Fluorescence by the Vacuum-uv Photolysis of Acetylene

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Acetylene as an intermediate reaction product plays an important role in hydrocarbon combustion with a close relation to chemiionization and chemiluminescence. In such processes, the production of polyacetylenes probably starts soot formation. Recently, acetylene and products involving acetylene reactions became of great interest for the comet tail chemistry and for the formation of acetylene-type molecules detected in interstellar space.

One way of studying acetylene reactions is the investigation of the C_2H_2 photolysis. In most of the papers which have been published it is indicated that several secondary reactions during the photolysis of acetylene in the vacuum-uv have to be attributed to reactions of metastable $C_2H_2^*$ molecules with C_2H_2 itself or with other reactants[1–4]. There is some additional evidence for long living $C_2H_2^*$ states in the 9 eV region from molecular beam experiments[5]. Also from the banded structure of the C_2H_2 absorption spectrum[6, 7] it may be concluded that relatively long living states become excited in the vacuum-uv for which predissociation must be very weak.

Electronically excited $C_2H_2^*$ can decompose into the following products:

$$\begin{array}{llll} \text{(a)} & & \nearrow C_2H + H\,, & \text{energy } E(C_2H_2^*) \geqq 115 \text{ kcal/mole,} \\ \text{(b)} & C_2H_2^* & \rightarrow C_2 \;\; + H_2\,, & \text{energy } E(C_2H_2^*) \geqq 147 \text{ kcal/mole,} \\ \text{(c)} & & \searrow CH \; + CH\,, & \text{energy } E(C_2H_2^*) \geqq 228 \text{ kcal/mole.} \end{array}$$

Previously, Stief et al.[2] have reported fluorescence from the photolysis of acetylene with the Kr-resonance line at 1236 Å (231 kcal/mole). The emission was also observed by irradiation with the Xe-line at 1295 Å (221 kcal/mole) but not with the Xe-line at 1470 Å (195 kcal/mole). These authors have attributed the fluorescence in the visible spectral region to the Swan bands, $C_2(A\,^3\pi_g \rightarrow X\,^3\pi_u)$. According to their mechanisms the electronically excited C_2^* radicals were formed by a slow decomposition of $C_2H_2^*$ through reaction path (b) which could be suppressed by the addition of inert gases in the torr region.

We have reinvestigated the fluorescence in the C_2H_2 system because the slow decomposition of $C_2H_2^*$ into electronically excited fragments seemed to be a very rare process due to competitive energy redistribution in the C_2H_2 molecule. On the other hand, if the emitter cannot be identified as C_2^*, two other emitters, $C_2H_2^*$ or C_2H^*, should be responsible for the fluorescence as it has been shown by the present work.

The fluorescence measurements were carried out in a conventional reaction chamber attached to a resonance lamp which was excited by a microwave discharge[8]. About 20% of the light intensity from such a Kr-resonance lamp occurs at 1165 Å which usually is not separated from the main intensity at 1236 Å. Acetylene was prepared by vacuum distillation of commercial gas. The fluorescence spectrum was analysed with a 1.5 m Fastie-Two-Mirror monochromator by photoelectric detection. The reaction chamber could also be used for mixing acetylene with atomic oxygen diluted by argon, in order to compare the fluorescence spectrum with the emission from an acetylene-oxygen atom flame under almost identical conditions. It is well known that the emission spectrum of such a flame shows the Swan bands[9, 10]. In a different apparatus in which the radiation from a Kr-resonance lamp was modulated by a mechanical chopper[11], the decay time of the fluorescence could be measured wiht a time resolution of about 0.05 μsec.

Figure 1 shows the fluorescence spectrum in comparison to the acetylene-oxygen atom flame spectrum, both with a resolution of $\Delta\lambda = 10$ Å. The two spectra show a very similar, apparent continuous emission starting at about 4000 Å (72 kcal/mole). This emission extends to the red with a spectral distribution which is mainly determined by the spectral sensitivity of the detection system. Swan bands can only be seen in the flame spectrum. Even with a spectral resolution of $\Delta\lambda = 0.5$ Å which became possible by a photon-counting technique[12], no structure in the fluorescence spectrum was detectable; this finding rules out any diatomic molecule as emitter of the fluorescence. Comparing the fluorescence intensity with that of the airglow reaction, $NO + O \rightarrow NO_2 + h\,\nu$, as a suitable standard[13], gave a rough estimate of 0.1% for the fluorescence yield.

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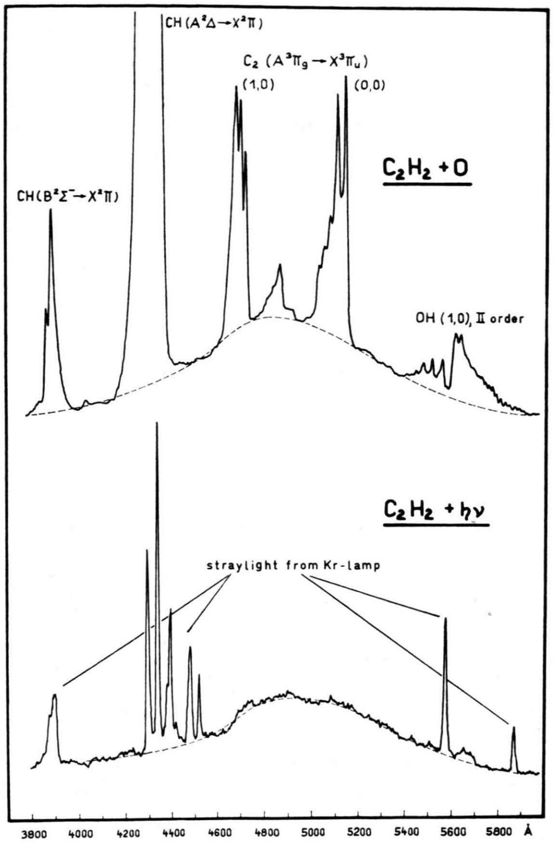

Fig. 1. Fluorescence spectrum from the C_2H_2 photolysis at 1236 Å and flame spectrum from the reaction $C_2H_2 + O$.

By varying the C_2H_2 pressure in the fluorescence cell, a natural lifetime $\tau = 6.2$ μsec and a rate constant $k = 1.5 \times 10^{-10}$ $\text{cm}^3 \times \text{molecule}^{-1} \times \text{sec}^{-1}$ for the quenching of the fluorescence by C_2H_2 was found, Figure 2. With these values and the quenching constants obtained from the stationary fluorescence experiments, rate constants for the quenching of X* by other inert gases were determined as given in Table 1:

Table 1. Quenching of the X* fluorescence, $\tau(X^*) = (6.2 \pm 1.0)$ μsec.

quenching gas	rate constant [$\text{cm}^3 \times \text{molecule}^{-1} \times \text{sec}^{-1}$]
C_2H_2	$(1.5 \pm 0.2) \cdot 10^{-10}$
H_2	$(8.3 \pm 1.5) \cdot 10^{-11}$
N_2	$(5.2 \pm 1.5) \cdot 10^{-11}$
Ar	$(6.4 \pm 1.5) \cdot 10^{-11}$

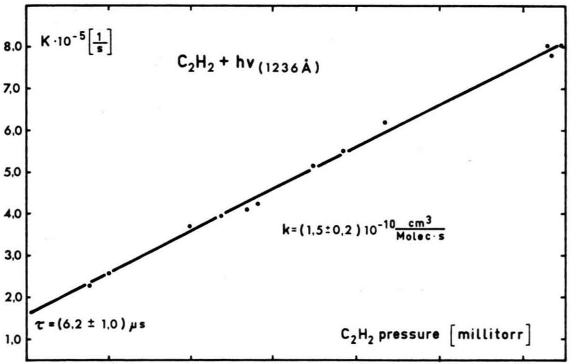

Fig. 2. Reciprocal decay-time of the X* fluorescence as a function of the C_2H_2 pressure.

Different pumping speeds through the reaction chamber did not influence the fluorescence intensity or the decay time of the X* emission.

It is concluded that the emitter X* has to be formed by a primary step in the C_2H_2 photolysis. The Swan bands as well as other diatomic emitters can definitively be excluded for the observed fluorescence, and $C_2H_2^*$ or C_2H^* remain as the only possible polyatomic emitters produced primarily by the C_2H_2 photolysis. From substituted acetylenes such as CH_3C_2H, $C_2H_5C_2H$, CNC_2H or C_4H_2 no fluorescence was observed by the photolysis at 1236 Å, except CN* violet bands in the case of cyanoacetylene. On the other hand, careful search in the vacuum-uv gave no indication of resonance fluorescence from $C_2H_2^*$.

None of the two possible emitters, $C_2H_2^*$ or C_2H^*, can be excluded or evidently prooved at the moment. But the fact that H_2 production which has been shown by isotope analysis to occur through reaction (b) [2] can be suppressed by CO_2 with a rate which is in good agreement with the measured lifetime of X* from the present work if gas kinetic collision frequency is assumed for the quenching of X* by CO_2, supports $C_2H_2^*$ as emitter. The reduction of C_2H_2 disappearance by the addition of N_2 [2] and the quenching of X* by N_2 are in close agreement, too.

$C_2H_2^*$ would be optically excited by a non-allowed transition with a quantum yield of 0.1%. For linear configurations the transition between upper states resulting in fluorescence could be seen in analogy to N_2 transitions. Transitions between bent states of C_2H_2 could explain the fluorescence as well. The forbidden optical transition to an upper bent state from the linear ground state would result in a rather complex vibrational structure of the emission spectrum as it is indeed observed for the fluorescence.

The apparent continuous emission from the acetylene-atomic oxygen flame is under further investigation. Energy transfer from highly excited CO* molecules [14, 15] to C_2H_2 might be responsible for this emission. In the $C_3O_2 + O + H$ system which shows all the other "hydrocarbon-like" emitters [10], the continuous emission was not observed.

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