Line Broadening in Multiphoton Processes with a Resonant Intermediate Transition

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The linewidth of the excitation spectrum for multiphoton ionization is found to be broadened much more severely than the cascade fluorescence originating from the resonant intermediate level. These results are due to the mutual effects of the ionizing and resonating transitions, which are not properly accounted for in perturbative treatments.

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Resonant intermediate transitions have been explored as a means to enhance the processes of multiphoton absorption in many experiments reported to date. It is observed,[1,2] however, that these processes often exhibit the effects of saturation and the overall enhancement appears to be rather limited. Although much effort has been spent on the theory of these processes,[3,4] much remains to be done to establish the nature of saturation in actual experiments. We have now performed experiments with an atomic beam of thallium and have made for the first time simultaneous observations of the ionization and the cascade fluorescence which result from transitions to the resonant intermediate level. The line shape of the excitation spectrum for multiphoton ionization is seen to become non-Lorentzian at high intensities of excitation and is broadened much more severely than the accompanying fluorescence. For some of the transitions studied, the fluorescence linewidth showed no broadening beyond the laser linewidth, whereas the ionization linewidth always increased with the laser intensity. These results disagree with theoretical analyses which treat ionization as a perturbation to a system of two strongly coupled energy levels, but can be understood in terms of both the two-step process of ionization, which involves excitation of an intermediate state, and ionization directly from the ground state. It is concluded that broadening of a resonant intermediate transition may be reduced drastically in the presence of ionization, but the ionization signal may always exhibit broadening induced by the resonating transition. This difference in the fluorescence and ionization line shapes is characteristic of multiphoton excitation involving a near-resonant intermediate transition, and may also be important in other experiments reported recently.[5,6]

Our experiments were performed with a tunable dye laser pumped by a frequency-doubled Nd-doped yttrium aluminum garnet laser. The output from the tunable laser is focused so as to intersect at right angles an atomic beam of thallium. The fluorescence signal emanating from the region of interaction is collected in a direction perpendicular to both the laser and atomic beams, and the ionization signal is measured with a pair of parallel plates placed near the region of interaction. In addition, an aperture could be placed near the interaction region to verify that effects attributable to inhomogeneous intensity distribution are insignificant.

Thallium was chosen for the experiments as it was convenient to study intermediate levels which could be reached through either a single-photon transition or a two-photon transition from the ground state. Figure 1(a) illustrates the process of three-photon ionization involving the $6P_{1/2} \rightarrow 7P_{3/2}$ (or $6P_{1/2} \rightarrow 7P_{1/2}$) transition as a two-photon intermediate resonance. Figures 1(b) and 1(c) depict the corresponding excitation spectra for the fluorescence and ionization signals at low and high intensities. The peaks therein are due to the hyperfine splitting of the ground state, with a known separation[7] of 0.7 cm^{-1}. Although the baseline appears to be elevated slightly at higher intensities, the linewidth of the fluorescence signal remains practically unchanged at 0.07 cm^{-1} (full width at half maximum) over the range of intensities used in our experiments. This linewidth is approximately twice the linewidth of the exciting laser beam, with negligible contributions from the natural linewidth (0.56×10^{-3} cm^{-1}) and the residual Doppler width (0.39×10^{-3} cm^{-1}) for this transition. On the other hand, the linewidth for the ionization signal increases monotonically with increasing laser intensity. At low intensi-

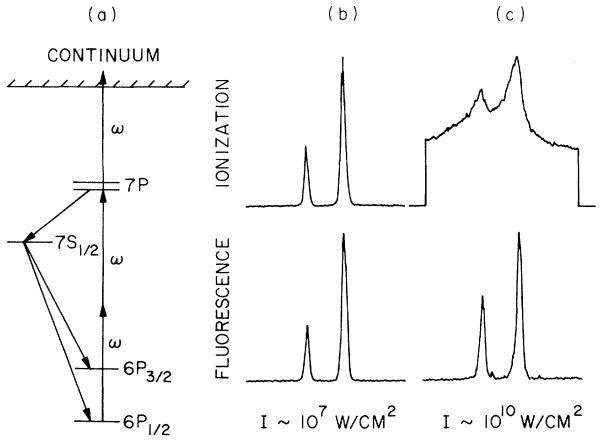

FIG. 1. (a) Energy-level diagram of thallium showing three-photon ionization. Population of the $7P$ level is inferred by observing fluorescence from the $7S_{1/2}$ level at either 5350 Å ($7S_{1/2} \rightarrow 6P_{3/2}$) or 3775 Å ($7S_{1/2} \rightarrow 6P_{1/2}$). The excitation spectra for the fluorescence and ionization signals are shown for low and high intensities in (b) and (c), respectively.

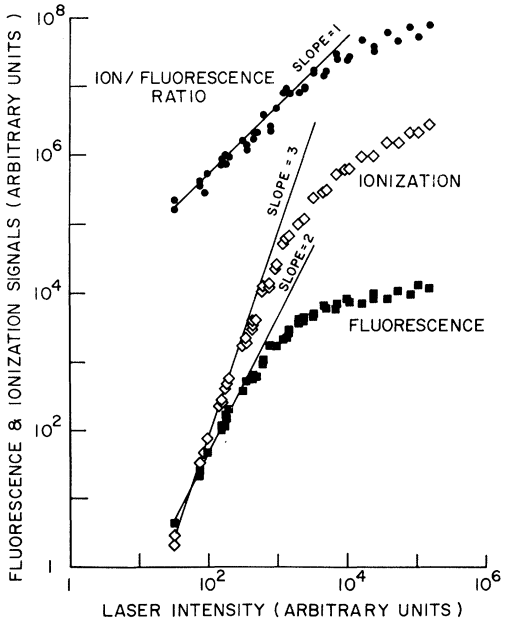

FIG. 2. Plot of the fluorescence and ionization signals as functions of the exciting intensity for the process of three-photon ionization involving the $7P_{3/2}$ state as the near-resonant intermediate level. The excitation frequency is in two-photon resonance with the $6P_{1/2} \rightarrow 7P_{3/2}$ transition.

ties, it reflects the laser linewidth similar to that of the fluorescence signal. At higher intensities, however, the peaks begin to show some broadening, and the baseline begins to rise. By scanning over a much wider spectral range, it was determined that what appears to be an elevated baseline is actually the center portion of a Lorentzian-like curve with an amplitude comparable to that of the narrower components. At the highest intensity used, the width of this curve reached the order of 10 cm^{-1}, or a factor of 140 broader than the corresponding fluorescence signal.

Figure 2 summarizes the intensity dependence of the fluorescence and ionization following the two-photon transition $6P_{1/2} \rightarrow 7P_{3/2}$ near 5688 Å. It is seen that both the two-photon fluorescence and three-photon ionization signals exhibit the usual off-resonance dependence at very low intensities; but they deviate significantly from these low-intensity dependences as the laser intensity is increased and eventually become sublinear with the laser intensity at still higher intensities. The ratio of the ionization signal to the fluorescence signal is seen to increase, as expected, as a linear function of the laser intensity at low intensity levels, but also begins to deviate from the linear dependence as the laser intensity is increased.

We have also studied the process of two-photon ionization involving a single-photon resonance near the $6P_{1/2} \rightarrow 7S_{1/2}$ transition at 3775 Å. The ionization signal for this process behaves similarly to that described above for the three-photon ionization. However, the corresponding fluorescence signal near 5350 Å also exhibits some broadening which reaches a few tenths of a wave number at higher laser intensities.

In our experiments, there was no shift[8] in the peaks of the fluorescence and ionization signals to within our laser linewidth, thus indicating that our experiments are largely free from Stark shifts and broadening. With a density of less than 10^{10} atoms/cm^3 used in our experiments, stimulated emission between levels is also unlikely.

In the absence of transitions away from the resonating levels, the effect of saturation of an absorption transition can be described adequately in terms of a model involving two levels only.[9] This is often the case for transitions in the microwave regime, but for the case of multiphoton excitation in the optical regime, depletion of population due to ionization must be taken into account. This can be done by including a continuum as well as the two bound levels in the model.[3,4,10] Within the framework of this model, ionization processes involving intermediate multiphoton resonances

(such as our $6P_{1/2} \rightarrow 7P$ transitions of thallium) can also be accommodated through the introduction of an effective multiphoton matrix element.[9] However, the solution of this model in closed form[4] is too complicated to offer any physical insight; and in arriving at a working expression, various approximations have to be made. These approximations either incorporate the effect of ionization as a perturbation,[3,10] or neglect terms higher order in the transition matrix elements to and from the ionization continuum.[4] One consequence of the former simplification is that all processes considered involve the excitation of the intermediate state, from which fluorescence occurs through radiative decay and ionization takes place through the absorption of an additional photon. According to this simple picture, the ionization and fluorescence signals would exhibit identical excitation line shapes, and their ratio would always be linearly proportional to the intensity of excitation. Our experimental results do not agree with this simple picture of an excited state as the sole origin of the observed fluorescence and ionization signals. Although this picture may be altered somewhat when transient effects are also taken into account, examination of our overall results indicates that it is unlikely that these effects could be responsible for the observed dependences.

From the reported values[11] for the matrix elements of the thallium transitions, one calculates the two-photon absorption cross section for the $6P_{1/2} \rightarrow 7P_{3/2}$ transition to be about 3×10^{-44} cm^4 sec and the radiative lifetime of the $7P$ state to be about 60 nsec. This would give a two-photon transition rate of 10^{13} sec^{-1} at an intensity level of 10^{10} W/cm^2, the maximum value used in our experiments. In the absence of ionization, the corresponding saturation parameter for this transition should be about 1×10^6, and the line shape should remain Lorentzian, but broadened by a factor of about 10^3 above the laser linewidth. This prediction is in sharp contrast with our fluorescence observation from the $7P$ state, which shows no measurable broadening, and is also different from the observed ionization line shape which indicates the presence of additional components with different degrees of broadening not anticipated from the approximate analyses.

The ionization cross section from the $7P$ state is estimated with use of the quantum-defect method to be about 1×10^{-17} cm^2. This indicates that the corresponding ionization rate should be higher than the two-photon transition rate of the $6P_{1/2} \rightarrow 7P_{3/2}$ transition for most of the intensity values used in our experiments, but should become lower than the latter for the highest decade of intensities indicated in Fig. 2, reaching a maximum value of 4×10^{11} sec^{-1} at the maximum intensity of 10^{10} W/cm^2.

In the case of two-photon ionization using the $7S_{1/2}$ state as the near-resonant intermediate level, both the ionizing transition from the $7S_{1/2}$ state and the intermediate $6P_{1/2} \rightarrow 7S_{1/2}$ transition are single-photon transitions. Their absorption cross sections are estimated to be about 0.3×10^{-17} cm^2 and 3×10^{-12} cm^2, respectively. It follows that the transition rate for the intermediate transition is always higher than the ionizing rate by about six orders of magnitude, and that the saturation parameter at the maximum intensity used should be about 7×10^7 in the absence of ionization. This degree of saturation would broaden the linewidth to 300 cm^{-1}, or a factor of 10^4 above the laser linewidth. Again, this value of broadening is orders of magnitude too large compared to the fluorescence width of 0.3 cm^{-1} and the ionization width of about 10 cm^{-1} observed in our experiments. In view of these results, it may be concluded that the presence of ionization significantly lessens the extent of saturation even when the ionization rate is very small compared to the rate of the resonating transition. The lessening of saturation was anticipated in some of the approximate treatments[4] to date; however, the extent to which this lessening may occur does not appear to have been appreciated fully, nor does the difference in line shapes appear to have been recognized.

The above observations can be understood in terms of the mutual effects of the ionizing and resonating transitions. Ionization from the intermediate level tends to remove the population in that level. At high ionization rates, electrons are removed from the intermediate level as soon as they are excited to that level so that saturation of the resonating transition will never set in. In general, population in the intermediate level can be increased only to the extent that the net transition rate between the resonating levels equals the rate of ionization from the upper resonating level. This means that saturation of the resonating transition may be lessened significantly, with a corresponding reduction in the power broadening of the fluorescence signal originating from the upper resonating level. Broadening of the observed ionization signal may be expected to behave differently, however, since this signal is due in part to

ionization from this intermediate level, and in part to ionization directly from the ground state. Since broadening of a transition is usually associated with a reduction in the peak intensity, it is reasonable to expect that the ratio of the ionization to fluorescence signals deviates from linearity when the ionization signal shows excess broadening as observed.

We have performed a quasi-steady-state analysis similar to that of Armstrong and O'Neil,[4] but without dropping the higher-order terms neglected in their analysis. Approximate results of our analysis indicate that the ionization line shape can in general be expressed as the sum of two Lorentzian components each with different degrees of broadening, and that this line shape reduces to that of the resonating transition in the limit of vanishing intensities. In addition, the fluorescence line shape may also exhibit a second component whose amplitude may become important under certain conditions. Our analytical results are in good qualitative agreement with experimental observations presented above. We are currently extending our analysis to include transient behavior, and reducing our laser linewidth towards its Fourier-transform limit so as to facilitate the detection of broadening induced at a much lower intensity level.

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