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ac Stark splitting in multiphoton excitation of atomic hydrogen in flames: Abnormal peak asymmetry due to pressure broadening

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The author develops a theory of ac Stark (or Autler-Townes) splitting occurring in double optical resonances, one of which is a two-photon transition. It includes both laser bandwidth and collisional broadening effects. Theoretical results are in excellent agreement with Goldsmith's observation of two-peaked structures in the multiphoton excitation spectra of atomic hydrogen in atmospheric-pressure flames. This is believed to be the first study demonstrating that the peak asymmetry in an ac Stark doublet can be reversed due to pressure broadening.

This Rapid Communication reports excellent agreement between theory and Goldsmith's unexpected observation of two-peaked resonance structures in the multiphoton excitation spectra of hydrogen atoms in a hydrogen-air diffusion flame.[1] We show that the phenomenon is ac Stark (or Autler-Townes) splitting[2] with abnormal peak asymmetry. This article is believed to be the first study demonstrating that the peak asymmetry in an ac Stark doublet is reversed due to pressure broadening.

Multiphoton excitation and detection of atomic hydrogen is of great interest in metrology and atomic physics,[3-5] diagnostics of plasma,[6,7] and combustion chemistry.[1,8-10] Previous reports[5,7,9,10] have discussed only power broadening and ac Stark *shifting* (but not ac Stark *splitting*) in hydrogen. On the other hand, ac Stark splitting in the optical frequency range has been pursued intensely as a research topic in its own right to understand the nonlinear interaction of strong laser radiation with matter. The splitting in the form of doublets in absorption or excitation spectra in double resonance experiments[11] have been observed in atoms other than hydrogen[12-14] and have been analyzed theoretically.[15-19] Attention in most experiments and theories so far has been confined to the low-pressure regime where collisional effects are unimportant compared to other decay and dephasing mechanisms. In particular, the unexpected observation[13] of reversed peak asymmetry in the doublet has stimulated further experimental[14] and theoretical[16-18] investigations, which attributed the reversed peak asymmetry to a laser bandwidth effect. It has been demonstrated[14,17,18] further that this abnormal peak asymmetry reverts back to normal when the pump laser detuning is larger than a few laser bandwidths. Unlike the earlier studies, the present work calls attention to (1) a new cause of abnormal asymmetry, namely, pressure broadening; and (2) that the above expected switching back to normal asymmetry at detuning beyond several laser bandwidths will not happen in the high-pressure regime.

In Goldsmith's experiment, hydrogen atoms were excited to the $3p$ level by two-photon absorption ($\lambda_a = 243$ nm) from the ground state to the $2s$ state followed by absorption of a third photon ($\lambda_b = 656$ nm), as shown by the inset of Fig. 1. The Balmer-α fluorescence to the $2s$ level was collected as a function of detuning of the *first* (a) laser around the $1s$-$2s$ resonance, while the frequency of the *second* (b) laser was kept fixed. Since only one intermediate level ($2s$) exists, one expects only one resonance peak. This was indeed the case observed for low intensity I_b of the second laser. However, at higher values of I_b, a second and smaller peak appeared as shown by the solid curve of Fig. 1. The beam geometry and detection were arranged to achieve spatial and temporal uniformity of the I_b beam, which was important for resolving the two peaks.[1]

I shall show that the appearance of the second peak is due to ac Stark splitting of the $2s$-$3p$ transition at high intensity of the second laser. The analysis employs the well-known density matrix equations of motion with the relaxation rates included.[15,16] The principal levels are the near-resonant $1s$, $2s$, and $3p$ levels (to be labeled 1, 2, and 3, respectively). By reducing the equations of motion coupling all the other hydrogenic states to these principal states and then making the rotating-wave approximation, we obtain the result that the states $1s$ and $2s$ are coupled by an effective two-photon Rabi frequency,

$$\chi_e \equiv \tfrac{1}{2}\sum_k \chi_{2k}\chi_{1k}/\Delta_{ka} , \qquad (1)$$

where the sum over k is carried over all the p states (including the continuum), the χ_{jk} are the single-photon Rabi frequencies, and the $\Delta_{ka} \equiv \omega_k - \omega_1 - \omega_a$ are the frequency detunings. Although the intensity of first laser ($I_a = 6\times 10^8$ W/cm^2) is about two orders of magnitude higher than that

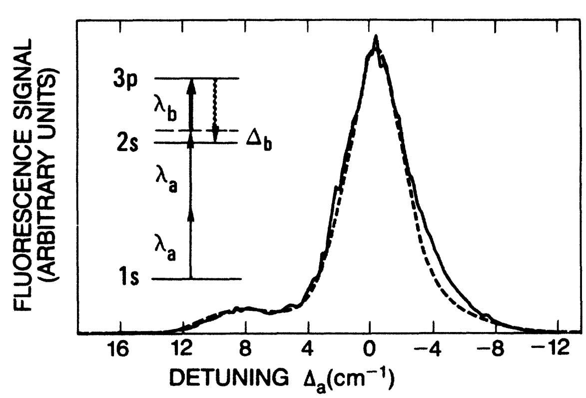

FIG. 1. Theoretical fit (dashed line) to the experimental (solid line) multiphoton excitation spectrum (Ref. 1) as function of the 243-nm (λ_a) laser detuning Δ_a, while the 656-nm (λ_b) laser detuning Δ_b is held fixed. The inset shows the multiphoton excitation scheme of the hydrogen atom.

of the second laser ($I_b = 4.4\times10^6$ W/cm^2) in the experiment, the value[20] of χ_e is only 0.015 cm^{-1} because of the large energy defects in the denominator of Eq. (1). In comparison, the 2-3 Rabi frequency[21] χ_b is 3.71 cm^{-1} at the above I_b value, and the relaxation rate of the hydrogenic states in the atmospheric pressure flame are in the order of 1 cm^{-1} (see below). Therefore, it is an excellent approximation to consider the first laser effectively as a weak probe.

The approximate bandwidths of the first and second lasers are $\gamma_a = 0.5$ cm^{-1} and $\gamma_b = 0.2$ cm^{-1}, respectively,[1] and are significant compared to other relaxation rates. We adopt the well-known phase-diffusion model[16] for each laser field by assuming that its bandwidth is due to phase fluctuations. There are better, but calculationally more difficult models[17,18] for the laser fields. But since pressure effect, rather than laser bandwidth effect, is dominant here, the phase-diffusion model is adequate for the present comparison with experimental data. We calculate stochastic averages (denoted by a bar) of the density matrix elements over the field fluctuations.

The dominant relaxation mechanism of the hydrogenic states in the flame at atmospheric pressure and at an estimated temperature of 2500 K is by collision with nitrogen, oxygen, hydrogen, and water molecules. The concentrations of these species in the observation region were not determined.[1] The collisional quenching rates of the $2s$ and the $3p$ states are estimated to be a few times 10^{10} s^{-1}, based on measurements on the $2s$ state[22,23] and the $3d$ state.[8] These values are to be compared to the radiative decay rate of 1.86×10^8 s^{-1} for the $3p$ level[21] and photoionization rates of the order 10^9 s^{-1} for the above laser intensities.[4,24] Since the laser pulses are about 5–6 ns,[1] we may make the steady-state approximation.

With the above approximations, we obtain[25] an analytic solution for the diagonal density-matrix element $\bar{\sigma}_{33}$ for the $3p$ level, which is proportional to the $3p$-$2s$ fluorescence collected in the experiment:

$$\bar{\sigma}_{33} = \frac{\frac{1}{4}\chi_e^2\chi_b^2 h}{4\Gamma_3\Delta_b^2 + \Gamma_3(\Gamma'_{32})^2 + \chi_b^2\Gamma'_{32}(1+\gamma_{31}/\gamma_{21})}\ , \tag{2}$$

where

$$h \equiv (pP + qQ)/(P^2+Q^2)\ , \tag{3}$$

$$P \equiv -\Delta_a^2 - \Delta_b\Delta_a + \tfrac{1}{4}\chi_b^2 + \tfrac{1}{4}\Gamma'_{31}\Gamma'_{21}\ , \tag{4}$$

$$p \equiv \tfrac{1}{2}\Gamma'_{32} + \tfrac{1}{2}\Gamma'_{31}\Gamma'_{32}/\gamma_{21}\ , \tag{5}$$

$$Q \equiv \tfrac{1}{2}(\Gamma'_{31} + \Gamma'_{21})\Delta_a + \tfrac{1}{2}\Gamma'_{21}\Delta_b\ , \tag{6}$$

$$q \equiv (\Gamma'_{32}/\gamma_{21})\Delta_a - (1 - \Gamma'_{32}/\gamma_{21})\Delta_b\ . \tag{7}$$

In the above expressions, γ_{ij} represents the total decay rate from state i to state j and Γ_i denotes the total decay rate from state i to all the other states. The effective transverse relaxation rates Γ'_{ij} are given in terms of the transverse relaxation rates Γ_{ij} and the laser (full width at half maximum) bandwidths γ_a and γ_b as follows: $\Gamma'_{21} = \Gamma_{21} + 2\gamma_a$, $\Gamma'_{32} = \Gamma_{32} + \gamma_b$, and $\Gamma'_{31} = \Gamma_{31} + 2\gamma_a + \gamma_b$. The detunings Δ_a and Δ_b are defined as $\Delta_a \equiv 2\omega_a - (\omega_{2s} - \omega_{1s})$ and $\Delta_b \equiv \omega_b - (\omega_{3p} - \omega_{2s})$.

The factor h in Eq. (2) contains, in general, two peaks as function of the first laser detuning Δ_a. In the limit of vanishing Γ'_{21} and Γ'_{31}, the peaks of h occur at the zeros of the energy denominator P:

$$\Delta_a^{\pm} \equiv \tfrac{1}{2}[-\Delta_b \pm (\Delta_b^2 + \chi_b^2 + \Gamma'_{31}\Gamma'_{21})^{1/2}]\ . \tag{8}$$

This is the origin of the two peaks observed in the experiment. The separation of the two peaks $\Delta_a^+ - \Delta_a^-$ depends on the detuning Δ_b and the intensity I_b ($\propto \chi_b^2$) of the second laser. Furthermore, the peak height $h_\pm$ at $\Delta_a^\pm$ is given by

$$h_\pm \propto \frac{1 + (1+\Delta_b/\Delta_a^\pm)(\Gamma'_{32} - \gamma_{21})/\gamma_{21}}{1 + (1+\Delta_b/\Delta_a^\pm)\Gamma'_{21}/\Gamma'_{31}}\ . \tag{9}$$

When the 3-2 transverse relaxation rate and the second laser bandwidth are large compared to the 2-1 decay rate (i.e., $\Gamma'_{32} \gg \gamma_{21}$), we see that the numerators in Eq. (9) have the dominant effect on the relative peak heights. Since by definition $\Delta_a^+ > 0$ and $\Delta_a^- < 0$, we have $\Delta_b/\Delta_a^+ < 0$ while $\Delta_b/\Delta_a^- > 0$ for $\Delta_b < 0$ (the case in the experiment); and hence $h_+ < h_-$, as shown in Fig. 1. Such peak asymmetry is called "abnormal" because it is reversed from that observed in the limit of narrow laser bandwidth and low pressure. In the latter limit, when both lasers are detuned to the red (i.e., $\Delta_a < 0$, $\Delta_b < 0$), overall three-photon energy conservation will be more difficult to satisfy than the mixed detuning case (i.e., $\Delta_a > 0$, $\Delta_b < 0$), resulting in the "normal" asymmetry $h_+ > h_-$.[12,15] Similarly, the abnormal peak asymmetry here can be understood as follows: At the *small* negative detuning Δ_a^- of the *first* laser (see Fig. 1), the detuning of the *second* laser is overcome by resonant absorption in the wings of the broad 2-3 transition line and of the second laser. Thus, the overall three-photon transition becomes a two-photon resonant transition plus a single-photon resonant transition. This is more probable than the pathway with the mixed detunings, whose two-photon transition is more off-resonant due to the relatively larger positive detuning Δ_a^+, thus giving rise to the abnormal asymmetry $h_+ < h_-$.

With $\chi_b = 3.71$ cm^{-1}, the estimated values[8,22,23] of $\Gamma'_{21} = 2.0$ cm^{-1}, $\Gamma'_{31} = 2.2$ cm^{-1}, and $\Gamma'_{32} = 3.2$ cm^{-1} for the experiment, the measured separation of the two peaks is used to determine the detuning Δ_b to be -7.3 cm^{-1} by Eq. (8); and the observed ratio of the peak heights is used to determine the ratio Γ'_{32}/γ_{21} to be 29.1 by Eq. (9). Then excellent agreement between theory (the dashed curve in Fig. 1) and the experimental (solid) curve is obtained by Doppler-averaging $\bar{\sigma}_{33}$ in Eq. (2) under the experimental conditions. This theoretical profile (normalized to the central peak maximum) is found to be sensitive to the values of Γ'_{21}, Γ'_{31}, and Γ'_{32}/γ_{21} (confirming its important role in determining the peak asymmetry as discussed above). But it is quite insensitive to the values of $\Gamma_3 (=1$ cm$^{-1})$ and $\gamma_{31}/\gamma_{21} (=0.9)$, each of which can be multiplied or divided by a factor of 10 without changing the *normalized* profile noticeably.

For the opposite detuning $-\Delta_b > 0$, the peak asymmetry will be reversed [i.e., $h_+(-\Delta_b) > h_-(-\Delta_b)$] by argument following Eq. (9). More precisely, $\Delta_a^{\mp}(-\Delta_b) = -\Delta_a^{\pm}(\Delta_b)$ from Eq. (8). Then it follows from Eq. (9) that (a) $h_+(-\Delta_b) = h_-(\Delta_b)$ and (b) $h_-(-\Delta_b) = h_+(\Delta_b)$. The relation (a) says that for the opposite detuning $-\Delta_b$, the peak

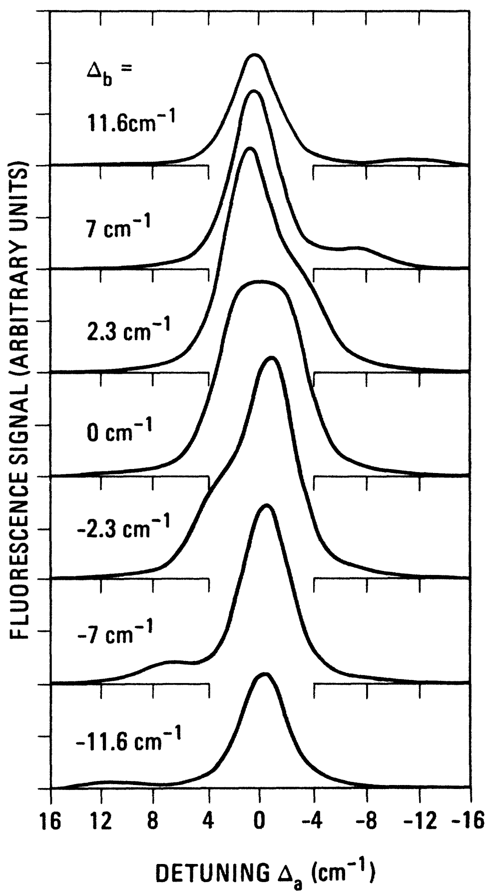

FIG. 2. Calculated multiphonon excitation spectra showing (a) the reversal of peak asymmetry for detunings Δ_b of opposite signs and (b) the persistence of abnormal peak asymmetry for detunings $|\Delta_b|$ up to about 60 times the 656-nm laser bandwidth.

height at Δ_a^+ is equal to that of the original detuning at Δ_a^-. This prediction[26] of asymmetry reversal at opposite signs of Δ_b is shown in Fig. 2 and is confirmed by a subsequent experiment.[27] Note that this reversed asymmetry is nevertheless abnormal for the opposite detuning.

Furthermore, both theory (see Fig. 2) and experiment[27] show that even when the second laser is detuned to ± 12 cm^{-1} (60 times the second laser bandwidth of 0.2 cm^{-1}), the peak asymmetry remains abnormal. This is contrary to results in the low-pressure regime where both observation[14] and theories[17,18] have shown that the abnormal asymmetry due to the second laser bandwidth reverts back to normal for detunings larger than a few bandwidths. In view of the discussion following Eq. (9), this persistence in abnormality can be understood easily in view of the large collisional broadening of the 2-3 transition and the relatively very broad wings of collisional line shapes. For the latter reason, a more precise treatment of the collisional line shape (or laser line shape for that matter) is not expected to qualitatively change these results.[28]

In conclusion, the above results clearly establish, for the first time, that pressure broadening (rather than laser bandwidth) causes abnormal peak asymmetry and that the abnormality persists at detunings very large compared to the laser bandwidth. They underscore the importance of considering ac Stark effects and their influence by pressure broadening in future applications of intense lasers to high-pressure environments. The theory is in excellent agreement with Goldsmith's observation[1] and its predictions[26] have been confirmed by a second experiment.[27] Other aspects and applications of the theory will be presented elsewhere.

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[25]The differences between the solution here and those in Refs. 15 and 16 arise essentially from (a) the *two-photon* coupling between levels 1 and 2, (b) the first laser serving as the weak probe, and (c) the collisional relaxation scheme among the levels being different from that of pure radiative decays. In fact, the steady-state approximation is more readily satisfied in the high-pressure regime. Therefore direct comparison between a steady-state solution and experimental data is possible here, but not in Refs.

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[28]For sufficiently large detunings Δ_b beyond the wings of the collisional line shape, the 2-3 transition would appear as a sharp line to the second laser and, in principle, the peak asymmetry should revert back to normal (i.e., $h_+ > h_-$ for $\Delta_b < 0$) because of overall three-photon energy conservation. But then the possibility of observing the much diminished h_- is questionable, and only one peak h_+ would be observed, corresponding to the usual nonresonant three-photon excitation of $3p$.