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The time development of adiabatic two-photon absorption: I. Low intensity regime

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Abstract. The time dependence of the two-photon absorption process is experimentally investigated in the low intensity regime as a function of laser linewidth, Doppler width, polarisation and delay between pulses, using 5 ns pulses at two different frequencies. Excellent agreement is found between experiment and the theoretical predictions of Allen and Stroud. The experiment augments and expands earlier work on the dependence of linewidth in the two-photon process. The lineshape of the Hänsch-type laser producing the pulses is shown to be best described by a Gaussian rather than a Lorentzian or as the result of an Ornstein–Uhlenbeck process.

1. Introduction

The literature of multiphoton processes is now very extensive as the *Multiphoton Bibliography* of Eberly and Karczewski (1977) and Eberly *et al* (1979a, b) demonstrates. Two-photon absorption has had a good deal of attention (Giacobino and Cagnac 1980), and the beautiful experimental work of Bjorkholm and Liao on resonant enhancement (Bjorkholm and Liao 1974), energy level shifts (Liao and Bjorkholm 1975) and lineshape (Bjorkholm and Liao 1976) for example, has meant that many aspects of the process have been examined in considerable depth. However, the detailed time development of the absorption process has not been examined experimentally although a good deal of theoretical work relating to it has been published.

Takatsuji (1975) developed the optical Bloch formulation for N non-resonant intermediate states and two fields, as did Grischkowsky *et al* (1975), while Schenzle and Brewer (1978) investigated transient phenomena. The more general problem of N photons from the same laser for a large number of non-resonant intermediate states was solved by Milonni and Eberly (1978). Adiabatic models to account for the role of pulsed excitation, particularly multiphoton ionisation rather than absorption, have been created by Armstrong and Baker (1980), McLean and Swain (1978) and Crance and Feneuille (1977) while examinations of the rate equation approach have been presented by Ackerhalt and Shore (1977), Salomaa (1977) and Swain (1980).

Recently Allen and Stroud (1982) developed a general theory which described the excitation of a high-lying atomic or molecular state by the absorption of N photons from N different lasers. It was assumed that no intermediate states were resonantly excited. The effects of saturation, Stark shifts, spontaneous emission and finite laser

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bandwidths were all included. In the most general case the formalism reduced to a set of equations analogous to the Bloch equations. In the regime where the incoherent processes destroy the Rabi oscillations the Bloch equations reduce to simple rate equations with a time dependent rate. This is when $\gamma_b + \gamma_L \gg \Omega^{(n)}(t), 1/\tau_p$, where γ_b and γ_L are the widths of the resonant atomic state and the laser radiation respectively, $\Omega^{(n)}(t)$ the composite Rabi frequency arising from the n-photon field and τ_p the pulse duration. If the phase diffusion model is used these rate equations are:

$$\langle \dot{x}_{bb} \rangle_L = -2\gamma_b \langle x_{bb}(t) \rangle_L - R(t)(\langle x_{bb}(t) \rangle_L - \langle x_{aa}(t) \rangle_L) \tag{1a}$$

$$\langle \dot{x}_{aa} \rangle_L = R(t)(\langle x_{bb}(t) \rangle_L - \langle x_{aa}(t) \rangle_L) \tag{1b}$$

$$R(t) = \frac{\sqrt{2\pi}}{\gamma_L} \frac{\mathcal{M}_{NPA}^2}{\hbar^{2n}} (\varepsilon^{(n)}(t))^2 \exp\left(-\frac{(\delta - \Delta(t))^2}{2\gamma_L^2} \right) \tag{1c}$$

where $\langle\ \rangle_L$ represents the ensemble average over the randomly fluctuating laser phase, x_{bb} the population of the excited state, x_{aa} the population of the lower state $\varepsilon^{(n)}(t) = |\varepsilon_1(t)||\varepsilon_2(t)|\ldots|\varepsilon_n(t)|$, δ the detuning from resonance, $\Delta(t)$ the Stark shift and $\mathcal{M}_{NPA}$ is the generalised N-photon electric dipole moment matrix element. When the laser intensities are weak and there is negligible saturation, these equations may trivially be extended to include Doppler broadening and reduce further by a series of adiabatic approximations to a simple double integral of the form

$$\begin{aligned} \langle x_{bb}(t) \rangle = \frac{2\mathcal{M}_{NPA}^2}{\hbar^{2n}} \mathrm{Re} \int_0^t dt' \exp[-2\gamma_b(t-t')\varepsilon^{(n)}(t')] \\ \times \int_0^{t'} dt'' \, \varepsilon^{(n)}(t'') \exp[-(\gamma_b + i\delta)(t'-t'') \\ -\tfrac{1}{2}(\gamma_D^2 + \gamma_L^2)(t'-t'')^2 + i(I(t') - I(t''))] \end{aligned} \tag{2}$$

for a Gaussian laser lineshape where γ_D is the Doppler width and $I(t) \equiv \int_0^t dt' \, \Delta(t')$. In general, we may write $(I(t') - I(t'')) = \Delta(t')(t'-t'')$ and in the low intensity regime careful choice of the frequencies of the two pulses makes this term negligible. Also if we choose to work exactly on resonance then $\delta = 0$ and the form for $\langle x_{bb}(t) \rangle$ becomes

$$\begin{aligned} \langle x_{bb}(t) \rangle = \frac{2\mathcal{M}_{NPA}^2}{\hbar^{2n}} \int_0^t dt' \exp[-2\gamma_b(t-t')\varepsilon^{(n)}(t')] \\ \times \int_0^{t'} dt'' \, \varepsilon^{(n)}(t'') \exp[-\gamma_b(t'-t'')] \exp[-\tfrac{1}{2}(\gamma_D^2 + \gamma_L^2)(t'-t'')^2] \end{aligned} \tag{3a}$$

for a Gaussian laser lineshape, and

$$\begin{aligned} \langle x_{bb}(t) \rangle = \frac{2\mathcal{M}_{NPA}^2}{\hbar^{2n}} \int_0^t dt' \exp[-2\gamma_b(t-t')\varepsilon^{(n)}(t')] \\ \times \int_0^{t'} dt'' \, \varepsilon^{(n)}(t'') \exp[-(\gamma_b + \gamma_L)(t'-t'')] \exp[-\tfrac{1}{2}\gamma_D^2 (t'-t'')^2] \end{aligned} \tag{3b}$$

for a Lorentzian laser lineshape. For the case of an Ornstein–Uhlenbeck process (see Yeh and Eberly 1981), we see that $-\gamma_L(t'-t'')$ will be replaced by $-\gamma_L(t'-t'') + \gamma_L\{1 - \exp[-(t'-t'')]\}/\gamma$ where γ is a cut-off parameter. Careful comparison with experiment consequently offers the possibility of testing the theory and also of determining which form of phase process best describes the type of pulsed laser employed.

2. Experiment

This work investigates the theoretical predictions for the simplest case possible, that of $N=2$ or two-photon absorption. The experiment involved the use of a two-wavelength pulsed tunable dye laser (Marx *et al* 1976) producing 5 ns (FWHM) duration pulses at 5784 and 5790 Å, which allowed on-resonant two-photon absorption in atomic sodium from the $3s\ ^2S$ ground state to the $4d\ ^2D$ state. The atomic sodium was contained in a quartz cell in a small oven maintained in the range about 220–250 °C. Excitation to the upper state was monitored by observing the decay from $4d\ ^2D$ to $3p\ ^2P$ at 5688 Å. The small difference between the excitation and fluorescence wavelengths made it necessary to employ a narrow-band pass filter to isolate the fluorescent signal, and great care had to be taken to minimise scatter from the cell. The advantage of observing the $4d\ ^2D$–$3p\ ^2P$ decay, however, compared with observing the cascade transition $4p\ ^2P$–$3s\ ^2S$ in the UV was that the time dependence of the upper level population could be monitored directly and was not convoluted with any subsequent decay. The fluorescence signal was examined using a digitised boxcar averager, the output of which could either be stored on magnetic cassette tape and played into a data-handling computer or plotted out in analogue form in the usual way. Sensible pulse averaging was ensured by using a discriminator which only allowed the boxcar to trigger when the input laser pulse had the chosen peak intensity.

The light from the laser at the two excitation frequencies, when the effective laser field $\varepsilon^{(n)}(t)$ was given by $|\varepsilon_1(t)||\varepsilon_2(t)|$, could be co-propagating or counter-propagating, thus leading to effective Doppler widths of 3.54 or 0 GHz. The laser linewidths could be adjusted by the insertion of etalons into the Hänsch-type cavities to yield 0.34 GHz or 3.60 GHz and greater. The available combinations of laser and Doppler width thus allowed a thorough investigation of the dynamics in the low intensity regime where the double integral expression for the population of the upper level was expected to hold.

It was necessary to ensure that the laser intensities used qualified as being in the 'low intensity regime'. The assumption in the theory is that the population of the upper level is essentially negligible and that there is, therefore, zero saturation. Under these circumstances, as equations (3*a*, *b*) show clearly, the peak fluorescent intensity should be proportional to the product of input laser peak intensities. In ensuring that this regime was invoked, a careful analysis of the linewidth and lineshape dependence of the two-photon process was possible.

2.1. *Effect of laser linewidth and lineshape*

In the limit that the Doppler width or the Gaussian linewidth is the dominant width such that $(\gamma_D^2+\gamma_L^2)^{1/2} \gg \tau_p^{-1}$, γ_b, Allen and Stroud show that

$$\langle x_{bb}(t)\rangle = \left(\frac{2\pi}{\gamma_L^2+\gamma_D^2}\right)^{1/2} \frac{\mathcal{M}_{NPA}^2}{\hbar^{2n}} \int_0^t dt' \exp[-2\gamma_b(t-t')(\varepsilon^{(n)}(t'))^2]$$

and that $\langle x_{bb}(t)\rangle \propto 1/(\gamma_L^2+\gamma_D^2)^{1/2}$, thus formally confirming the heuristic theory of Marx *et al* (1978), which they experimentally verified by varying γ_L when exciting sodium by taking two photons from the same laser. In this work, however, the two-excitation photons had different frequencies and the co-propagating and counter-propagating beams of different frequency allow the Doppler width, γ_D, to be 3.54 GHz or about 0 GHz.

To calculate the theoretical fluorescent response it was necessary to compute the double integral given in equation (3). It was consequently necessary to measure the input laser intensity as a function of time and to fit it by a least-squares routine to an analytic curve. It was found that a curve of the form $\varepsilon = At^n \exp(-kt)$ gave a good representation and having determined the parameters A, n and k the expression could be inserted into the double integral and the values of $\langle x_{bb}(t)\rangle$ calculated. The relative peak heights were then readily obtainable.

We see in figures 1 and 2 that the peak fluorescent intensity I_F plotted against the peak value of the product $I_1 I_2$ is perfectly linear. Also for $\gamma_D = 0$ and $\gamma_D = 3.54$ GHz we find a different ratio of gradients. The laser linewidth was measured by observing the fringe visibility in a Michelson interferometer and was found to be 0.34 ± 0.02 and 6.60 ± 1.32 GHz depending upon whether the etalons were in or out of the Hansch cavities. It may be seen that, not surprisingly, the broader emission was difficult to measure with great precision. The experimental ratio of slopes in figures 1 and 2 may be compared with the values calculated from equations 3(a), 3(b), the equivalent form for an Ornstein–Uhlenbeck process and also for the limiting form cited above which agrees with the heuristic theory value. Table 1 shows the experimentally observed and predicted values. Quite clearly only the Gaussian laser linewidth gives satisfactory consistent agreement and we may conclude that the Hänsch type, N_2-pumped, tunable dye laser of this type is well described by a Gaussian lineshape output. Not surprisingly the heuristic theory is also found to be entirely satisfactory.

This simple measurement, while defining the range of usable laser intensity, has thus provided the best evidence so far available as to the nature of laser linewidth dependence of two-photon absorption and in addition has commented on the spectral distribution of the output of a Hänsch-type laser.

2.2. Time dependence

In the intensity regime so defined, the full time dependence of the fluorescent response may be calculated from the double integral. For the four permutations of γ_L and γ_D

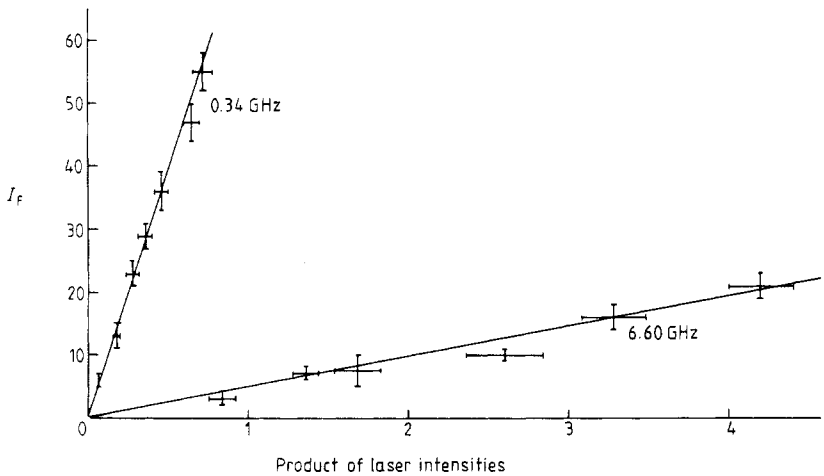

Figure 1. Fluorescent intensity plotted against the product of input laser intensities for $\gamma_L = 0.34$ GHz and 6.60 GHz, where $\gamma_D = 0$. Counter-propagating beams. Experimental ratio of gradients is 16.19 ± 1.14. Theoretical ratio of gradients is 17.85 ± 3.85.

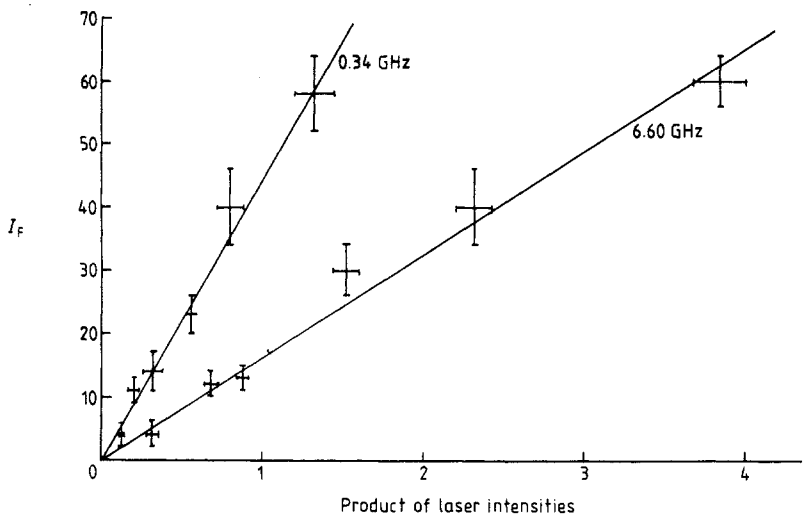

Figure 2. Fluorescent intensity plotted against the product of input laser intensities for $\gamma_L = 0.34$ GHz and 6.60 GHz where $\gamma_D = 3.54$ GHz. Co-propagating beams. Experimental ratio of gradients is 2.71 ± 0.30. Theoretical ratio of gradients is 2.78 ± 0.61.

Table 1. Comparison of slopes of I_F plotted against $I_1 I_2$ for two laser linewidths for Doppler broadening of 0 and 3.54 GHz.

	$\gamma_D = 0$ GHz	$\gamma_D = 3.54$ GHz
Experimental value	16.19 ± 1.14	2.71 ± 0.30
Gaussian lineshape	17.85 ± 3.85	2.78 ± 0.61
Heuristic theory	19.41 ± 5.17	2.79 ± 0.63
Lorentzian lineshape	16.43 ± 2.70	6.92 ± 1.36
Ornstein–Uhlenbeck process (for best value of $\gamma = 12$ GHz)	6.76 ± 0.78	2.72 ± 0.40

which are possible, only the Gaussian form given by equation (3*a*) gives agreeable results. Clearly, as table 1 implies, the other formulations lead to incorrect ratios of the relative peak heights. The comparison of theory and experiment can be seen in figures 3 and 4. We should stress that only one curve has been normalised to the experimental peak height, the others have their relative positions defined by the theory because the input pulses were sustained at a constant intensity and so the remarkable quality of the agreement of theory and experiment becomes very clear.

The form of the laser field $\varepsilon^{(n)}(t)$ also allows the effect of delay between one pulse and the other to be investigated. If one pulse is delayed with respect to the other by means of an optical delay in the path of one of the counter-propagating beams, then $\varepsilon^{(n)}(t) = |\varepsilon_1(t)||\varepsilon_2(t+\tau)|$. The double integral given by equation (3*a*) was calculated for a range of values of τ and the theoretical comparison with experiment is shown in figure 5, again to excellent advantage. Clearly significantly larger delays, where $\tau \geq \tau_p$ do not yield measurable results.

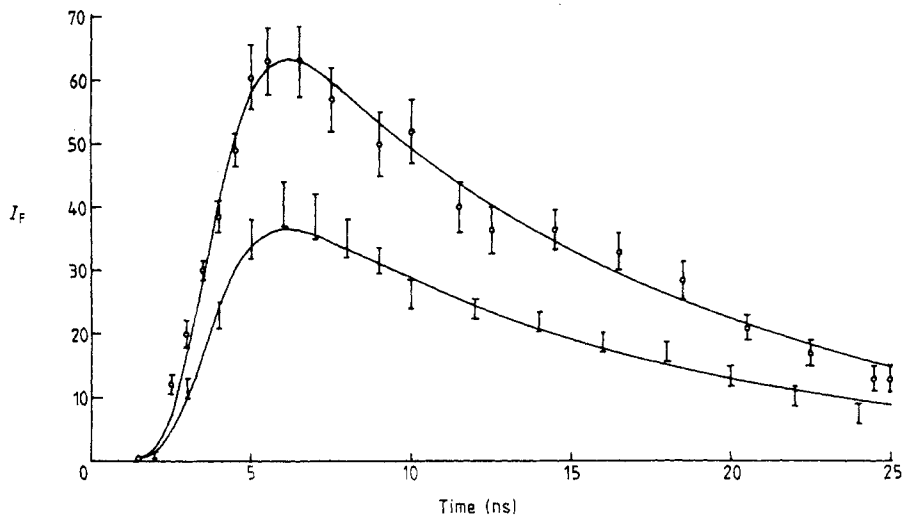

Figure 3. The theoretical and experimental time development of two-photon absorption for $\gamma_D = 3.54$ GHz. Co-propagating beams. ——, theoretical curve; ○, laser bandwidth = 0.34 GHz; I, laser bandwidth = 3.60 GHz.

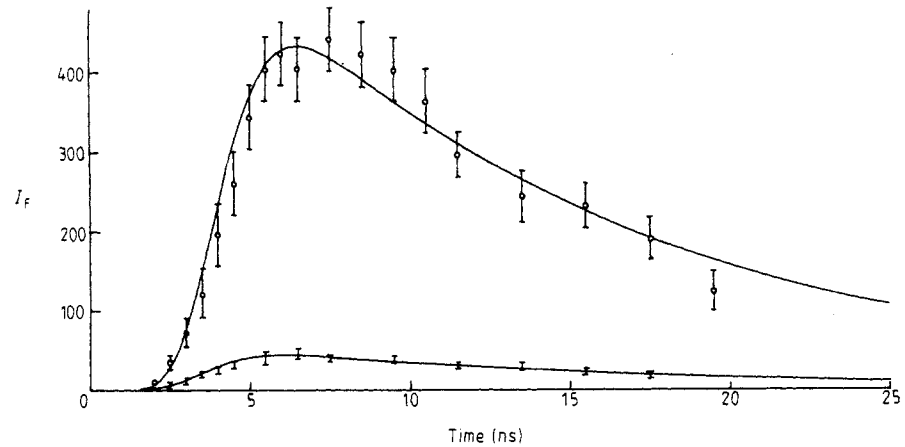

Figure 4. Theoretical and experimental time development of two-pohoton absorption for $\gamma_D = 0$. Counter-propagating beams. ——, theoretical curve; ○, laser bandwidth = 0.34 GHz; I, laser bandwidth = 3.60 GHz.

It should be noted that in the low intensity regime the polarisation of the light should only influence the peak height through the N-photon absorption electric dipole matrix element which comes outside the double integral; the time dependence of the process should not alter. This was confirmed by comparing the results of linearly polarised and circularly polarised light for which the theoretical matrix elements have the ratio 1.5. The peak heights were found to be in the ratio 1.46±0.08 and after renormalisation are shown together with the predicted theoretical curve in figure 6. Clearly there is no difference in time dependence.

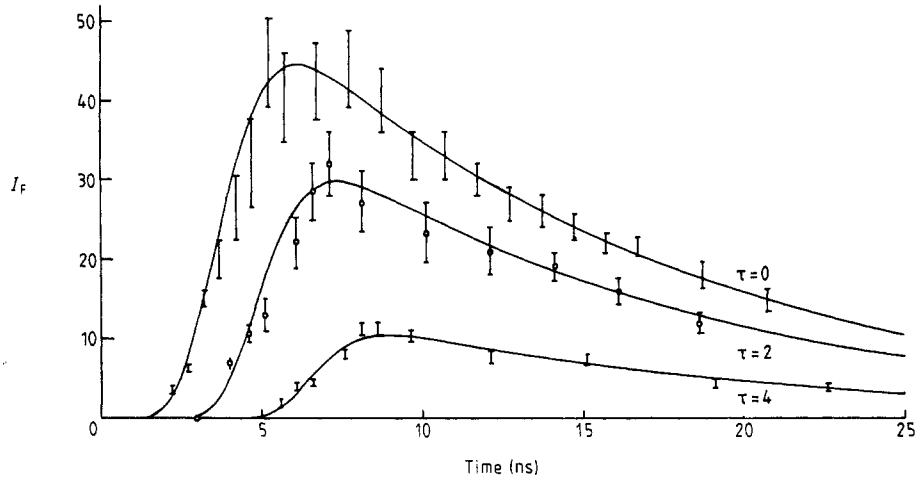

Figure 5. The effect of delay between pulses in two-photon absorption. ——, theoretical prediction; τ, the delay between pulses in ns is given. $\gamma_L = 3.60$ GHz, $\gamma_D = 0$ GHz.

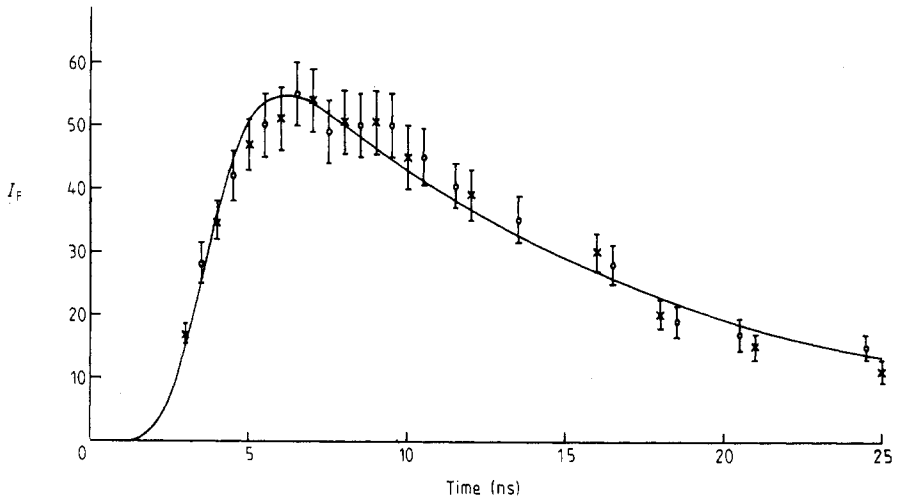

Figure 6. The demonstration that the time dependence of the fluorescence is independent of excitation polarisation. Only the peak heights of the linearly and circularly polarised curves have been normalised. ‡, linear polarisation; ○, circular polarisation. $\gamma_L = 3.60$ GHz, $\gamma_D = 3.54$ GHz.

3. Conclusions

Excellent agreement has been demonstrated in the low intensity regime between theory and experiment for the time-development of two-photon absorption. The approach used has also realised an analysis of the role of laser and atomic bandwidths and of the spectral shape of the laser emission. However, when the intensity of the excitation pulses is increased so that saturation begins to play a role, the appropriate

theory is the rate-equation theory of equation (1), and it is necessary to take careful cognisance of the role of the Stark shift. A detailed analysis of the rate-equation regime will be reported in a second paper.

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