PHYSICAL REVIEW A VOLUME 21, NUMBER 6 JUNE 1980

Radiative emission from singlet superexcited levels of H_2

J. Breton,* P. M. Guyon,† and M. Glass-Maujean‡

L.U.R.E. Laboratoire commun Centre National de la Recherche Scientifique et Université Paris-Sud, 91405 Orsay, France

(Received 20 November 1979)

The high-resolution fluorescence-excitation spectrum of H_2 from 850 to 720 Å allows us to identify fluorescent levels lying above the $H(n=1)+H(n=2)$ dissociation threshold and even above the ionization threshold. Below the ionization limit (804 Å $<\lambda$) fluorescence remains a competitive decay channel for nearly all the excited levels except the $3p\pi\,{}^1\Pi_u^+$ and $4p\sigma\,{}^1\Sigma_u^+$. Above the ionization limit we still observe fluorescence from many levels mainly of ${}^1\Pi_u^-$ symmetry. The whole vibrational progression of the $3p\pi\,{}^1\Pi_u^-$ up to $v'=17$ is observed. In addition fluorescence is observed from few levels lying above the $H(n=3)+H(n=1)$ dissociation limit.

I. INTRODUCTION

Fluorescence of molecular hydrogen excited by electron impact (or by a discharge) has been extensively studied in the past. The high-resolution visible spectra of Dieke[1] extending from the near ultraviolet to the infrared region provide a huge amount of information particularly on the triplet states. While Crosswhite and Dieke assigned 15 singlet levels lying higher than the dissociation limit $H(n=2)+H(n=1)$, they assigned more than 150 such triplet levels, 50 of them lying higher than the ionization limit. This differing numbers of singlet and triplet states identified may be due to a different behavior of the singlet levels regarding dissociation or simply to the inadequate knowledge of the first singlet gerade excited state $E,F\,{}^1\Sigma_g^+$. Not all of the lines in Dieke's spectrum are assigned.

More recently, Sroka[2] observed vacuum ultraviolet fluorescence from singlet levels lying higher than the dissociation limit and even higher than the ionization limit. His wavelength resolution, however, was limited and he was not able to assign the fluorescent levels. Roncin *et al.*,[3] observed vuv lines emitted from $3p\pi\,{}^1\Pi_u^-$ levels lying higher than the ionization limit.

High-resolution vuv fluorescence spectra are difficult to obtain since lines emitted from superexcited levels are expected to be very weak. Another way to observe them is to look at the fluorescence-excitation spectrum. When excited by absorption of vuv photons, H_2 molecules radiate in the vuv region ($\rightarrow X\,{}^1\Sigma_g^+$) and in the visible region ($\rightarrow E,F\,{}^1\Sigma_g^+$).[4] If the incident photons are sufficiently well defined in energy to allow absorption on a particular rotational line, no selection is needed on the fluorescence to identify the fluorescent level. We have previously reported preliminary results using this method.[4] In this work, we observed fluorescence from levels lying between the dissociation $H(n=2)+H(n=1)$ and the ionization limits, and even higher, i.e., above the ionization limit. However the resolution was not high enough at the time to assign the fluorescent levels unambiguously. We have improved the resolution greatly and are now able to identify them.

II. EXPERIMENTAL SETUP

Most of the experiment has been described previously.[4] The vacuum uv continuum of synchroton radiation of Orsay is dispersed by a 1-m normal-incidence monochromator. A typical 0.06-Å bandwidth (~9 cm^{-1}) achieved at 800 Å allows the selective excitation of individual rotational levels. Wavelength calibration is obtained by comparison of the observed absorption spectrum with published data.[5]

The monochromatic vuv light passes through a differentially pumped cell (Fig. 1) where the pressure of hydrogen is maintained at 10^{-2} torr. The pressure achieved in the monochromator is about 10^{-6} torr, so as to minimize absorption outside of the fluorescence detection region. The transmitted light is detected using a salicylate-coated window, fluorescence is detected through a quartz window by a refrigerated EMI-9558-QB or 9635-A photomultiplier, without any filter. The 9635-A photomultiplier is blind to the red part of the visible spectrum and therefore cannot detect $H\alpha$(6563-Å) radiation which can occur for incident wavelength shorter than 749 Å. Both photomultipliers are sensitive to the blue light; for incident wavelengths shorter than 722 Å, the fluorescence observed is mostly due to $H\beta$ atomic radiation (4860 Å). An exit diaphragm on the cell is used to avoid stray light from the salycilate hitting the fluorescence detector.

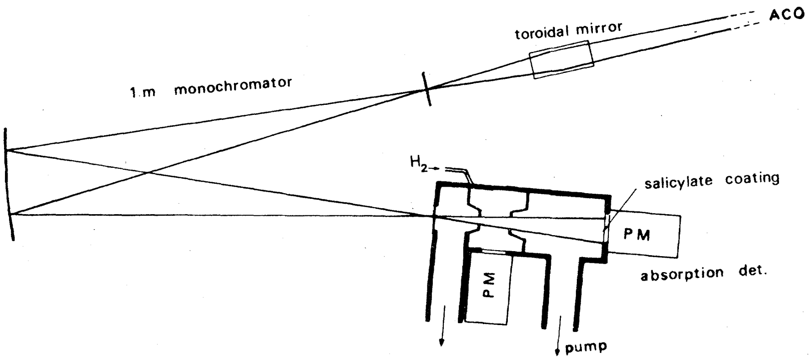

FIG. 1. The experimental setup.

III. RESULTS

The fluorescence-excitation spectra were recorded at high (0.06-Å) and low (0.15-Å) resolution in order to combine selectivity and sensitivity over the 845–720 Å spectral range. The intensities of the fluorescent lines have not been used for a quantitative evaluation, because emission occurs over a wide spectral range for which the sensitivity of the photomultiplier presents great variations. Part of the high-resolution excitation spectrum and absorption spectrum is shown in Fig. 2(a) corresponding to the region between the dissociation and ionization thresholds. In Fig. 2(b), a "low"-resolution excitation spectrum is drawn for comparison, corresponding to a range above the ionization limit.

The absorption of photons *between 845 and 804* Å excites molecular levels whose decay channels are only predissociation and (or) fluorescence. We have observed fluorescence from *nearly all the excited levels except* the $3p\pi\ ^1\Pi_u^+$ (all v' and N'), $4p\sigma\ ^1\Sigma_u^+$ (all v' and N') levels which are all missing in the fluorescence spectrum. The lines observed in absorption and not detected in fluorescence are all associated with the $^1\Sigma_u^+$ or $^1\Pi_u^+$ states and represent roughly one line in three. The levels which do not fluoresce are tabulated in Table I. This information on fluorescence is in perfect agreement with previous predissociation rate measurements[6,7]: We see that all the levels which do not fluoresce are very strongly predissociated, while all the strongly predissociated levels are not observed to fluoresce. In addition, wherever predissociation is not complete, i.e., less than 80%, we observe fluorescence corresponding to the remaining 20%.

TABLE I. The levels, excited in the 804–845 Å spectral range, which are not observed to fluoresce. X_d is the predissociation rate measured previously.

	V'	N'	X_d[a]
$3p\pi\ ^1\Pi_u^+$	≥3	≥1	1
$4p\sigma\ ^1\Sigma_u^+$	≥1	≥0	1
$4p\pi\ ^1\Pi_u^+$	1	3	>0.8
	2	≥2	>0.8
	3	≥1	>0.8
$5p\sigma\ ^1\Sigma_u^+$	0	3	>0.5
	2	≥0	>0.8
$7p\sigma\ ^1\Sigma_u^+$	0	3	>0.8
	1	≥0	>0.9
$8p\sigma\ ^1\Sigma_u^+$	0	≥0	>0.7

[a] P. M. Guyon, J. Breton, and M. Glass-Maujean, Ref. 7 and unpublished data.

For incident wavelengths *shorter than 804* Å the excited molecular levels may be also preionized. By comparing Fig. 2(a) and 2(b) we see at once that preionization is a much more efficient decay channel than predissociation: The lower two spectra in Fig. 2(b) show that only few lines survive in emission. This is not unexpected, but the fact that a few lines remain is remarkable in view of the results for other molecules. Those lines are reported in Table II.

It is seen from Table II that nearly all the observed emission lines originate from levels of $^1\Pi_u^-$ symmetry, and most of them from low Rydberg states with $3\leq n\leq 7$. This is again not unexpected since we know that the $^1\Pi_u^-$ states are very stable with regard to dissociation[7] and the low Rydberg states are hardly preionized because the vibrational excitation has to change by more than one quantum.[8] However, our results show that this rule has a few exceptions: Out of the 60 observed excited levels five have Π^+ or Σ^+ symmetry, but emission from all of them is very weak.

The predissociation[7] and preionization[8] rates previously measured are displayed for discussion in Table II. One can see that the various data agree well on the whole; the only exceptions are the $5p\pi\ ^1\Pi_u$ and $6p\pi\ ^1\Pi_u$ states where the sum of

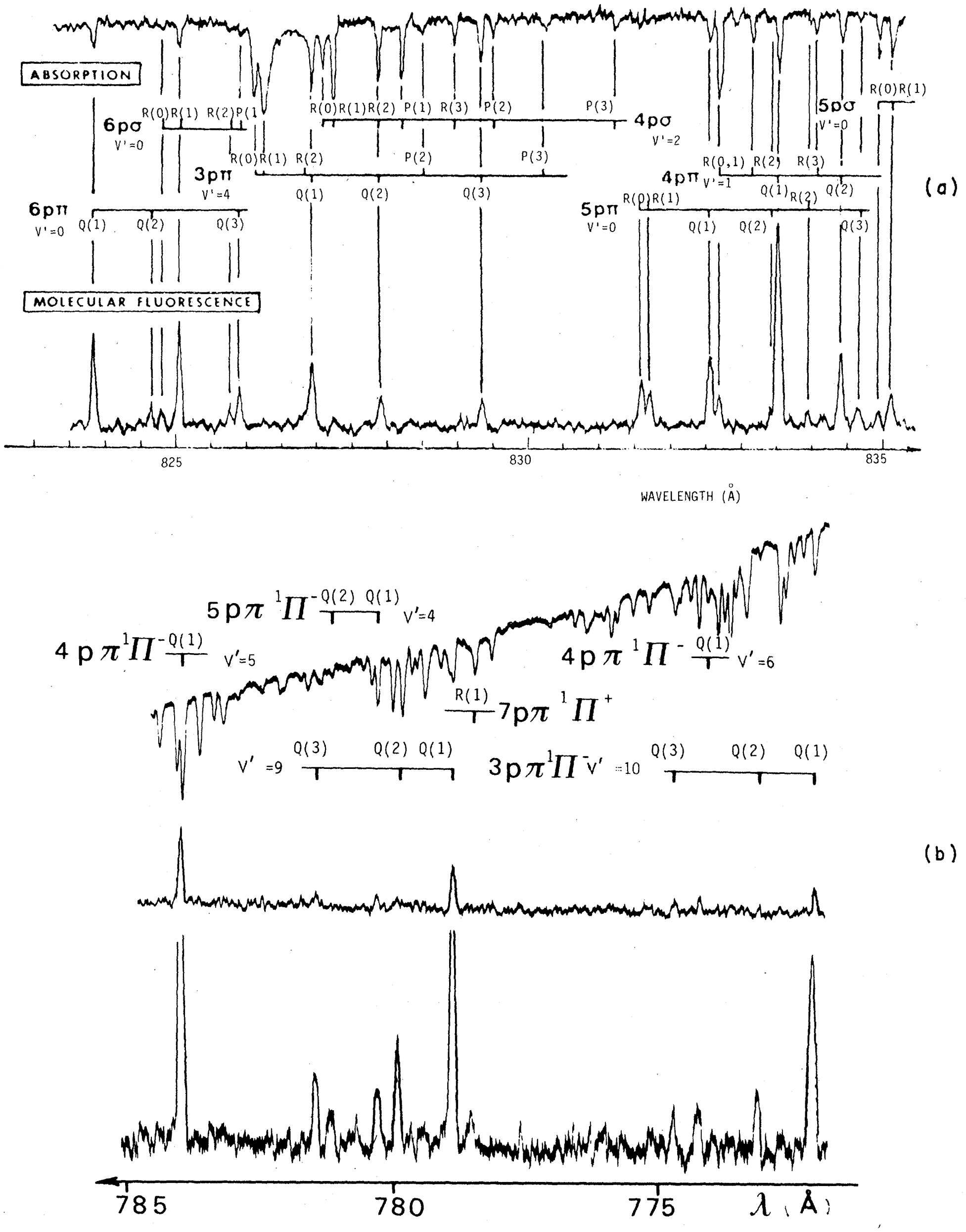

FIG. 2. Part of the high-resolution fluorescence-excitation spectrum and absorption spectrum. (a) In the energy range between dissociation and ionization limits; (b) above the ionization limit. A "low"-resolution excitation spectrum is drawn below for comparison.

nonradiative decay rates is as large as 1.1 in some cases even without including the fluorescence rate. This may be due to overestimated preionization rates, or more simply, to the uncertainties of these rates which from Ref. 8 can be inferred to be at least ~10%.

The absorption spectrum has not yet been fully analyzed at wavelengths shorter than 760 Å.[5,9] We have therefore extrapolated Dehmer and Chupka's values to higher values of v' in the $3p\pi$, $4p\pi$, and $5p\pi$ states. In this way we have been able to identify all the vibrational levels of the $3p\pi\ {}^1\Pi_u^-$ state up to $v' = 17$ which is the last bound level, as shown by the Birge-Sponer plot of Fig. 3.

Nevertheless some lines remain unassigned. They may originate from high rotational levels of the ground state; information about transitions is limited because most available absorption data have been taken with hydrogen cooled to 78 K.

An interesting feature is that some of these

TABLE II. Wavelengths and identification of the absorption lines which are responsible for observed fluorescence. The ionization X_i and predissociation X_d rates measured previously in Refs. a and b, respectively, are reported for comparison.

λ (Å)	$np\lambda, v'$	X_i [a]	X_d [b]
803.95	$5p\pi, 2Q(1)$	0.94	<0.05
3.57	$5p\pi, 2R(2)\ \Pi^+$		<0.2
3.24	$2R(0)R(1)\ \Pi^+$	0.98	0.07 ± 0.05
797.67	$3p\pi, 7Q(3)$		0.2 ± 0.1
6.96	$4p\pi, 4Q(3)$		
6.17	$3p\pi, 7Q(2)$		0.15 ± 0.05
5.89	$6p\pi, 2Q(1)$	0.81	0.3 ± 0.1
5.80	$11p\pi, 1Q(1)$		
5.60	$4p\pi, 4Q(2)$		
5.18	$3p\pi, 7Q(1)$	0	
4.96	$12p\pi, 1Q(1)$		
4.70	$4p\pi, 4Q(1)$	0.08	<0.3
4.30	$13p\pi, 1Q(1)$		
3.80	$5p\pi, 3Q(3)$		
3.00	$7p\pi, 2Q(3)$		
2.50	$5p\pi, 3Q(2)$		<0.2
1.66	$5p\pi, 3Q(1)$	0.4	<0.2
1.41	$7p\sigma, 2R(0)\ \Sigma^+$	~0.5	
0.98	$7p\pi, 2Q(1)$		
789.80 (±0.05)			
9.13	$3p\pi, 8Q(3)$		
7.63	$3p\pi, 8Q(2)$		<0.1
6.61	$3p\pi, 8Q(1)$	0	
5.93 (±0.05)			
5.68	$9p\pi, 2Q(1)$		<0.1
4.04	$4p\pi, 5Q(1)$	0.06	
3.74	$6p\pi, 3Q(1)$	1.00	
3.46	$4p\pi, 5R(1)\ \Pi^+$	0.18	0.7 ± 0.1
2.13	$12p\pi, 2Q(1)$		
1.53	$3p\pi, 9Q(3)$		
1.25	$5p\pi, 4Q(2)$		<0.15
0.38	$5p\pi, 4Q(1)$	0.90	
779.99	$3p\pi, 9Q(2)$		
8.95	$3p\pi, 9Q(1)$	0	0.2 ± 0.1
8.60	$7p\pi, 3R(1)\ \Pi^+$		
4.79	$3p\pi, 10Q(3)$		
4.36	$4p\pi, 6Q(1)$	0.80	
3.24	$3p\pi, 10Q(2)$		
2.75	$6p\pi, 4Q(1)$	0.95	0.10 ± 0.05
2.19	$3p\pi, 10Q(1)$	0	0.20 ± 0.10
0.10	$5p\pi, 5Q(1)$	1.09	<0.5
769.80	$13p\pi, 3Q(1)$		
8.98	$3p\pi, 11Q(3)$		
8.13	$7p\pi, 4Q(1)$		
7.34	$3p\pi, 11Q(2)$		
6.29	$3p\pi, 11Q(1)$	0	0.3 ± 0.1
5.58	$4p\pi, 7Q(1)$	0.93	
5.00 (±0.05)			
2.98 (±0.05)			
2.41 (±0.05)	$3p\pi, 12Q(2)$		
1.23	$3p\pi, 12Q(1)$	0	
760.00 (±0.05)			
758.63 (±0.05)			
8.20	$3p\pi, 13Q(2)$ $7p\pi, 5Q(1)$		
7.65	$4p\pi, 8Q(1)$	0.80	
7.04	$3p\pi, 13Q(1)$		

TABLE II *(Continued)*

λ (Å)	$np\lambda, v'$	X_i[a]	X_d[b]
3.76 (±0.05)	$3p\pi$, 14Q(1)		
2.95 (±0.05)	$3p\pi$, 15Q(2)		
2.36 (±0.05)	$5p\pi$, 7Q(1)		
1.35 (±0.05)	$3p\pi$, 15Q(1)		
0.59 (±0.05)	$4p\pi$, 9Q(1)		
749.82 (±0.05)	$3p\pi$, 16Q(1)		
9.15 (±0.05)	$3p\pi$, 17Q(1)		
7.95 (±0.1)			
738.70 (±0.1)			
7.80 (±0.1)			

[a] P. M. Dehmer and W. A. Chupka, J. Chem. Phys. 65, 2243 (1976).

[b] P. M. Guyon, J. Breton, and M. Glass-Maujean, Chem. Phys. Lett. 68, 314 (1979).

unassigned lines occur at wavelengths shorter than 749 Å, which means that they originate from levels which lie even above the dissociation limit corresponding to H($n=1$)+ H($n=3$). The continuum of the $3p\pi\ ^1\Pi_u^-$ state may induce the predissociation of the other $^1\Pi_u^-$ states, through vibronic interaction. This mechanism seems, therefore, not very efficient.

IV. CONCLUSION

We have observed fluorescence from singlet excited levels lying higher than the ionization limit and even higher than the dissociation H($n=1$) + H($n=3$) limit. These fluorescent levels belong mostly to the $3p\pi\ ^1\Pi_u^-$, $4p\pi\ ^1\Pi_u^-$, $5p\pi\ ^1\Pi_u^-$, $6p\pi\ ^1\Pi_u^-$, and $7p\pi\ ^1\Pi_u^-$ states. The triplet fluorescent superexcited ungerade levels observed in the Dieke's[1] early work all belong to the $3p\pi$, $4p\pi$, $5p\pi\ ^3\Pi_u^-$ states. We conclude that there must be a great similarity between the singlet and triplet emission of H_2. Dieke was not able to assign many of the singlet lines because he had little information at his disposal on the double-minimum $E,F\ ^1\Sigma_g^+$ lower state. Our results prove that emission lines originating from very high $np\pi\ ^1\Pi_u^-$ levels must be present in Dieke's spectra.

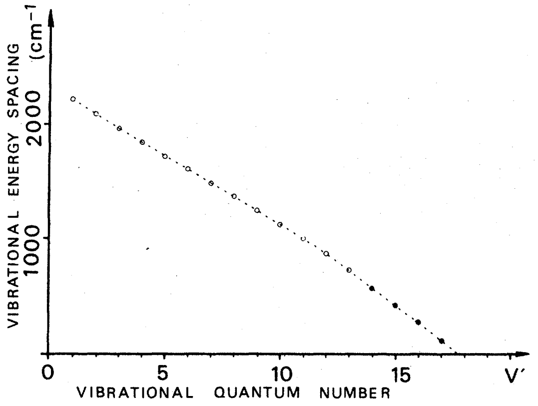

FIG. 3. The Birge-Sponer plot of the $3p\pi\ ^1\Pi_u^-$ levels. The closed circles correspond to our extrapolation.

Another point may be emphasized: The importance of the symmetry properties of the electronic eigenfunction of the molecule. The dynamics of the $np\pi$ states present a much greater similarity between triplet and singlet states than between Π^- and Π^+ states.

ACKNOWLEDGMENTS

The authors would like to thank the Laboratoire de l'Accélérateur Linéaire in Orsay for their technical help in operating the storage ring. They gratefully acknowledge Dr. Ch. Jungen for reading the manuscript and for helpful comments.

---

*Also at Laboratoire d'Electrodynamique des Gaz Ionisés, Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05, France.

†Also at Laboratoire des Collisions Atomiques et Moléculaires, Université Paris-Sud 91405 Orsay, France.

‡Also at Laboratoire de Spectroscopie Hertzienne de l'E.N.S., 4 place Jussieu, 75230 Paris Cedex 05, France.

[1] G. H. Dieke, *The Hydrogen Molecule Wavelength Tables*, edited by H. M. Crosswhite (Wiley, New York, 1972).

[2] W. Sroka, Phys. Lett. 28A, 784 (1969).

[3] J. Y. Roncin, H. Damany, and C. Jungen, Communication to the Fourth International Conference on vuv, Hamburg, 1974 (unpublished).

[4] P. Borrell, P. M. Guyon, and M. Glass-Maujean, J. Chem. Phys. 66, 818 (1977).

[5] S. Takezawa, J. Chem. Phys. 52, 2575 (1970).

[6] M. Glass-Maujean, J. Breton, and P. M. Guyon, Phys. Rev. Lett. 40, 181 (1978).

[7] P. M. Guyon, J. Breton, and M. Glass-Maujean, Chem. Phys. Lett. 68, 314 (1979).

[8] P. M. Dehmer and W. A. Chupka, J. Chem. Phys. 65, 2243 (1976).

[9] G. Herzberg and Ch. Jungen, J. Mol. Spectrosc. 41, 425 (1972).