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Highly nonlinear, sign-varying shift of hydrogen spectral lines in dense plasmas

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Hydrogen H_α shift is measured in a plasma characterized by a noticeable coupling due to a high electron density ($N_e \geqslant 2\times10^{18}\,\mathrm{cm}^{-3}$) and a relatively low temperature ($T=8900\,\mathrm{K}$). The plasma is produced by a single laser breakdown in an underwater medium, creating a stable and radially homogeneous plasma. The results cannot be explained by the known contributions to the shift, which predict shifts by a factor of 2 greater than the experimental shifts. A contribution called dipole ionic-electronic shift (DIES) is introduced. The data presented in this work constitute the experimental discovery of this phenomenon. Indeed, the total theoretical shifts obtained taking into account the DIES are in excellent agreement with our experimental values.

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I. INTRODUCTION

A study of optical properties of plasmas characterized by a noticeable coupling usually encounters experimental difficulties because it needs stable and homogeneous plasmas of a high electron density N_e and a relatively low temperature T. Underwater laser plasmas correspond to such conditions ($N_e > 10^{18}\,\mathrm{cm}^{-3}$; $T \leqslant 10^4\,\mathrm{K}$) and a complete description of their physical parameters has been done recently by elaborated spectroscopic methods [1].

In the present paper, the shift of the hydrogen H_α emission line is studied as a function of electron density for a fixed temperature in underwater laser plasmas. To our knowledge, this is the first experimental study of H_α shift in such conditions. The electron density N_e and the temperature T are independently measured by using Ca and K emission lines obtained from chloride salts added to the water sample.

The experimental results cannot be explained by the known contributions to the shift [2–4] which predict shifts by a factor of 2 greater than the experimental shifts. We introduce here a theoretical contribution called a dipole ionic-electronic shift (DIES). Its main feature is a highly nonlinear, sign-varying dependence on N_e.

We also allow for another strong coupling phenomenon called an acceleration of (perturbing) electrons by the ion field (AEIF). The paper [5], where the AEIF was introduced, focused on how the AEIF reduces the width of spectral lines. In the present paper, we extend the effect of the AEIF to the shift of spectral lines.

We show that after taking into account the DIES and the AEIF, the total theoretical shifts become in excellent agreement with our experimental shifts.

II. EXPERIMENT

A Nd:YAG laser ⟨⟨*L*⟩⟩ of 10 ns duration and an energy ranging from 36 mJ to 60 mJ is focused into the liquid by a 50 mm focal length fused silica lens ⟨⟨*F*⟩⟩ (Fig. 1). The quartz cell ⟨⟨*C*⟩⟩ contains the water sample and prevents any external pollution. The fresh solutions of KCl and $CaCl_2$ analytes are prepared from chlorine salts. The K and Ca concentrations obtained after dissolution are 187 μg/ml and 276 μg/ml.

The spark light is observed at the right angle, perpendicular to the path of the laser pulses, through an achromatic cemented doublet ⟨⟨Do⟩⟩ and an optical fiber ⟨⟨OF⟩⟩ up to the spectroscopic device. It is composed of a Chromex 500-IS spectrometer ⟨⟨*S*⟩⟩ and a 1024 photodiode array detector ⟨⟨De⟩⟩ with 700 channels intensified. They are monitored with an optical multichannel analyzer OMA2000 and a personal computer.

The dispersion of the detection system is 0.8 Å/channel so that most of the H_α profile is observed. The photodiode array is carefully calibrated in wavelengths units with neon, xenon, krypton, and argon low pressure emission lamps. The spectral emission of a tungsten lamp is used to take into account of the relative sensitivities of the detector channels. The instrumental function of the detection device is obtained from the Ar I (763.51 nm) line observed in argon low pressure lamp spectra. This line is sufficiently narrow so that it can be considered as the δ function for our spectroscopic system.

III. THEORY

There are several sources of the center of gravity shift (CGS) of hydrogen or hydrogenlike spectral lines in plasmas (only these lines are considered below). The primary source of the CGS is a pure electronic shift (ES) [2]. A pure ionic CGS is zero [4]. However, ionic contributions to the CGS can arise due to a coupling with electrons.

One of such *coupled* contributions to the CGS originates from the simultaneous allowance for both the ion-quadrupole corrections to the intensities and the electron impact shifts of individual Stark components. This shift, which we call here the quadrupole ionic electronic shift (QIES) was presented in [4]. The electron impact shifts entering the QIES were calculated in [4] using the standard theories (ST)—the semiclassical approaches [6,7] where the entire dynamic interaction of the electron microfield with the radiator was treated perturbatively and without the recognition of its strong coupling with the ion microfield. Therefore, the QIES consists of the product of two factors, originated from the ion quadrupole corrections and from the electron impact shifts, respec-

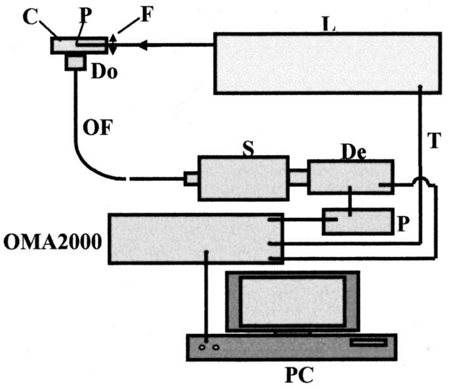

FIG. 1. *Experimental setup*. L = laser; F = focusing lens; P = plasma; C = cell; Do = imaging doublet; OF = optical fiber; S = spectrometer; De = intensified detector; T = electrical trigger; P = pulser; OMA2000 = optical multichannel analyzer; PC = personal computer.

tively, but the latter (electronic) factor is calculated without the allowance for its strong coupling with the ion microfield.

In the present paper, while treating the CGS, we go beyond the ST and employ two major *strong coupling phenomena*, which become more and more effective with the increase of the plasma density and/or with the decrease of the plasma temperature. The first phenomenon is a *direct* coupling of the electron and ion microfields, manifested by the acceleration of (perturbing) electrons by the ion field (AEIF). The paper [5], where the AEIF was introduced, focused on how the AEIF reduces the width of spectral lines. In the present paper, we extend the effect of the AEIF to the shift of spectral lines. In the next section, it will be demonstrated that for our experimental conditions, *the AEIF significantly reduces both the ES and the QIES*.

The second phenomenon is an *indirect* coupling of the electron and ion microfields, where the radiator acts as an intermediary. The strong indirect coupling was first introduced in paper [8], where the generalized theory (GT) of Stark broadening was presented (the latest, advanced version of the GT can be found in [9]). Both paper [8] and paper [9] focused primarily on how this strong indirect coupling modifies the width of spectral lines. Below we show that this strong indirect coupling contributes also to the CGS of spectral lines. Since this new contribution to the CGS results from a ''cross fertilization'' between the ion-*dipole* interaction with the radiator and the electron impact shifts of individual Stark components, we call it the dipole ionic electronic shift (DIES).

The physics behind the AEIF and the corresponding formalism were already presented in [5]. Therefore, our main focus here is the presentation of the DIES.

Let us consider a Stark component resulting from the radiative transition between an upper Stark state $\alpha = (n_\alpha, q_\alpha, m_\alpha)$ and a lower Stark state $\beta = (n_\beta, q_\beta, m_\beta)$. Here $q_\alpha = n_{1\alpha} - n_{2\alpha}$ and $q_\beta = n_{1\beta} - n_{2\beta}$, where $(n_{1\alpha}, n_{2\alpha})$ and $(n_{1\beta}, n_{2\beta})$ are the corresponding parabolic quantum numbers. The electron impact shift s of this component in the ST (see, e.g., [4]) can be represented in the form

$$s(q_\alpha,q_\beta)=[n_\alpha{}^2 q_\alpha b_\alpha - n_\beta{}^2 q_\beta b_\beta] f(N_e,T_e),$$

$$f(N_e,T_e)=(3\pi\hbar N_e/m_e{}^2)[2m_e/(\pi T_e)]^{1/2}, \qquad (1)$$

$$b_\gamma = \mathrm{Im}\int_0^\infty dZ\, C_\gamma(Z)/Z, \qquad \gamma=\alpha,\beta.$$

Here $C_\gamma(Z)$ is a so-called broadening function and Z is a scaled impact parameter of the perturbing electron [6,7]. In the ST, the shift function b_γ is independent of quantum numbers and is a constant equal to $\pi/2$ [7].

As in paper [4], we consider a pair of lateral Stark components corresponding to radiative transitions $(n_\alpha, q_\alpha) \rightarrow (n_\beta, q_\beta)$ and $(n_\alpha, -q_\alpha) \rightarrow (n_\beta, -q_\beta)$. Obviously, in the ST, $s(-q_\alpha, -q_\beta) = -s(q_\alpha, q_\beta)$. Since in the dipole approximation with respect to the ion microfield, these two Stark components have equal intensities, then in the ST, the CGS of this pair is $[s(q_\alpha,q_\beta)+s(-q_\alpha,-q_\beta)]/2=0$. The summation of the CGS over all such pairs of lateral Stark components of the spectral line still yields zero. An allowance for central (unshifted) Stark components characterized by $q_\alpha = q_\beta = 0$ does not change the result since for them $s(0,0)=0$.

However, in the GT, the broadening function C_γ, and consequently the shift function b_γ, depend on quantum numbers through dimensionless parameters χ_γ and Y_γ entering C_γ in the GT:

$$\chi_\gamma = k/n_\gamma, \quad k=(n_\alpha q_\alpha - n_\beta q_\beta);$$

$$Y_\gamma = [3n_\gamma\hbar/(2m_e v)]^2 F/e, \quad \gamma=\alpha,\beta. \qquad (2)$$

Here v is the velocity of the perturbing electron and F is the strength of the ion microfield. We emphasize that in the GT, the shift function b_γ depends both on even and *odd* powers of χ_γ. Therefore, in the GT, the CGS of the same pair of Stark components differs from zero: $[s(q_\alpha,q_\beta)+s(-q_\alpha,-q_\beta)]/2 \neq 0$. Consequently, the CGS of the entire spectral line can be expressed as

$$d_{\mathrm{DIES}} = \left\{ \sum_{k>0} g_k f(N_e,T_e)[n_\alpha{}^2 q_\alpha b_D(\chi_\alpha, Y_\alpha) - n_\beta{}^2 q_\beta b_D(\chi_\beta, Y_\beta)] \right\} \bigg/ \sum_{\mathrm{all}\ k} g_k, \qquad (3)$$

$$b_D(\chi_\gamma, Y_\gamma) = [b(\chi_\gamma, Y_\gamma) - b(-\chi_\gamma, Y_\gamma)]/2, \quad \gamma=\alpha,\beta,$$

where g_k are intensities of the Stark components. Physically, this shift, DIES, originates from the fact that in the GT, the perturbing electron scatters differently on the atomic Stark states characterized by the same absolute value but the opposite signs of the averaged dipole moment. We emphasize that, in the ST, there was no such difference in the electron scattering.

A more explicit formula for the function $b(\chi_\gamma, Y_\gamma)$ that controls the DIES can be obtained as follows. First, we enter the expression for $C(\chi_\gamma, Y_\gamma, Z)$ given by Eq. (30) of [6] into the second line of Eq. (1). Second, we substitute variable Z by variable $\varepsilon(Z)$ given by Eq. (31) of [6] and integrate over

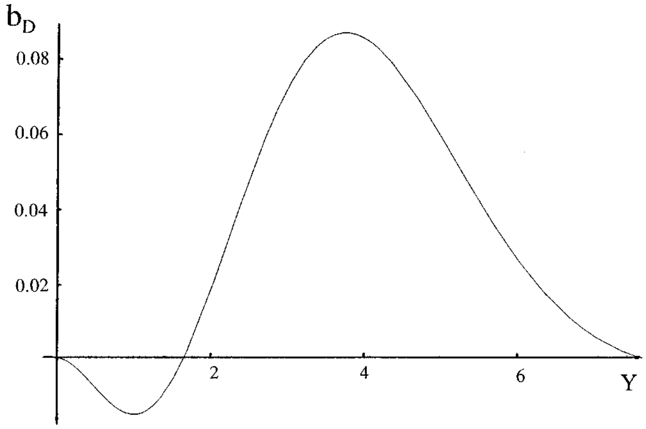

FIG. 2. Function $b_D(\chi,Y)$, controlling the dipole ionic-electronic shift (DIES), versus dimensionless parameter $Y=[3n\hbar/(2m_e v)]^2 F/e$ for a typical Stark component characterized by $\chi=1$ [parameter χ is defined in Eq. (2)].

ε, the integration being possible analytically. Third, we substitute variables x_1, x_2 from Eq. (30) of [6] by variables $\varphi_1=\tan^{-1}x_1$, $\varphi_2=\tan^{-1}x_2$. Finally, we substitute variables φ_1, φ_2 by variables $y=(\varphi_1-\varphi_2)/2$, $z=(\varphi_1+\varphi_2)/2$ and arrive at

$$\begin{aligned}b(\chi,Y)=(3\pi/16)\int_0^{\pi/2}dy\int_{y-\pi/2}^{\pi/2-y}dz\\ \times\{(\cos 2y+\cos 2z)J_1(u)/u\\ +2(\cos 2y-3\cos 2z)[J_2(u)/u^2-2J_3(u)/u^3]\\ +2[(\chi\cos z-\sin y)^2/(\chi^2-2\chi\sin y\cos z\\ +\sin^2 y)][J_3(u)/u-2J_4(u)/u^2]\},\end{aligned}\tag{4}$$

$$\begin{aligned}u(\chi,Y)=Y[4(\sin 2y)/(\cos 2y+\cos 2z)]\\ \times(\chi^2-2\chi\sin y\cos z+\sin^2 y)^{1/2}.\end{aligned}\tag{5}$$

Here $J_j(u)$ are the Bessel functions ($j=1,2,3,4$); suffix γ at χ and Y is omitted for brevity. Again, it is clearly seen from Eqs. (4) and (5) that $b_D(\chi_\gamma,Y_\gamma)=[b(\chi_\gamma,Y_\gamma)-b(-\chi_\gamma,Y_\gamma)]/2\neq 0$.

Further, we studied analytically the asymptotics of the function $b_D(\chi,Y)$. For the case of $Y\ll\min(1,1/\chi)$ we obtained

$$b_D(\chi,Y)\approx-\{\pi\chi Y/[8(\chi^2+1)^{1/2}]\}\ln\{1/[64Y(\chi^2+1)^{1/2}]\}.\tag{6}$$

Equation (6) shows two features of the DIES: (1) at relatively small ion fields F (and consequently, at relatively small values of Y), the DIES is *red*; (2) as the ion field F increases, the DIES reaches an extremum, then diminishes by the absolute value, and then becomes *blue*. The fact that for relatively large F the DIES is blue can be also seen from another asymptotics we obtained. Namely, for the case of $1/\chi\ll Y\ll 1$, we found that

$$b_D(\chi,Y)\approx 1/(90\chi^3 Y^2).\tag{7}$$

Our numerical calculations of the function $b_D(\chi,Y)$ confirmed this *highly nonlinear, sign-varying* behavior of DIES. Figure 2 shows the function $b_D(\chi,Y)$ versus Y for $\chi=1$. It is seen that at relatively small Y, the function $b_D(1,Y)$ is negative (the shift is red), but at relatively large Y it becomes positive (the shift is blue), and that *the primary extremum* of this function is on the positive (*blue*) side. We emphasize that $Y\propto F/v^2\propto N_e^{2/3}/T_e$. Therefore, dense plasmas of a moderate temperature should be the most favorable for the observation of the DIES, where it is expected to be blue. As T_e increases and/or N_e decreases, the DIES should become red and its absolute value should become relatively small.

IV. FINAL RESULTS AND DISCUSSION

Spectra of K and Ca emission lines are unfolded from the instrumental function by a reconvolution method [10,11]. The doublet lines K I (766.49 nm, 769.90 nm), Ca II (393.37 nm, 396.85 nm) are corrected on reabsorption by a theoretical method described in detail in [1]. The method is based on finding the optical depths τ_{10},τ_{20} at the center of the doublet components from the ratio I_{10}/I_{20} of the observed central intensities using the fact that $\tau_{10}/\tau_{20}=2$. For our diagnostic lines, the central optical depths are found to be 0.8 for K I (766.49 nm) and 0.5 for Ca II (393.37 nm). This method is applicable to doublet lines in a homogeneous medium. For our experimental conditions, the drops of N_e and T from the

TABLE I. Experimental and theoretical H_α shifts $\Delta\lambda$ as a function of electron density N_e in underwater laser plasma. The temperature T is equal to 8900 K for the whole set of electron density values. Expt=experimental shift; ES=electronic shift; QIES=quadrupole ionic-electronic shift; AEIF=acceleration of electrons by the ion field; DIES=dipole ionic-electronic shift; tot=total shift. Positive values are red shifts.

N_e (10^{18} cm^{-3})	$\Delta\lambda_{\mathrm{expt}}$ (Å)	$\Delta\lambda_{\mathrm{ES+QIES}}$ (Å)	$\Delta\lambda_{\mathrm{ES+QIES+AEIF}}$ (Å)	$\Delta\lambda_{\mathrm{DIES}}$ (Å)	$\Delta\lambda_{\mathrm{tot}}$ (Å)
2.0	7.1±1.4	12.4	8.9	−1.7	7.2
2.1	7.4±1.5	13.0	9.3	−1.8	7.5
2.3	7.7±1.5	14.2	10.0	−2.1	7.9
2.4	8.1±1.6	14.9	10.4	−2.2	8.2
2.5	8.2±1.6	15.5	10.8	−2.3	8.5
2.8	9.4±1.8	17.5	12.0	−2.7	9.3
3.0	9.5±1.9	18.7	12.7	−3.0	9.7

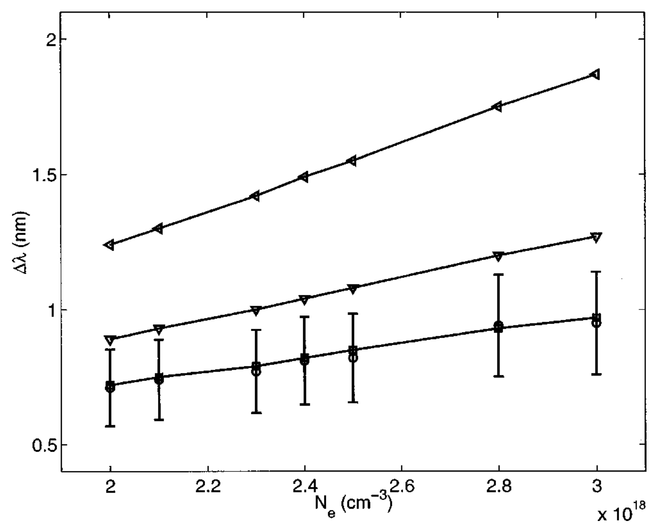

FIG. 3. Experimental and theoretical H_α red shifts $\Delta\lambda$ as a function of electron density N_e in underwater laser plasma. The temperature T is equal to 8900 K for the whole set of N_e values. ○: Experimental; ◁: ES+QIES; ▽: ES+QIES+AEIF; □: Total (ES+QIES+AEIF+DIES).

center to the edge are only 7% and 10%, respectively. Therefore, the method is applicable.

The predominant broadening mechanism for emission lines in underwater plasmas is the Stark broadening. Due to the high electron density and the relatively low temperature, the Doppler broadening is negligible. The electron density N_e is deduced from the Stark width of the deconvoluted (and corrected for the reabsorption) line K I (766.49 nm) using the Stark broadening parameters from [12], which are in excellent agreement with the experimental Stark broadening parameters for this line [15]. The values of N_e for different shots are found to be in the range of $(2-3)\times10^{18}\,\mathrm{cm}^{-3}$.

We emphasize that measurements of the H_α widths in the same underwater laser plasma were published by some of us previously [1]. The experimental H_α widths turned out to be noticeably smaller than predicted by the ST [6]. Only the allowance for the AEIF (in frames of an advanced generalized theory for the electron and ion-dynamical broadening) brought the theoretical H_α widths in agreement with the experimental ones as shown in [5]. In distinction, the widths of the line K I (766.49 nm) are practically unaffected by the AEIF for the following reason. The AEIF is effective when the separation R of the perturbing ion from the radiator satisfies the inequality: $W<R<D$, where W is the electron Weisskopf radius and D is the Debye radius. However, for the line K I (766.49 nm) under our experimental conditions, we have $W\approx D$, so that the AEIF is practically disabled. We note that the value of W for the H_α line (rigorously derived from first principles in the generalized theory [8,9]) is more than three times smaller than for this K I line, thus allowing the AEIF to work for a part of the ion ensemble. So, the experimental widths of both lines are consistent with each other and correspond to the densities deduced from them.

The Ca II (393.37 nm) and Ca I (422.7 nm) lines are observed at the same time in the emission spectra. The temperature T is obtained from their integrated intensities ratio, employing the Saha formula at the known electron density N_e. The value of T is found to be 8900 K for the entire above range of the electron densities.

We note that the optical thickness of the singlet line Ca I (422.7 nm) was checked by measuring its integrated intensity I versus the concentration C of Ca for $137\,\mu\mathrm{g/ml}<C<320\,\mu\mathrm{g/ml}$. In the optically thin case, I should be proportional to C. We found by this method that the line was optically thin for $C<300\,\mu\mathrm{g/ml}$.

The relative inaccuracy of N_e and T is about 15%. We deduce from the experimental N_e and T values that local thermodynamic equilibrium criterion [12] is fulfilled.

The influence of the instrumental function on H_α profiles is negligible because the instrumental function width is only less than 5% of the H_α width. The H_α shift is obtained by a synthetic method which consists in minimizing the quadratic error between the experimental spectrum and a theoretical one. The theoretical line profile for this procedure was chosen as a superposition of the Lorentzian (for the central Stark components) and the generalized Holtsmarkian [13] (for the lateral Stark components) with statistical weights equal to 366/943 and 577/943, respectively. Here 366/943 and 577/943 are the corresponding statistical weights of the central and lateral Stark components of the H_α line. Then, a second degree polynome is added to fit the underlying continuum. The H_α experimental shift precision is estimated to be 20%.

The comparison of the experimental and theoretical H_α shifts is presented in Table 1 and Fig. 3. It is seen that the previously known contributions to the shift (ES plus QIES) overestimate it by a factor of 2. By taking into account the reducing factor due to the AEIF, the situation gets better, but a significant discrepancy still remains. Only the further allowance for the DIES brings the total theoretical shift into agreement with the experimental values.

Thus the present work seems to constitute the experimental discovery of a *very unusual* shift: the DIES. In distinction to all previously known shifts, the DIES is *highly nonlinear and sign varying*. The most favorable conditions for observing the DIES correspond to the plasmas of high densities but of relatively low temperatures, where the DIES is blue. It is the very range of N_e and T where we experimentally studied the H_α shift; to our knowledge, this is the first study of the shift of hydrogen spectral lines in such conditions.

Finally, we note that the DIES is more sensitive to the temperature than to the density. We illustrate this by considering paper [14], where the experimental study of the H_α shift was conducted at $N_e=(1-10)\times10^{18}\,\mathrm{cm}^{-3}$, but at $T=5.6-10.4\,\mathrm{eV}$, that is at temperatures significantly higher than in our experiment. For the conditions of [14], the absolute value of the DIES is several times smaller than for our conditions and it does not contribute significantly to the total shift. The discrepancies of up to 40% between the conventional theory and the measured shift, seen from Table II and from Fig. 8 of [14], result primarily from neglecting the AEIF. The allowance for the AEIF would bring the theoretical shifts in agreement with the values measured in [14].

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