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Classification

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## Lifetimes of radiative excited levels of H<sub>2</sub>

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**Résumé.** — Nous avons mesuré, par la technique de fluorescence résolue dans le temps, la durée de vie de niveaux de H<sub>2</sub> excités par photoabsorption. Pour certains d'entre eux, la fluorescence n'est qu'un canal de désexcitation parmi d'autres : prédissociation et préionisation. Ces mesures permettent, à partir des valeurs des taux de dissociation et d'ionisation, d'obtenir une valeur absolue pour les probabilités de dissociation, d'ionisation et pour les durées de vie radiatives de ces états.

**Abstract.** — Lifetimes of photoexcited levels of H<sub>2</sub> were measured by the time resolved fluorescence technique. For many levels, fluorescence is one decay channel among others : predissociation and autoionisation. From published predissociation and autoionization yields, absolute values of predissociation probabilities, autoionization probabilities and radiative lifetimes are deduced.

### 1. Introduction.

In the past few years, many lifetime measurements were performed on H<sub>2</sub> excited levels [1-9] but only one of them refers to optically-allowed excited levels : the Lyman and Werner systems [1]. They are of interest in the physics of planetary atmospheres [10] and will provide a test to *ab initio* calculations.

In the present work we report lifetime measurements of photoselected excited levels. Most of them are lying above the H(1S) + H(*n* = 2) dissociation limit and a few of them above the ionization limit.

The excitation spectrum of visible molecular fluorescence of H<sub>2</sub> was observed from 860 Å to 740 Å and was reported previously [11]. The fluorescent levels, when excited by photoabsorption from the fundamental levels, mostly radiate back to the X levels but for a small amount, to the excited E, F <sup>1</sup>Σ<sub>g</sub><sup>+</sup> levels emitting visible photons. Fluorescence does remain a competitive decay process *versus* predissociation [12] and even preionization [13].

Predissociation [12] and ionization [13] yields were measured for many excited levels. The lifetime measurement provides an absolute measurement of the dissociation and/or the ionization probabilities.

The lifetimes are measured directly on the exponential decay of the fluorescence.

### 2. Experiment.

The VUV continuum of the synchrotron radiation source at Orsay is dispersed by a 1 m normal incidence monochromator. A typical 0.05 Å bandwidth can be achieved at 800 Å, to allow the selective excitation of individual rotational levels but in most cases, the flux was too small and a bandwidth of 0.2 Å was generally used. Wavelength calibration is obtained by comparison of the absorption spectrum with published data [14]. The monochromatic light passes through a differentially pumped cell where the pressure can be maintained from 10<sup>-3</sup> to a few 10<sup>-2</sup> torr and measured by a Baratron Gauge. Molecular fluorescence is detected through a plexiglass light-pipe by a refrigerated photomultiplier, without any filter. The RTC-XP2020 photomultiplier used for most of the cases is blind to the red part of the visible spectrum. Some of

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the measurements were made with a RTC-56 TVP photomultiplier sensitive up to 7000 Å.

The synchrotron radiation is pulsed with a 1-ns-width and 73.433 ns between pulses. The fluorescence observed is very faint, much less than 1 photon by exciting pulse and a single photon technique can very easily be achieved : the fluorescence photon when detected opened the start gate of a Time to Amplitude Converter, the following synchrotron radiation pulse was used with an appropriate delay at the stop gate of the T.A.C., as the synchrotron radiation pulses provide a very performant clock, no frequency fluctuation would shade the signal. Then the output of the T.A.C. is used to feed a multi-channel analyser. A typical decay curve is shown on figure 1. To present the decay in the usual way, the curve was inverted. The decay curves were fitted by an exponential curve and the error bars estimated from the fitting.

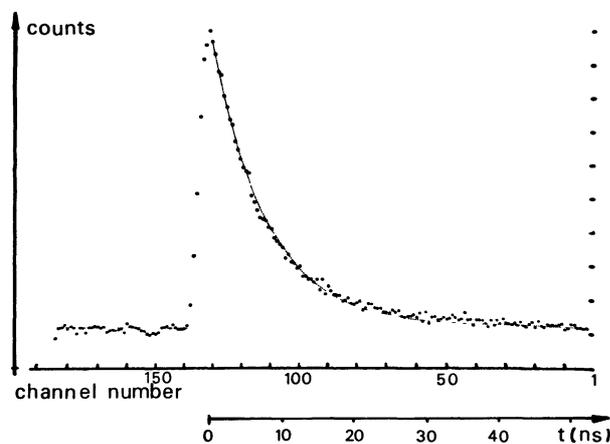


Fig. 1. — Decay curve observed at 8 mtorr from the  $4p\sigma^1\Sigma_u^+ v' = 0 J' = 3$  level. The dotted line is an exponential fit.

### 3. Experimental results and discussion.

First, for the fluorescence decays, no variations were observed depending on the spectral range detected. No cascades were found, and the study of the rising slope of the signal confirmed that the fluorescence detected was due to the emission of the levels directly excited by the VUV pulse. A very easy calculation can prove then that all these emissions are toward the E, F levels, contrarily to Böse and Hunder observation [15].

Because of the differential pumping necessary for this experiment (for more details, see Ref. [16]), pressure could not be varied on a large range, therefore it is not surprising if no variation with pressure could be detected in the lifetime values for the  $np^1\Pi_u$  and  $1\Sigma_u$  levels with  $n = 3$  and 4 (Fig. 2).

On figure 3 are plotted the measured emission probability values for the  $5p\pi^1\Pi_u^- v' = 0 J' = 1$  level with the pressure ; by exception, in this case, the pressure range was extended to 50 mtorr : and varia-

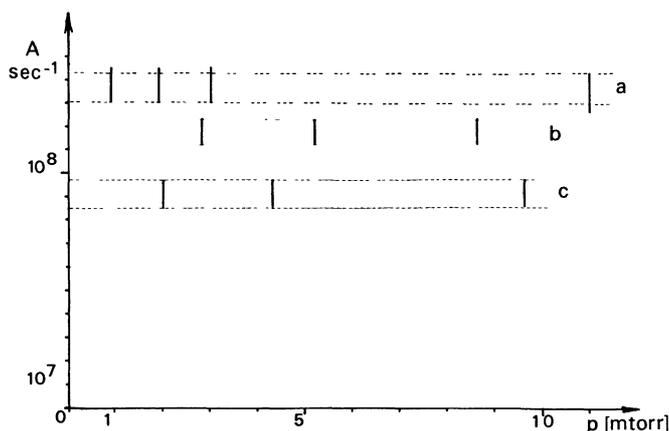


Fig. 2. — Decay probabilities measured at different pressure values, with the extrapolations

- (a) decay probabilities from the  $4p\pi^1\Pi_u^- v' = 3 J' = 1$ .  
 (b) decay probabilities from the  $4p\sigma^1\Sigma_u^+ v' = 0 J' = 3$ .  
 (c) decay probabilities from the  $3p\sigma^1\Sigma_u^+ v' = 4 J' = 2$ .

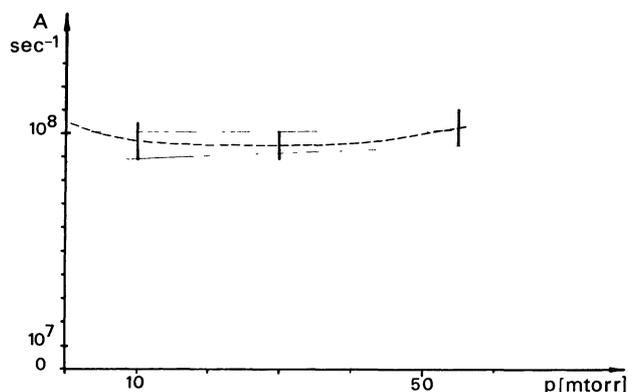


Fig. 3. — Decay probabilities from the  $5p\pi^1\Pi_u^- v' = 0 J' = 1$  level measured at different pressure values. ... represents the performed extrapolation neglecting the multiple diffusion. --- is for a possible extrapolation, taking multiple diffusion into account.

tions were observed. It is possible that collisional quenching and multiple diffusion [17] are competing in this pressure range as the value at 50 mtorr seems to indicate. If that was confirmed, our reported lifetime values would be in slight error (no more than 10 %).

For a few cases the absorption lines R(0) R(1) were not well resolved and then only a mean value on the two rotational  $J' = 1$  and 2 levels could be measured.

The results are summarized on table I for the levels lying below the dissociation limit for which fluorescence is the only possible decay channel, and on table II for the levels lying above it and below the ionization limit. For the second ones, photon emission and predissociation can compete, and the observed decay time  $\tau$  of the fluorescence is the combination

Table I. — Measured lifetimes of levels lying below the dissociation limit : H(1S) + H(n = 2).  $\tau_{\text{Ryd}}$  are calculated assuming a Rydberg law (see text).

Level	$v'$	$J'$	Excitation line Å	$\tau$ (ns)	$\tau_{\text{Ryd}}$ (ns)
3p $\sigma$ 1 $\Sigma_u^+$	4	2	R(1) 855.57	11.0 ± 0.7	5.0
4p $\sigma^1$ $\Sigma_u^+$	0	1 } 2 }	R(0) 855.11 } R(1) 855.27 }	7.6 ± 0.6	6.2
		3	R(2) 855.90		
		1 } 2 }	R(0) 848.19 } R(1) 848.15 }		
4p $\pi$ 1 $\Pi_u^+$	0				

Table II. — Measured lifetimes of levels lying above the dissociation limit H(1S) + H(n = 2) and below the ionization limit. The predissociation yields  $\chi_d$  are measured values from reference [12].  $A_{\text{diss}}$  and  $\tau_{\text{rad}}$  are deduced from  $\tau$  and  $\chi_d$ .  $\tau_{\text{Ryd}}$  is as in table I.

Level	$v'$	$J'$	Excitation line	$\tau$ (ns) (this work)	$\chi_d$ [12]	$A_{\text{diss}}$ (s <sup>-1</sup> )	$\tau_{\text{rad}}$ (ns)	$\tau_{\text{Ryd}}$ (ns)	
4p $\pi$ 1 $\Pi_u^+$	1	1	R(0) 832.66 } R(1) 832.68 }	1.2 ± 0.6 }	0.65 ± 0.15	(8.0 ± 5.0) · 10 <sup>8</sup>	5.0 ± 4.0	7.1	
		2							
1 $\Pi_u^-$	1	1	Q(1) 833.50	7.3 ± 0.2	< 0.03	< 4 × 10 <sup>6</sup>	7.4 ± 0.3	7.1	
		2	Q(2) 834.38	7.1 ± 0.3	< 0.06	< 8 × 10 <sup>6</sup>	7.3 ± 0.5		
		3	Q(3) 835.68	7.6 ± 0.4	< 0.04	< 5 × 10 <sup>6</sup>	7.8 ± 0.6		
	2	1	Q(1) 819.33	7.2 ± 0.2	< 0.05	< 7 × 10 <sup>6</sup>	7.4 ± 0.4	7.3	
		3	Q(3) 821.53	7.2 ± 0.3	< 0.05	< 7 × 10 <sup>6</sup>	7.4 ± 0.5		
	3	1	Q(1) 806.44	7.2 ± 0.2				7.4	
		2	Q(2) 807.33	7.0 ± 0.3					
5p $\pi$ 1 $\Pi_u^+$	0	1	R(0) 831.66	15.0 ± 3.0	< 0.15	< 1.2 × 10 <sup>7</sup>	17.0 ± 5.0	13.4	
		2	R(1) 831.55	11.7 ± 1.0	< 0.1	< 9 × 10 <sup>6</sup>	12.4 ± 1.7		
1 $\Pi_u^-$	0	1	Q(1) 832.55	10.5 ± 1.0	< 0.03	< 3 × 10 <sup>6</sup>	10.7 ± 1.2	13.4	
1 $\Pi_u^+$	1	1	R(0) 816.77 } R(1) 816.74 }	6.9 ± 0.3	0.4 ± 0.2 0.7 ± 0.2				13.8
		2							
1 $\Pi_u^-$	1	1	Q(1) 817.60	12.3 ± 0.3	0.10 ± 0.05	(8.0 ± 4.0) · 10 <sup>6</sup>	13.7 ± 1.1	13.8	
5p $\sigma$ 1 $\Sigma^+$	0	0	P(1) 836.03	3.7 ± 0.5				12.0	
		1	R(0) 834.89	3.2 ± 0.3					
		2	R(1) 835.07	2.5 ± 0.5					
	1	2	R(1) 820.44	8.0 ± 0.5				14.0	
4	R(3) 822.12	3.3 ± 0.3							

of the photon emission probability  $A_{\text{rad}}$  and of the predissociation probability  $A_{\text{diss}}$  (in s<sup>-1</sup>):

$$1/\tau = A = A_{\text{rad}} + A_{\text{diss}}.$$

For most of the studied levels, the predissociation yield ( $\chi_d = A_{\text{diss}}/A$ ) was measured [12]. Then absolute predissociation probabilities (in s<sup>-1</sup>) and radiative lifetimes (in ns,  $\tau_{\text{rad}} = 1/A_{\text{rad}}$ ) can be deduced, table II.

For levels lying above the ionization limit, results are summarized on table III. The observed lifetime is then such as

$$1/\tau = A = A_{\text{rad}} + A_{\text{diss}} + A_{\text{ion}}$$

the autoionization yield was measured [13] and autoionization probabilities  $A_{\text{ion}}$  theoretically calculated [13]. A comparison between the theoretical value and the value deduced from the measured yield and the observed lifetime can be made.

No theoretical calculated values of the radiative lifetime are available for these levels except for  $n = 3$  [18]. Another possible approach is to consider all the  $n\pi$  levels as Rydberg ones and to use the  $1/n^3$  emission probability rule with the theoretical published Born-Oppenheimer 3p $\sigma$  and 3p $\pi$  values; the figures in last column of the tables were obtained in such a way.

Table III. — Measured lifetimes of levels lying above the dissociation and the ionization limits. Predissociation yields  $\chi_d$  and auto-ionization yields  $\chi_i$  are measured values from references [12] and [13]. For the auto-ionization probabilities  $A_{\text{ion}}$ : a is from reference [13] and b from reference [20].

Level	$v' J'$	Excitation line (Å)	$\tau$ (ns) (this work)	$\chi_d$ [12]	$\chi_i$ [13]	$A_{\text{diss}}$ ( $\text{s}^{-1}$ )	$A_{\text{ion}}$ ( $\text{s}^{-1}$ ) theoretical	$A_{\text{ion}}$ ( $\text{s}^{-1}$ ) deduced	$\tau_{\text{rad}}$ (ns)	$\tau_{\text{Ryd}}$ (ns)
4 $p\pi^1 \Pi_u^-$	4 1	Q(1) 794.70	$6.2 \pm 0.3$	$< 0.3$	0.08	$< 5 \times 10^7$	$1.2 \times 10^7$ (a)	$(1.3 \pm 0.1) \cdot 10^7$	$8.4 \pm 2.0$	7.6
	2	Q(2) 795.60	$6.7 \pm 0.3$							
	3	Q(3) 796.96	$3.6 \pm 0.5$							
	5 1	Q(1) 784.04	$7.1 \pm 0.4$		0.06		$6.9 \times 10^7$ (a)	$(8.5 \pm 0.5) \cdot 10^6$	7.7	
5 $p\pi^1 \Pi_u^+$	2 1	R(0) 803.24	$1.1 \pm 0.5$	$0.07 \pm 0.05$	1.0	$(1.0 \pm 0.9) \cdot 10^8$	$2.0 \times 10^9$ (b)			
	2	R(1) 803.25		$0.07 \pm 0.05$	0.96	$(1.0 \pm 0.9) \cdot 10^8$				

It fairly agrees for the  $n\pi\pi$  levels, then we can say that  $^1\Pi_u^-$  levels have fairly Rydberg behaviours.

The predissociation study of the  $4p\pi^1\Pi_u^-$  levels [19] provided a determination of their radiative lifetimes:  $7 \pm 1$  ns which is in excellent agreement with the measured values. In this case, we can see that the radiative lifetime, as expected, varies very slowly with  $J'$  and  $v'$  and is not much affected by the symmetry  $\Pi^+$  or  $\Pi^-$ , contrary to the predissociation probability.

It does not seem to be the same for the  $5p\pi v' = 0$  levels but the apparent variations may be due to an improper correction for the combined effect of collisions and multiple diffusion.

An interesting point is the  $5p\pi^1\Pi_u^+ v' = 2 J' = 1, 2$  levels. They lie above the ionization limit. They are known to be mostly preionized [13] but also to be predissociated and still to radiate [12]. The preionization of these levels was studied by Jungen and Dill using MQDT [20]; they showed that the  $J' = 1$  level presents a very narrow profile in absorption  $\Delta\sigma = 0.011 \text{ cm}^{-1}$  which corresponds to a ionization probability of  $2.07 \times 10^9 \text{ s}^{-1}$ , which may be compatible with a small predissociation and a small remaining fluorescence (the observed decay time  $1.1 \pm 0.5$  ns is a limit for our technique, a deconvolution of the response function would be necessary, but we had no

mean to measure the response function correctly). If we accept for the radiative lifetime the value measured for  $v' = 1$ :  $13.7 \pm 0.9$  ns ( $A_{\text{rad}} \gtrsim 7 \times 10^7 \text{ s}^{-1}$ ), the fluorescence yield is then of the order of 7%, the same value as for the predissociation yield ( $7 \pm 5\%$ ) [12].

Using all these figures one obtains a total decay probability of  $2.2 \times 10^9 \text{ s}^{-1}$  ( $\tau = 0.45$  ns) in fair agreement with the measured decay probability of  $(9.0 \pm 4.0) \cdot 10^8 \text{ s}^{-1}$  ( $1.1 \pm 0.5$  ns). The calculated ionization probability may be a little overestimated.

All the observed values are not so easily interpreted; for instance the  $4p\pi^1\Pi_u^- v' = 4 J' = 3$  presents an abnormally small lifetime while the  $5p\sigma^1\Sigma_u^+ v' = 1 J' = 2$  presents a very large one, maybe due to an accidental coupling, or a wrong assignation. Most  $5p\sigma$  observed values well agree with the observed predissociation yields of the order of 50% [21] and with a radiative lifetime of  $\simeq 7$  ns.

#### 4. Conclusion.

These lifetime measurements provide a complement to the predissociation-yield study allowing the determination of absolute values for small predissociation probabilities and of radiative lifetimes.

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