neutral particles, the large Coulomb cross section for collisions between charged particles, and rapid three-body recombination all tend to promote equilibration. Thus, equilibration is likely for a wide range of circumstances at high temperatures when the electron density is of the order of or greater than, say, 10^{22} m^{-3}, with the exception of very rapid transients, steep gradients, or strong electric fields. This has been supported by careful experimental measurements such as those of Schram (ref. 1) and Emmons (ref. 2).

The success and verification of LTE assumptions at high electron densities, as well as the obvious pragmatic simplification, has led to their assertion at lower electron densities at temperatures below 10,000K. For example, a review of the papers on thermal plasmas at the Ninth International Symposium on Plasma Chemistry and those published since then in the Journal of Plasma Chemistry and Plasma Processing indicate that LTE is by far the most common description even at lower temperatures. The purpose of this paper is to review the applicability and limitations of the LTE assumption at the lower electron densities encountered for temperatures below approximately 10,000K. We first briefly review possible forms of nonequilibrium, then after discussion of our experimental facilities, present evidence that partial local thermodynamic equilibrium between bound and free electrons is often a good model for recombining noble-gas plasmas. However, admixtures of nitrogen or hydrogen in such plasmas can destroy the validity of this simplification. The principle effects of departures from LTE are argued to be incorrect evaluation of the plasma radiation source strength and errors resulting from the common use of emission spectroscopy for plasma diagnostics, particularly with regard to the widely used LTE temperature measurement.

FORMS OF NONEQUILIBRIUM

The review of recent articles on thermal plasmas mentioned in the preceding section indicates that when departures from equilibrium are considered the most common, particularly in modeling papers, are differences between electron and gas temperatures, and the effects of finite ionization/recombination rates in causing nonequilibrium electron densities with respect to ground-state populations. The former effect occurs in the presence of significant electric fields, that is in the plasma source itself, or when there are very steep gradients--and is relatively well recognized and understood. The influences of the latter effect, particularly in recombining plasmas which are virtually characteristic of plasma chemistry applications, have not been as well considered and are the principle theme of this paper. In particular, the coupling between the populations of bound electronic states and the electron density in a recombining plasma can have major effects on the local emission or radiation and the utility of standard emission diagnostics. On the other hand, effects on the overall energy balance, **except for radiation and the possible importance of recombination energy release**, and on the fluid mechanics may be relatively minor, except perhaps for electron effects on the thermal conductivity. Of course, both electron-temperature and electron-density nonequilibrium will have important effects on the electrical properties and behavior of a plasma. At lower temperatures still, chemical (as well as vibrational) nonequilibrium is surely of importance in many plasma chemistry applications, including energy balances as well as species fluxes to surfaces. Methods of describing chemical nonequilibrium in neutral gases are now well in hand, although reaction rates are not always satisfactorily known. But the coupling between plasma effects and chemistry has received much less attention. The role of electron-density nonequilibrium in influencing chemical reactions is one such possibility (ref. 3). Another, described later in this paper, is the possibility that neutral-particle chemical reaction rates can drive electron-density nonequilibrium in plasmas containing molecular ions.

EXPERIMENTAL FACILITY

The measurements described here were conducted with a nominally 50 kW TAFA model 66 RF induction torch, powered by a LEPEL model t-50-3 power supply operating at a frequency of 4 MHz. The vertical 5-coil torch has a 7.5 cm inner diameter and an inner length of 26.5 cm measured between the gas injection plate and the 5 cm exit nozzle, which is 6 cm above the upper coil. The present experiments were conducted using a water cooled quartz test section which is shown schematically in Figure 1. The test section has an inner diameter of 5 cm and a length of 18 cm above the nozzle exit. Spectroscopic measurements reported at the "nozzle exit" were made 1 cm downstream of the nozzle with the test section removed. Similarly, measurements reported at the "test section exit" were made in the free-jet 1 cm downstream of the test section exit. The power supply and torch, and the test section cooling water systems were separately instrumented with thermocouples and flowmeters to independently obtain calorimetric energy balances for comparison with those obtained from spectroscopic measurements.

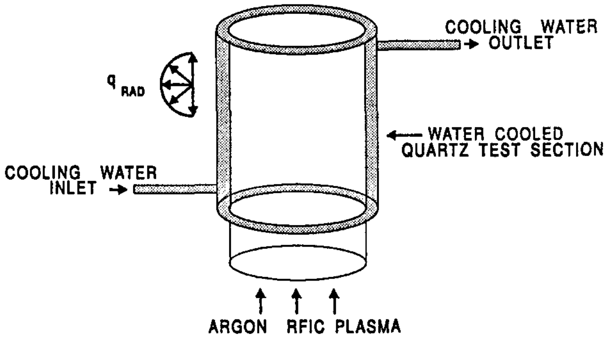

Figure 1.
Schematic of quartz test section.

Plasma emission measurements were made using a SPEX model 1400-II 3/4 meter scanning monochromator fitted with a Hamamatsu model R1104 photomultiplier tube. Absolute intensity calibrations were obtained by means of a tungsten strip lamp, with a calibration traceable to NBS standards. Temperature measurement of the tungsten filament was made using a Pyro-micro disappearing filament optical pyrometer and is the principal source of uncertainty in the absolute intensity calibration (approximately 5%). Ultraviolet calibration was obtained using a calibrated quartz-halogen, type FEL, tungsten coiled-coil filament lamp. A narrow bandpass interference filter was also used to increase background rejection for the UV calibrations. A 4 mirror, dual translation stage, two lens optical collection system that enabled lateral and axial translational scans of the plasma emission is shown qualitatively in Figure 2. Data sets acquired using a Stanford Research Systems model SR510 lock-in amplifier were transferred to and stored on a laboratory computer for processing. Lateral traverses of the plasma emission were transformed to radial variations using an Abel inversion technique.

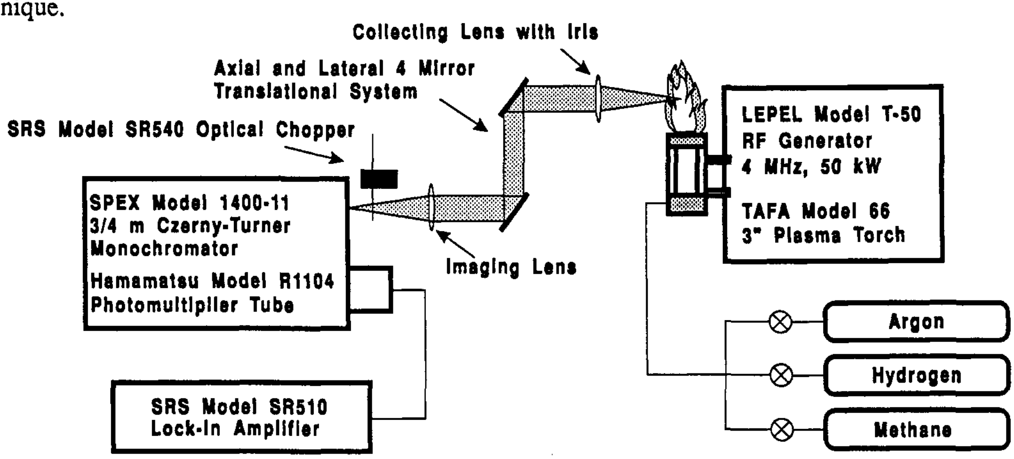

Figure 2. Experimental schematic for emission measurements.

Laser induced fluorescence measurements of a hydrocarbon plasma were performed using the same facility as described above, with the exception of a 7 cm nozzle and test section in place and a water-cooled flat-plate substrate placed parallel to the flow within the test section. This experiment is shown schematically in Figure 3 with the test section omitted for clarity. In this experiment, R-branch lines of the $A^2\Delta(v=0)$ - $X^2\Pi(v=0)$ system of CH (centered at approximately 431.5 nm) are pumped using a laser sheet generated with a Spectra Physics DCR-4G Nd:YAG pumped PDL-2 dye laser. The resultant fluorescence is collected through the same optical train used for the emission measurements, and the majority of Q-branch lines are detected by a photomultiplier tube after being spectrally isolated by a monochromator. Plasma background emission is overcome by using the pulsed laser in conjunction with a gated integrator.

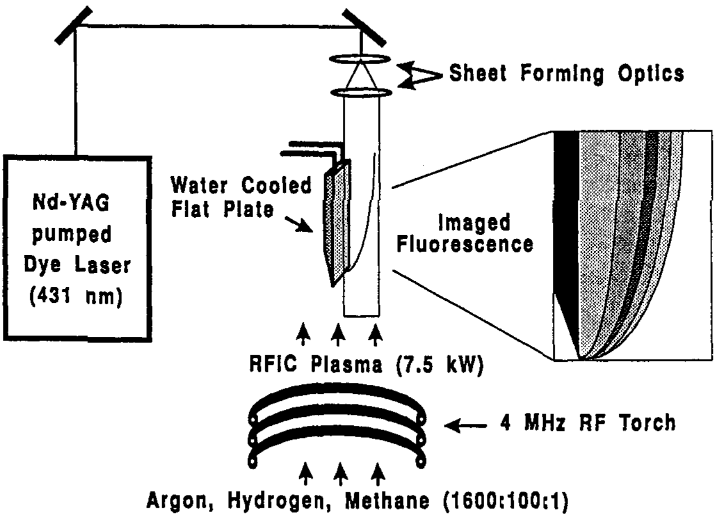

Figure 3.
Experimental schematic of the CH laser induced fluorescence experiment.

NOBLE-GAS EXPERIMENTS

Atmospheric pressure argon plasmas have been used to investigate the applicability of LTE assumptions to noble gas plasmas of moderate temperatures and electron densities (< 10,000 K, 10^{22} m^{-3} respectively). In these experiments, emission diagnostics are used to assess the plasma state at several locations downstream of the excitation source. Absolute line intensities, relative line intensities, and absolute continuum intensities are used to determine electronic state populations, electron density, and associated temperatures. The measurement of excited electronic state populations and electron density allows the applicability of LTE assumptions to be tested at the conditions of interest.

If a plasma is truly in a state of LTE, temperatures describing the absolute and relative electronic level populations, as well as their relation to the density of free electrons, will be the same. Recombining argon plasmas in the temperature and electron density range of 5000 - 8500 K, 10^{20} - 10^{22} m^{-3} respectively, downstream of the inductively coupled plasma torch, have been investigated in this manner and found to exhibit non-LTE behavior (refs. 4,5). This is due to the relatively slow electron-ion three-body recombination rates. Nevertheless the plasma is found to maintain partial local thermodynamic equilibrium, or PLTE. In this state of PLTE, excited electronic states and free electrons are mutually in partial equilibrium at the Boltzmann temperature T_B, as given by the excited state Saha equation:

$$\frac{n_e^2}{n_j} = \frac{2g_i}{g_j}\left(\frac{2\pi m_e k T_B}{h^2}\right)^{3/2} \exp\left(\frac{-\varepsilon_{j\lambda}}{kT_B}\right)$$

where $\varepsilon_{j\lambda}$ is the ionization energy of the jth excited level, g_i represents the ion partition function, and the other symbols have their usual meaning. The absolute populations of bound and free electrons, however, deviate from LTE with the ground state by a non-equilibrium factor, α, given by:

$$\frac{n_j}{g_j} = \alpha\left(\frac{1}{g_1}\right)\left(\frac{p}{kT_B}\right) \exp\left(\frac{-\varepsilon_j}{kT_B}\right)$$

$$\left(\frac{n_e^2}{n_1}\right) = \alpha\left(\frac{2g_i}{g_1}\right)\left(\frac{2\pi m_e k T_B}{h^2}\right)^{3/2} \exp\left(\frac{-\varepsilon_i}{kT_B}\right)$$

Although emission measurements allow only confirmation of PLTE in the argon plasmas to electronic levels as low as j=3, preliminary absorption measurements indicate that PLTE in fact extends to j=2 for the range of conditions investigated. Since the partial equilibrium is maintained by collisions between excited electronic states and free electrons, the Boltzmann temperature T_B should agree with the free electron translational temperature T_e. This is supported by detailed collisional-radiative models (ref. 6) which show equilibration, at sufficiently high electron densities, between the electron temperature T_e and the Boltzmann slope temperature T_B of high lying bound electronic levels. Analysis of the electron energy equation in the regions downstream of the excitation source indicates relatively small differences between the electron temperature T_e and the heavy particle gas temperature T_g.

The importance of accurately accounting for deviations from LTE can be illustrated by the interpretation of argon radiative source strength measurements. Measurements of the volumetric radiative source strength of argon (ref. 4) are shown in Figure 4 as interpreted with the assumption of LTE as opposed to those interpreted taking into account effects of the observed PLTE . Since the bound and free electrons responsible for the radiative emission of the plasma are, for the most part, overpopulated with respect to their LTE values, we can see that the value obtained using LTE assumptions drastically overpredicts the low temperature values of radiative source strength. Also shown in Figure 4 are the measurements of Emmons, who made use of LTE arguments in his data reduction, as well as a proposed upper bound curve, based on the argument that the observed radiation must fall off with decreasing temperature at least as fast as a Boltzmann factor corresponding to the population of the second excited level at 13.1 eV. We see in this case that the use of LTE temperatures for determining the plasma state and interpreting measurements is unsatisfactory.

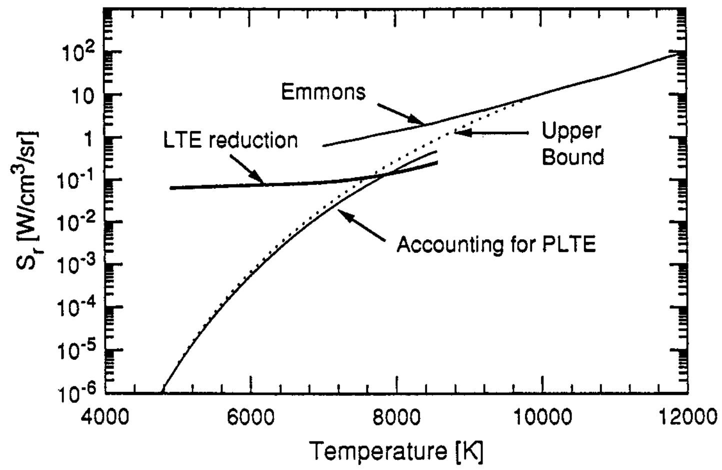

Figure 4.
Radiative source strength of argon.

MORE COMPLEX PLASMAS

If noble-gas thermal plasmas are less simple to describe and measure than is sometimes assumed, thermal plasmas containing mixtures of species and ions, particularly including molecules, are still more complex. In our laboratory, temperature and radiation source-strength measurements for atmospheric-pressure air have been performed using the induction-plasma facility described in the earlier. Figure 5 shows a comparison of the measured radiation source strength with the predictions of the NASA NEQAIR program (ref. 7) as modified by our group to include more accurate transition probabilities (ref. 8). Unlike the argon experiments, agreement between LTE temperatures, the O-atom Boltzmann temperature, and the N_2^+ rotational temperature suggests that LTE conditions are achieved. This is further supported by comparison of the electron density based on the ground-state Saha equation and the LTE temperature with a measured electron density from Stark broadening of hydrogen lines, with a small amount of hydrogen added specifically for this purpose. In the temperature range shown, where there are no previous direct experimental measurements of the radiation source strength, the agreement with the revised calculation is encouraging, and in itself indirectly supports LTE in these circumstances. It is plausible to attribute this to the dominance of molecular collisions and the relatively slow flow transients in these experiments.

At the other extreme, we have mixed small amounts of nitrogen or hydrogen with argon under conditions similar (but not necessarily identical) to those of the noble-gas experiments of the preceding section. It is found that under conditions where the plasma is still strongly recombining at the test-section exit the presence of the diluent causes marked departures from partial local thermodynamic equilibrium between the bound and free electrons. (Specific details of these measurements are given by another paper at this Symposium (ref. 9)). Typical results are shown in Figure 6 where the normalized population of the 4p bound state of argon is shown for varying diluent concentrations. In this Figure, an

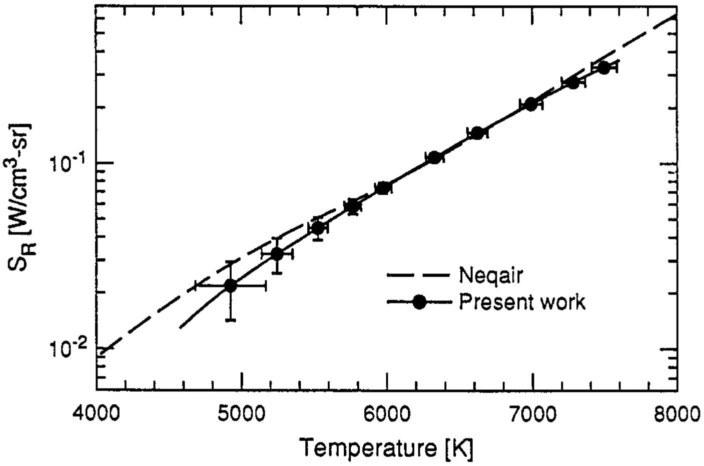

Figure 5.
Radiative source strength of air.

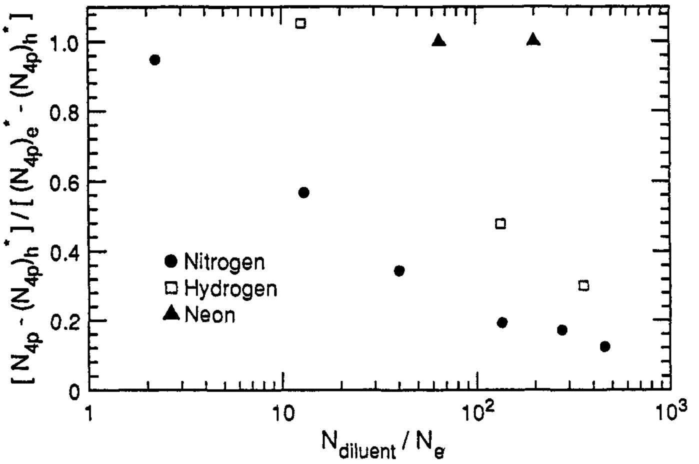

Figure 6.
Quenching of argon 4p bound electronic level.

ordinate value of 1 indicates that the 4p level population is in partial equilibrium with the free electrons, while a value of 0 indicates that the 4p level population is in LTE with the ground state. The decrease of the normalized values from unity as the diluent concentration is increased can be described as quenching of the bound-state populations. This quenching will lower the effective radiation source strength and invalidate PLTE diagnostics, such as the line to continuum temperature method (ref. 10). It seems likely that this quenching results from exothermic exchange reactions such as:

$$\mathrm{Ar(4s) + H(1) \Rightarrow Ar(3p) + H(2)}$$

An approximate collisional/radiative model, incorporating four levels of argon and four levels of hydrogen with reactions such as the foregoing, is successful in interpreting the qualitative behavior shown in Figure 6.

An interesting aspect of these experiments is that for the plasmas with nitrogen addition the elevated nonequilibrium electron density appears to be governed not by the usual electron three-body recombination, but rather by the (neutral) recombination of N to N_2. Based on calculations for these conditions using CHEMKIN (ref. 11) with rates from (ref. 12 and 13), the concentration of electrons and ionic species is governed by rapid dissociative recombination of N_2^+ and charge exchange between N_2^+, N^+, and Ar^+. According to the CHEMKIN calculations, a partial equilibrium of these reactions establishes the charged-particle concentrations relative to N_2 and N, at least for nitrogen concentrations greater than 1%. More specifically, the CHEMKIN calculations for our conditions support to a good approximation the readily derived result that for partial equilibrium of the dissociative-recombination and charge exchange reactions:

$$\frac{n_e \mathrm{Ar}^+ / \mathrm{Ar}}{(n_e \mathrm{Ar}^+ / \mathrm{Ar})^*} = \frac{\mathrm{N}^2 / \mathrm{N}_2}{(\mathrm{N}^2 / \mathrm{N}_2)^*}$$

Here (   )* denotes the equilibrium value of the concentration ratio in question. Similar results are obtained for N_2^+ and N^+, with Ar^+/Ar on the left-hand side replaced by N_2^+/N_2 or N^+/N. It is then the relatively slow recombination of N to N_2 through the test section that maintains and governs the electron-density overpopulation. This effect, if substantiated, may be of considerable importance for a range of plasma chemistry applications where molecular ions are present.

CONCLUSIONS

Our experience with recombining inductively coupled plasmas at temperatures below 10,000 K and electron densities below 5×10^{21} m^{-3} indicates that LTE is not a reliable assumption for plasma diagnostics or plasma modeling. However, for a pure argon plasma partial equilibration between bound and free electrons can be a useful and practical approximation. Under PLTE conditions, electron density and electron temperature must be separately measured, for example, by continuum radiation and the line to continuum temperature method. The validity of this approximation can be checked by accessing several bound states with sufficient energy separation. Under PLTE conditions, the nonequilibrium radiation source strength is independent of the ground-state density and proportional to the square of the nonequilibrium electron concentration.

Plasmas consisting of mixtures of species including molecules are considerably more complex. Under certain conditions (such as our air experiments) molecular collisions may result in LTE. But this surely must be independently checked for particular conditions, and the check is more complicated because of the possibility of chemical and vibrational nonequilibrium. The addition of relatively small amounts of nitrogen or hydrogen to a recombining plasma otherwise in PLTE has been shown to produce a quenching of excited state populations, invalidating the usefulness of the PLTE approximation. Under such circumstances, one must resort to direct measurements. Stark broadening and absolute continuum intensities in the visible (as well as other methods) can be used for a direct measurement of the electron density. For the electron temperature, we have used the variation of the recombination radiation intensity with wavelength in the UV (ref. 14). This method assumes only a Maxwellian electron translational velocity distribution function and a satisfactory knowledge of the recombination cross section through the so-called Biberman factor. Application of this method to our well-diagnosed argon plasmas shows good agreement under PLTE conditions with Boltzmann and line to continuum temperatures. For the gas temperature, since rotational equilibrium is likely for many conditions of interest, measurement of the relative intensities of rotational lines will in principle yield a rotational temperature which often can safely be assumed equal to the gas translational temperature. However, if this is done by conventional emission spectroscopy the usual Abel inversion of multiple lines can lead to unreliable results. We are currently exploring measurements of rotational temperature (as well as species concentration) in the boundary layer over a substrate in diamond deposition experiments using laser-induced fluorescence. However, these laser-based point measurements are notably difficult to perform in a luminous plasma, as evidenced by the scarcity of reported verified results. The scattering measurements of line width recently reported by Snyder and Reynolds (ref. 15) are a notable exception. Another possibility for the measurement of the gas temperature is the use of wavelength tunable diode lasers to obtain Doppler line widths. Because of the weak temperature dependence and occurrence of other forms of broadening this measurement must be performed with unusual precision to provide useful results (ref. 16).

In summary, then, we conclude that for noble-gas thermal plasmas LTE is not a safe assumption, but that in many circumstances PLTE provides a practical description for both diagnostics and modeling. Unfortunately, for mixtures and molecular plasmas no such general description appears applicable, and each case must be analyzed for its own particular characteristics. Under these circumstances, direct measurement of plasma parameters such as temperature and electron density may be the only reliable approach. Since most current techniques are in fact indirect, this presents a major challenge for experimentalists.

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