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TIME RESOLVED SPECTROSCOPY OF A PULSED DISCHARGE THROUGH  
WATER VAPOR : OBSERVATION OF EMISSIONS FROM THE  $C^2 \Sigma^+$  STATE  
OF OH

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ABSTRACT : the (0-9)  $C^2 \Sigma^+ - A^2 \Sigma^+$  band of OH and a complex emission located around 1850 Å are both observed as a function of time in a pulsed discharge through water vapor. The results are discussed in the light of Felenbok's interpretation of the origin of the 1850 Å emission.

INTRODUCTION

In 1957, Michel<sup>(1)</sup> observed in the spectrum of a hollow-cathode discharge through water vapor a series of lines in the region 1700 to 1900 Å (subsequently called 1850 group). These emissions do not show any typical structure. By observing the spectrum of H<sub>2</sub>O - D<sub>2</sub>O mixtures, Michel concluded that the emitter of the 1850 group contains only one hydrogen atom. He suggested that a nonlinear molecule like O<sub>2</sub>H or O<sub>2</sub>H<sup>+</sup> whose electronic spectra are still presently unknown could be responsible for the complexity of the 1850 group.

Owing to the relative positions of the known potential curves of OH favouring the application of the Franck-Condon principle, Felenbok<sup>(2)</sup> in 1963, put forward the

hypothesis that the 1850 group should correspond to the overlap of bands starting from vibrational levels  $v'=0$  and 1 of the  $C^2\Sigma^+$  state of OH to vibrational levels near the dissociation limit of its fundamental  $X^2\Pi_1$  state. Felenbok and Czarny<sup>(3)</sup> have tentatively assigned the vibrational levels of the  $X^2\Pi_1$  state involved in the transitions to be  $v''=10$  to 16. This assignation is based on an extrapolation of the curve  $\Delta G(v+\frac{1}{2})$  as a function of  $v+\frac{1}{2}$  of the  $X^2\Pi_1$  state to fit the dissociation energy of this state. To our knowledge, no detailed spectroscopic analysis has been published which would give a definitive answer to that problem. This note reports an attempt to throw further light on this question.

It is well known that different spectroscopic emissions starting from a common electronic level are governed by the mean radiative lifetime of this level. So the intensity decay curves of these emissions versus time must show the same behaviour for the same physical conditions in the discharge. Thus it is possible to check the validity of Felenbok's interpretation by comparing the experimental decay of intensity of the  $(0-9)C^2\Sigma^+ - A^2\Sigma^+$  band at  $2683.5 \text{ \AA}$  (the most intense band of this system recently reobserved under high resolution by Carlone and Dalby<sup>(4)</sup>) and of the  $(0-15,16) C^2\Sigma^+ - X^2\Pi_1$  bands which following Felenbok and Czarny must be identified with the 1850 group. If the decay curves are not similar, this identification must be definitively rejected. On the other hand if the curves have the same behaviour this will strongly support Felenbok's interpretation. However this analogous behaviour of the curves will not absolutely settle the question because different electronic states may have the same lifetime.

## RESULTS

The emissions are excited in a pulsed hollow cathode discharge through streaming water vapor. The

rectangular high voltage pulses are applied to the hollow-cathode tube at a rate of 25 cycles/sec. These pulses are produced by a generator using switched 3C45 hydrogen thyratrons (see for example<sup>(5)</sup> for a basic circuitry). They are  $2 \cdot 10^{-6}$  sec wide, their amplitude is 1500 V, the fall time is shorter than  $15 \cdot 10^{-9}$  sec. After the excitation has ceased the decay curve of the selected spectral emissions is registered as a function of time by a sampling method (see for example<sup>(6,7)</sup>). The measurements are punched in a digital form for a least squares analysis by the aid of a computer.

The selection of the spectral emission to be measured is performed by a 0.75 m Czerny-Turner spectrometer (SPEX 1800 - II) flushed with dry nitrogen. The advantage of this apparatus is its easy conversion from a spectrograph into a monochromator. So it is possible to carefully examine the photographic spectrum of the discharge before performing monochromatic measurements. This was particularly important for the (0-9)  $C^2\Sigma^+ - A^2\Sigma^+$  band in order to properly select the monochromator bandpass to avoid the superposition of Fe lines of the cathode. The spectrum has revealed the existence of a continuum very probably due to  $H_2$ <sup>(8)</sup> covering the full spectral region accessible with one exposure (1750 to 3500 Å). Being so blended by a continuum the emissions at 2683.5 and 1850 Å must show decay curves which are at least a superposition of two exponentials.

Two typical decay curves versus time of the intensity of the (0-9)  $C^2\Sigma^+ - A^2\Sigma^+$  band at 2683.5 Å and of the 1850 Å group are reproduced respectively in Fig. 1 and 2 on a semilogarithmic scale. These curves result from the mean of a series of 8 measurements for a water vapor pressure in the discharge of 1 mm Hg.

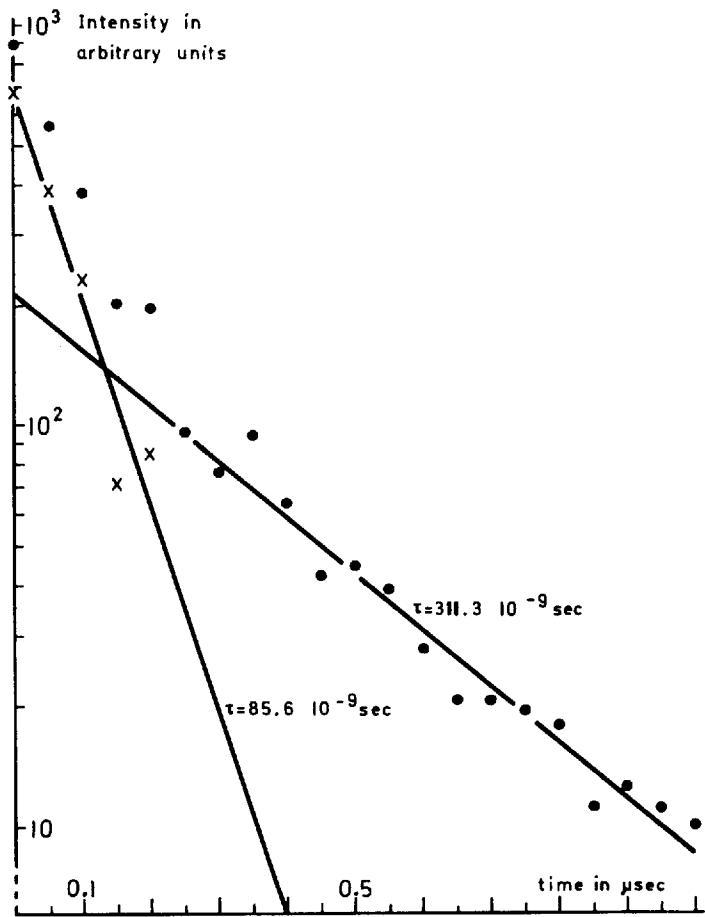


Fig. 1. Typical intensity decay curve of the (0-9)  $C^2\Sigma^+ - A^2\Sigma^+$  band of OH at 2683.5 Å.

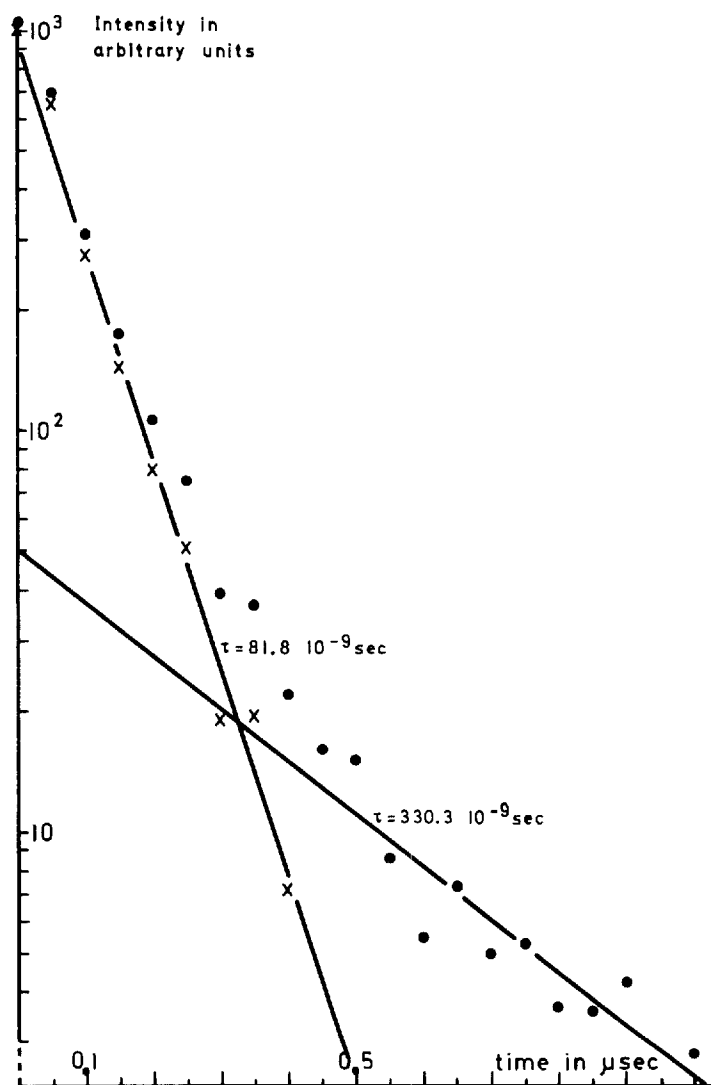


Fig. 2. Typical intensity decay curve of the 1850 Å group.

Table 1 gives the exponents deduced from the least squares treatment of 136 experimental decay curves obtained for each emission considered here at a water vapor pressure of 1 mm Hg in the discharge. The quoted limits are the standard deviations.

TABLE 1

	$(0-9)C^2\Sigma^+ - A^2\Sigma^+$ band of OH at 2683.5 Å	1850 Å group
First exponential	$\tau = 80.0 \pm 5.2 \cdot 10^{-9}$ sec	$\tau = 78.9 \pm 2.7 \cdot 10^{-9}$ sec
Second exponential	$\tau = 325.7 \pm 10.2 \cdot 10^{-9}$ sec	$\tau = 319.7 \pm 8.3 \cdot 10^{-9}$ sec

Obviously the differences from one column to the other between the corresponding values for  $\tau$  may be considered as insignificant because they largely fall within the standard deviations.

As foreseen two exponentials have been found<sup>(9)</sup> One of these is certainly due to the  $H_2$  continuum present at both wavelengths, the other value of  $\tau$  being characteristic of the upper electronic levels of the 1850 group and of the 2683.5 Å band of OH.

### CONCLUSION

This result, although as already mentioned being not an absolute argument, strongly suggests to identify the upper electronic state of the 1850 group with the  $C^2\Sigma^+$  state of OH. Thus, in future attempts to a detailed spectroscopic analysis of the 1850 group, Felenbok's interpretation is to be

first of all carefully considered. Our conclusion would have been reinforced if the same results were observed under widely different pressure conditions. Unfortunately owing to the fixed distance between the electrodes of the discharge tube it was not possible to vary the pressure conditions by more than a factor of two without disturbing the stability of the discharge. It is worthy noting that the  $\tau$  values obtained from the decay curves under these conditions of pressure have not shown any significant change larger than the standard deviations.

The attribution of the lifetimes reported in Table 1 to their corresponding electronic state :  $C^2\Sigma^+$  of OH or  $a^3\Sigma_g^+$  of  $H_2$  (which decays to the repulsive  $b^3\Sigma_u^+$  state with emission of the continuous radiation) is of a limited interest. Indeed due to numerous secondary processes in electrical discharges under fairly high pressure, the lifetimes measured in these conditions are generally far from representing the true radiative decay of the excited electronic states. Nevertheless we have attributed the large value of  $\tau (>300 \cdot 10^{-9} \text{ sec})$  to the  $a^3\Sigma_g^+$  state of  $H_2$  for the following reason. The photographic spectrum clearly shows that the 1850 Å group is much more intense than the continuum at this wavelength while at 2683 Å the continuum is fairly intense as compared to the  $(0-9)C^2\Sigma^+ - A^2\Sigma^+$  band. By comparison of the intensities at the origin of the short and long decay curves respectively in Fig. 1 and Fig. 2, we arrive at the above conclusion. The lifetime actually admitted is only around  $11 \cdot 10^{-9} \text{ sec}$  for the  $a^3\Sigma_g^+$  state of  $H_2$  at zero pressure<sup>(10)</sup>. The very large discrepancy between the lifetime at zero pressure and ours is certainly due to strong secondary processes governing the rate of population of the  $a^3\Sigma_g^+$  state. As already mentioned the intensity of the  $H_2$  continuum seems to depend strongly on such processes<sup>(8)</sup>. Even in discharge through molecular hydrogen the continuum intensity depends also strongly, beyond the electrical conditions in the discharge, on secondary phenomena due to pressure and gas purity<sup>(11)</sup>.



It is useless to propose some identification of the secondary processes involved in the particular observations realized here on the  $H_2$  continuum. Indeed, if the long decay part of the curves could be observed for delays much longer than the limit of 1  $\mu$ sec (imposed here by the signal to noise ratio), it is highly probable that more than one long exponential decay would be necessary to fit the observations<sup>(12)</sup>. Nevertheless this remark of fundamental importance for the absolute determination of lifetimes has no influence on our conclusion regarding Felenbok's interpretation, this conclusion being based on relative observations performed in the same physical conditions.

If we admit that deactivation is the only process acting after the direct excitation of OH in the discharge, then the small value of  $\tau$  ( $\approx 80 \cdot 10^{-9}$  sec) would represent in our interpretation of the results a lower limit for the lifetime of the  $C^2\Sigma^+$  state of OH. In the case where multiexponential long decay curves would be necessary to fit the observations at large delays, the  $80 \cdot 10^{-9}$  sec value would be slightly reduced<sup>(12)</sup>.

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