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On the mechanism of CH_3 radical formation in hot filament activated CH_4/H_2 and C_2H_2/H_2 gas mixtures

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Abstract

Resonance enhanced multiphoton ionization spectroscopy has been used to determine relative number densities of CH_3 radicals in a hot filament chemical vapour deposition (HF-CVD) reactor designed for diamond growth, as a function of process gas (i.e. both CH_4/H_2 and C_2H_2/H_2 gas mixtures), position (d), filament temperature (T_f) and local gas temperature (T_g). The similar CH_3 radical number density profiles observed upon activation of the two feedstock gas mixtures suggest that CH_3 radical formation in both cases is dominated by gas phase chemistry, in contradiction of the current consensus which invokes surface catalysed hydrogenation as the means of inducing the necessary C–C bond fission in the case of C_2H_2/H_2 gas mixtures. Three body addition reactions involving C_2H_2 (and C_2H_4), together with H atoms and H_2 molecules, are identified as probable reactions requiring further study in order to provide a proper description of diamond CVD using a C_2H_2/H_2 gas feed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diamond chemical vapour deposition; Methyl radicals; Laser spectroscopy; Acetylene

1. Introduction

The gas phase chemistry underpinning diamond chemical vapour deposition (CVD) following activation of CH_4/H_2 gas mixtures in, e.g. a hot filament (HF) reactor is by now fairly well understood. The consensus view assumes H atom production at, and diffusion away from, the filament surface and subsequent H atom abstraction from CH_4 molecules in the gas phase, resulting in formation of CH_3 radicals. These are generally accepted as the major growth species in low power, hydrogen rich deposition environments [1]. It has also long been recognized that diamond CVD occurs with comparable facility when using alternative hydrocarbon/H_2 process gases, including C_2H_2/H_2 process mixtures [2], but the detailed chemistry involved in this latter case remains a matter of some controversy. The analogous abstraction reaction

$$C_2H_2 + H \rightleftharpoons C_2H + H_2 \tag{1}$$

is endothermic by ~30 kJ mol^{-1} while possible bimolecular addition reactions like

$$C_2H_2 + H_2 \rightleftharpoons C_2H_3 + H \tag{2}$$

that might initiate the conversion of C_2H_2 into C_1 hydrocarbons, are very endothermic [3,4]. Yet a variety of in situ studies have demonstrated C_2H_2 conversion into CH_4 within the deposition chamber and that the C_2H_2/CH_4 mixing ratio at typical process temperatures is essentially independent of the hydrocarbon feedstock gas used [5–8], and demonstrated the pres-

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ence of significant CH_3 radical densities in both HF [9,10] and microwave [11] activated C_2H_2/H_2 gas mixtures. Toyoda et al. [9] considered both gas phase and surface catalysed mechanisms for $C_2H_2 \rightarrow CH_3$ conversion but were unable to distinguish which, if either, was the dominant contributor to the measured CH_3 concentrations. Zumbach et al. [8] compared measured $C_2H_2/C_2H_4/C_2H_6$ concentration ratios in a HF-activated C_2H_2/H_2 gas mixture with the results of model calculations which included gas phase chemistry only. Their simulations suggested no conversion from C_2H_2 to any other hydrocarbon, in marked contradiction to the experimental observation; they, therefore, concluded, almost by default, that $C_2H_2 \rightarrow CH_3$ conversion must involve adsorption, hydrogenation and subsequent desorption on hot surfaces within the reactor. Having reviewed the available thermodynamic and kinetic data relating to the various C_2H_x hydrocarbon species, Goodwin and Butler [1] reached a similar conclusion that heterogeneous conversion on the reactor walls (or the growing diamond surface) is the most likely route for C–C bond fission.

The present study forms part of an on-going program aimed at providing more direct and quantitative measures of both production and loss processes of H atoms and CH_3 radicals in a HF-CVD reactor [10,12]. Here we use $2+1$ resonance enhanced multiphoton ionization (REMPI) spectroscopy, at laser wavelengths ~ 333 nm [13–15], to monitor methyl radical number densities, henceforth $[CH_3]$, in situ, and with sub-millimetre spatial resolution, as a function of distance (d) from the HF using both CH_4/H_2 and C_2H_2/H_2 process gas mixtures, and as a function of mixing ratio and filament temperature, T_f. The $[CH_3]$ profiles derived in the case of CH_4/H_2 gas mixtures are compared with spatially resolved measurements using cavity ring down spectroscopy [16,17], and with complementary HF-CVD modelling studies [18,19]. The very obvious similarities between $[CH_3]$ profiles measured using CH_4/H_2 and C_2H_2/H_2 gas mixtures encourage the view that $C_2H_2 \rightarrow CH_3$ conversion occurs via gas phase chemistry; possible mechanisms are considered.

2. Experimental

The apparatus and procedures have been described previously [10,12]. Briefly, the CVD chamber comprises a six-way cross (base pressure $< 10^{-2}$ torr), equipped with quartz windows to allow transmission of the probe laser beam. A third window at right angles to, and in the same horizontal plane as, the laser axis allows viewing of the HF with a two-colour optical pyrometer. The HF (250 μm diameter Ta wire, seven turns, ~ 3 mm coil diameter) is mounted on a cradle suspended beneath a linear transfer mechanism mounted on the top flange, which is also equipped with the necessary electrical feed-throughs. The mechanism allows vertical translation of the HF by ≤ 25 mm, with a positional precision < 1 mm, relative to the fixed laser focus and the tip of the negatively biased Pt probe wire used for ion collection. Power is supplied from a DC power supply (operating in constant current mode) via the feed-throughs to one side of the HF (the other is grounded). The CH_4 (or C_2H_2) and H_2 process gases are metered using separate mass flow controllers, premixed in a manifold and enter the reactor through a port located above the cradle assembly; typical flow rates and operating pressures are 100 sccm (total) and 20 torr, respectively. The reactor is operated with, typically, 1% CH_4 in H_2 for 6–8 h prior to any measurements in order to carburize the HF.

CH_3 radicals are detected by $2+1$ REMPI using excitation wavelengths ~ 333 nm [13–15] generated by a Nd-YAG pumped dye laser (Quanta-Ray DCR-2A plus PDL-3) operating at 10 Hz, using a DCM/LDS698 dye mixture and subsequent frequency doubling (in KDP). The UV radiation is separated from the dye fundamental using a Pellin-Broca prism, attenuated to energies < 1.5 mJ pulse^{-1} and focused into the centre of the reactor (20 cm f.l. quartz lens). Some of the UV light exiting the reactor is diverted into a cuvette containing dilute Rhodamine 6G solution, and the resulting fluorescence monitored by a photodiode to allow power-normalization of the REMPI measurements. The transient REMPI current signal resulting from each laser pulse, and that from the photodiode monitoring the UV power, are passed to a digital oscilloscope and thence, via a GPIB interface, to a PC for storage and subsequent analysis.

3. Results and discussion

Fig. 1a displays a power normalized $2+1$ REMPI spectrum of the origin band of the $(3p_z;{}^2A''_2 \leftarrow \tilde{X}\,{}^2A''_2)$ transition of the CH_3 radical obtained using a 1% CH_4 in H_2 gas mixture at a distance $d = 4$ mm below the bottom of the HF maintained at 2475 K. The spectrum is dominated by the Q branch, with weak O, P, R and S branch structure contributing to the broad underlying pedestal [13]. The accompanying simulation (above) employs the appropriate zero and second rank tensor components to describe the two photon transition amplitude (with relative weightings 1:2.5), spectroscopic constants $\nu_0 = 59955$ cm^{-1}, $B' = 9.51$ cm^{-1} and $C' = 4.62$ cm^{-1} for the $3p_z;{}^2A''_2$ electronic state [15] (the quartic distortion constants were all set to the corresponding ground state values), literature values for the ground state spectroscopic constants [20], an excited state predissociation that scales with the N′ and K′

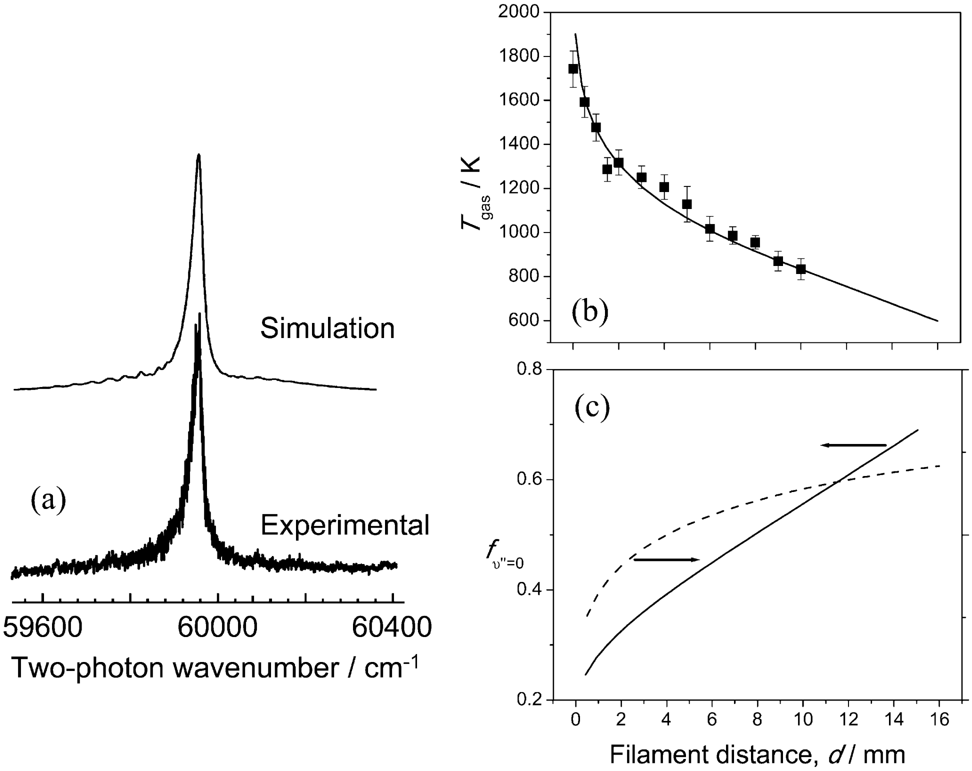

Fig. 1. (a) 2 + 1 REMPI spectrum of the $CH_3(3p_z;{}^2A''_2 \leftarrow \tilde{X}{}^2A''_2)$ transition obtained using a 1% CH_4 in H_2 gas mixture, $T_f = 2475$ K and probing at $d = 4$ mm together with (above) a best-fit simulation of the origin band contour, using spectroscopic parameters listed in the text and $T_g = 1150$ K. (b) Plot showing variation of T_g with d, obtained from H atom Doppler lineshape measurements using 20 torr of pure H_2 and $T_f = 2360$ K; the solid curve is a fit to the data using Eq. (3). (c) Plot illustrating the variation of the correction factors f_c and $f_{\upsilon''=0}$ with T_g (after Redman et al. [12]).

rotational quantum numbers as parameterized by Heinze et al. [15], a predissociation broadened linewidth of $\Delta\nu = 12$ cm^{-1} for transitions involving the non-rotating $N' = K' = 0$ level, and a rotational temperature of 1150 K. This temperature, estimated from band contour analysis, agrees well with that determined (for the same d, T_f and gas pressure and mixing ratio) from fitting the Doppler lineshape of the H atom $n = 2 \leftarrow n = 1$ two photon transition at 243.1 nm [12] and, given that the collision frequency at these temperatures and pressure is $> 10^8$ s^{-1}, is taken as a reliable indicator of the local gas temperature, T_g.

The aim of the present work is to determine relative values of $[CH_3]$ as a function of d, T_f, the hydrocarbon source gas, and its mixing ratio and mole fraction. The experimental measurable, however, is a power normalized REMPI signal - usually monitored at just one wavelength within the $CH_3(3p_z;{}^2A''_2 \leftarrow \tilde{X}{}^2A''_2)$ origin band, and at the prevailing T_g. As discussed previously [10,15], converting such a measurement into the required relative number densities requires knowledge of T_g, as a function of d, and correction factors to compensate for the facts that: (i) the origin band contour; and (ii) the fraction of the total CH_3 population that is in the probed $\upsilon'' = 0$ level, both vary with T_g [15]. The radial dependence of T_g in our HF reactor has been explored in detail, via H atom Doppler lineshape measurements [10,12,21], and shown to be well described by a model function of the form

$$T_g(d) = T_{d=0}\left\{1 - \left[1 - (T_L/T_{d=0})^2\right] \times \ln(d/R_f)/\ln(L/R_f)\right\}^{0.5} \quad (3)$$

where $T_{d=0}$ and T_L are the gas temperatures very close to the filament and at a distance L from the filament, respectively, and R_f is the filament radius [18]. Fig. 1b shows a representative T_g vs. d profile, measured for $T_f = 2360$ K, and serves to illustrate that the measured near filament gas temperature, $T_{d=0}$, is $\sim(T_f - 500)$ for all relevant filament temperatures. Temperature discontinuities of this magnitude have now been reported in several in situ studies of HF-CVD reactors [22–26] in accordance with expectations based on the early work of Langmuir [27], and have been assumed in all subsequent conversions of measured CH_3 REMPI signals to relative number densities. Given T_g, Fig. 1c summarizes the two temperature dependent factors by which the measured REMPI signal must be divided in order to complete this conversion [10]. f_c is obtained by calculating the $CH_3(3p_z;{}^2A''_2 \leftarrow \tilde{X}{}^2A''_2)$ origin band rotational contour for various temperatures in the range $600 < T_g < 1700$ K and then determining the fraction that falls within the bandwidth of the REMPI probe laser centred at 59 950 cm^{-1} (assumed Gaussian). The second correction term, $f_{v''=0}$, allows for the fact that the REMPI probe wavelength only samples that fraction of the total CH_3 radical population that is in its ground vibrational state; the temperature dependence of $f_{v''=0}$ is readily calculable given the relevant normal mode frequencies [28] and the assumption of local thermodynamic equilibrium.

Fig. 2 highlights similarities in the deduced relative $[CH_3]$ values (i.e. the measured 2 + 1 REMPI signals after power normalization and correction by the scaling factors shown in Fig. 1a) when using CH_4/H_2 and C_2H_2/H_2 process gas mixtures. Fig. 2a shows the variation of $[CH_3]$ with carbon content in the process gas mixture (expressed as percentage carbon) introduced into the reactor, while (b) depicts the way in which $[CH_3]$ increases with T_f. These trends appear to be independent of the carbon atom source and, taken together with the previous findings that comparable diamond CVD occurs with when using either CH_4/H_2 or C_2H_2/H_2 process gases [2], hint at a homogeneous CH_3 radical formation mechanism. Such a suggestion is reinforced by measurements of the radial dependence of $[CH_3]$ arising with these two process gas mixtures such as those shown in Fig. 3. Fig. 3a shows CH_3 REMPI signals measured using a 1% CH_4 in H_2 gas mixtures at $T_f = 2475$ K as a function of d, and the radial dependent *total* CH_3 number density after inclusion of the temperature dependent corrections for f_c and $f_{v''=0}$ described previously. The former is in good accord with that reported by Kruger, Zare and co-workers [16,17], who used cavity ring down spectroscopy (CRDS) to monitor the CH_3 column density (via the $3s;\tilde{B}^2A'_1 \leftarrow \tilde{X}^2A''_2$ origin band at 213.9 nm) in a HF activated CH_4/H_2 gas mixture. The deduced $[CH_3]$ is found to be almost independent of d close to the filament, and then to decline monotonically with increasing d — in marked contrast to the measured H atom number density which peaks at $d = 0$ [12,22,24,29].

Fig. 3b shows that the extent of the 'plateau' region of near constant $[CH_3]$ increases with T_f. Such radial profiles may be rationalized by assuming $[CH_3]$ to be determined largely by the gas phase equilibrium (1) and that, though the H atom number density falls with increasing d, the total gas number density (and thus the CH_4 number density) increases with d because of the reciprocal relationship between number density and T_g (at constant pressure). Finally, Fig. 3c compares the deduced radial dependent $[CH_3]$ profiles for the 1% CH_4 in H_2 mixture with those obtained using, respectively, 0.5% and 1% C_2H_2 in H_2. In order that these data could be plotted on a common vertical scale the hydrocarbon feed gas was switched from CH_4 to C_2H_2 and back, whilst maintaining T_f, a constant H_2 flow rate, and the laser output and focussing. C_2H_2/H_2 gas mixtures yield smaller absolute $[CH_3]$ values for a given input carbon mole fraction and T_f, but the general form of their radial profiles are similar to those found using CH_4/H_2 gas mixtures.

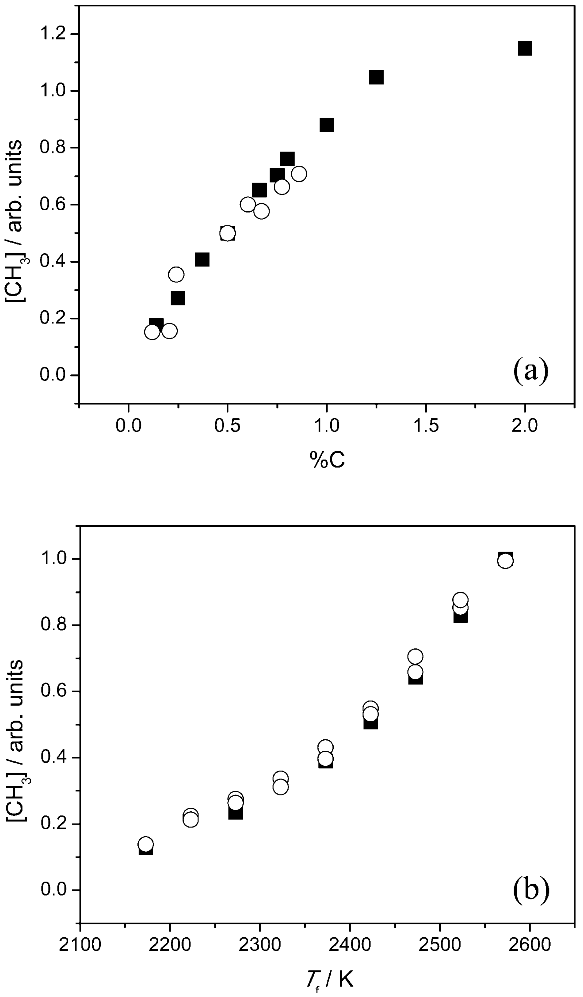

Fig. 2. (a) CH_3 number densities deduced by scaling 2 + 1 REMPI signals measured at 59 950 cm^{-1} using CH_4/H_2 (■) and C_2H_2/H_2 (○) gas mixtures, probing at $d = 4$ mm, plotted as a function of percentage of added carbon. Each data set displays corrected relative number densities, but these number densities have then been scaled arbitrarily so as to match at 0.5% C content and to highlight the similar dependence upon %C. (b) Plots showing variation of CH_3 number density with T_f using CH_4/H_2 (■) and C_2H_2/H_2 (○) gas mixtures, probing at $d = 4$ mm in each case. Again, the two data sets have been rescaled vertically to match at $T_f = 2575$ K to illustrate their similarity.

The present measurements were all made in the absence of any diamond film or heated substrate, and the reactor walls are both cold and distant. The forms of the $[CH_3]$ vs. d plots are largely insensitive to whether the carbon is initially introduced as CH_4 or C_2H_2, and to the hydrocarbon/H_2 mixing ratio and T_f. All of these observations suggest the need for an

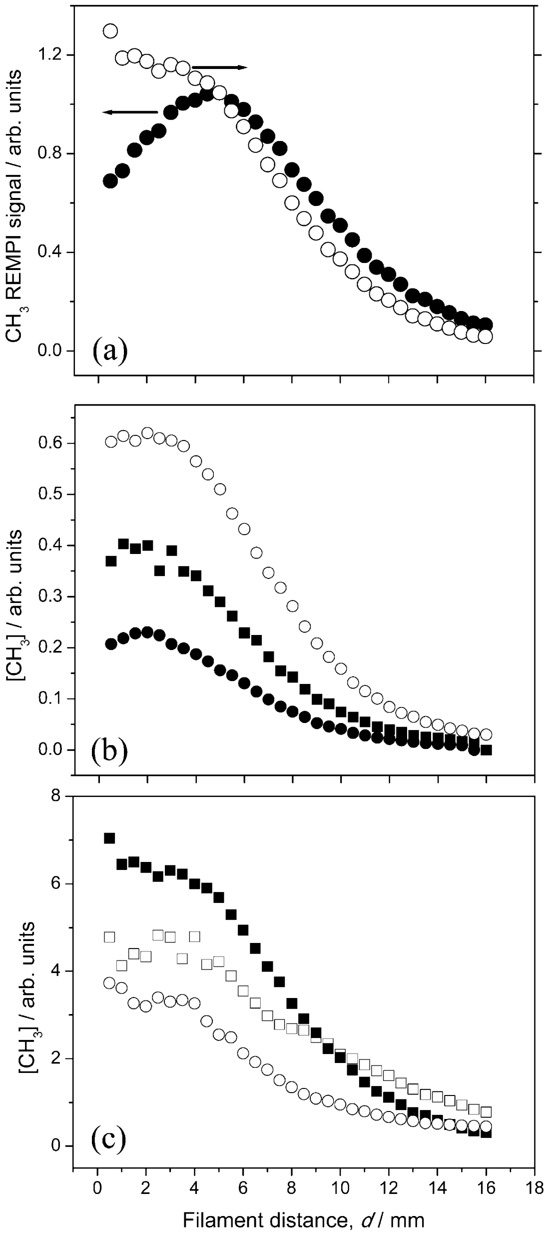

Fig. 3. (a) CH_3 REMPI signals (●), as a function of d, measured using a 1% CH_4 in H_2 gas mixture and $T_f = 2475$ K, together with (○) the d dependence of the total $[CH_3]$ obtained by scaling the measured REMPI signals with the temperature dependent sensitivity factors f_c and $f_{v''=0}$. (b) d dependence of the deduced total $[CH_3]$ from 1% CH_4 in H_2 gas mixtures with $T_f = 2275$ K (●), 2375 K (■) and 2475 K (○). The relative number densities from these separate experiments have been scaled to match the measured $[CH_3]$ vs. T_f data shown in Fig. 2b. (c) Deduced radial dependent $[CH_3]$ profiles for 1% CH_4 in H_2 (■), 0.5% C_2H_2 in H_2 (○) and 1% C_2H_2 in H_2 (□) mixtures, with $T_f = 2475$ K. Switching from CH_4 to C_2H_2 and back, whilst maintaining T_f and a constant H_2 flow rate, allows plotting of these various data sets on a common vertical scale.

explanation based on homogeneous gas phase chemistry, involving H atoms and the hydrocarbon precursor. Clearly, the endoergicity of the forward reaction (1) mitigates against simple H atom abstraction as an important precursor to C–C bond fission but, consistent with speculation advanced by Toyoda et al. [9], we propose that three body reactions such as

$$C_2H_2 + H \rightleftharpoons C_2H_3^{\#} \xrightarrow{M=H_2} C_2H_4 + H \qquad (4)$$

and

$$C_2H_4 + H \rightleftharpoons C_2H_5^{\#} \xrightarrow{M=H_2} C_2H_6 + H \qquad (5)$$

(where # implies a transitory activated complex) provide a purely gas phase route to eventual C–C bond cleavage. Simple probability arguments dictate that the third body M will almost inevitably be H_2, which is the reactant needed to drive the reaction through to the exothermic products. Clearly, there is a pressing need for further kinetic studies of these elementary reactions at temperatures and pressures (of H_2) relevant to diamond CVD environments; the companion paper [30] describes recent investigations of this gas phase chemistry in the context of a realistic three-dimensional model of the Bristol CVD reactor.

4. Conclusions

2 + 1 REMPI spectroscopy has been used to determine relative number densities of CH_3 radicals in a HF-CVD reactor designed for diamond growth, as a function of position (d) and local gas temperature (T_g). The CH_3 radical number densities arising in dilute CH_4/H_2 and C_2H_2/H_2 gas mixtures are observed to exhibit similar radial profiles, being almost independent of d close to the filament, and thereafter to decline monotonically with increasing d. These direct measurements strongly suggest that CH_3 radical formation in both CH_4/H_2 and C_2H_2/H_2 process gas mixtures is dominated by gas phase chemistry, in contradiction of the current consensus which invokes surface catalysed hydrogenation as the means of inducing the necessary C–C bond fission in the latter case.

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