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LIFETIME OF CdH AND CdD $A^2\Pi$ STATE EXCITED BY A DYE LASER

A. JOURDAN, J. M. NEGRE, J. DUFAYARD and O. NEDELEC

Laboratoire de Spectrométrie Physique, Université Scientifique et Médicale,
B.P. 53, 38041 Grenoble Cedex, France

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Résumé. — La durée de vie des niveaux excités $A^2\Pi_{1/2}$ et $A^2\Pi_{3/2}$, $v' = 0$ et 1, de CdH et CdD a été mesurée par excitation optique au moyen d'un laser à colorant pulsé.

Abstract. — The radiative lifetimes of the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$, $v' = 0$ and 1, excited states of CdH and CdD have been measured by pulsed dye laser excitation.

1. **Introduction.** — Pulsed dye laser excitation is a new technique particularly suitable for lifetime measurements [1, 2]. In this paper, we report the possibility of studying alkaline earth hydrides by this technique at a pressure sufficiently low that the collisional relaxation probability is small compared to the radiative decay probability. Up to now, the spectra and the Zeeman effect, in diatomic metal hydrides, have been studied by conventional techniques only.

2. **Experiment.** — CdH may be obtained in the ground state from cadmium excited states reacting with H_2 [3, 4] :

The $A^2\Pi \rightarrow X^2\Sigma$ fluorescence is then subsequently excited by means of a dye laser, the fluorescence decay leading to the measurement of the mean radiative lifetime.

A block diagram of the apparatus is given in figure 1. We use an electrodeless discharge in cadmium vapor and hydrogen to obtain the free radical. This

discharge is turned off during the excitation of the hydride by the laser pulse to avoid the presence of continuous light and also of fields and charged particles which may relax the excited states of this polar molecule. The temperature of the cell is kept constant during the experiment at $T \simeq 500$ K so that the cadmium vapour pressure is about 10^{-3} torr. A continuous flow of H_2 passes through the cell and the pressure may be varied from 10^{-3} to 10 torr.

An AVCO C 5 000 A N_2 laser working at 100 Hz pumps a dye laser made in our laboratory according to Hänsch's model [5], with an expander telescope ($\times 15$) and a 600 lines/mm diffraction grating working in the fifth order. The dye pulse duration is about 3 nanoseconds. An upper limit for the width of the laser line, measured on a fluorescence spectrum (Fig. 2) is about 0.25 Å. The fluorescent light emitted by the $A^2\Pi \rightarrow X^2\Sigma^+$ transition of CdH is focused on the slit of a Jobin-Yvon HRS 1 monochromator.

FIG. 1. — Block diagram of the apparatus.

FIG. 2. — CdH $A^2\Pi_{1/2}$ 0-0 band fluorescence obtained by scanning the dye laser wavelength.

A photomultiplier (EMI 9816) with a time spread of 3 nanoseconds is used. The signal is recorded with a Boxcar Integrator PAR model 162 via a Tektronix 75 ns delay line. The Boxcar is triggered by a photodiode receiving the dye laser pulse.

3. Results. — The $A^2\Pi$ excited state of CdH is characterised most closely by Hund's coupling case (a). Each band of the $A^2\Pi \rightarrow X^2\Sigma$ transition is divided into two sub-bands originating from $A^2\Pi_{3/2}$ and $A^2\Pi_{1/2}$. Each sub-band is composed of six branches [6, 7].

We have excited the $A^2\Pi$, $v' = 0$ and 1, states from the ground state $X^2\Sigma^+$, $v'' = 0$. The organic dyes employed to produce wavelengths from 4 000 Å to 4 500 Å are : diphenylstilbene popop, dimethyl popop, 7-diethylamino 4 methylcoumarin. Figure 2 shows the fluorescent light obtained by varying the wavelength of the dye laser providing the excitation of the CdH $A^2\Pi_{1/2}$ ($v' = 0$) state. The emitted light is focused on the photomultiplier and the delay of the boxcar gate is fixed.

The same experiment has been made with CdD which has a $A^2\Pi \rightarrow X^2\Sigma^+$ transition in the same wavelength region as CdH. After laser excitation of the 0 and 1 vibrational states of $A^2\Pi$, we have observed the emission of several bands (Table I) most of which had not been reported previously.

We have measured the lifetime τ of the $A^2\Pi$ states of CdH and CdD. The fluorescent light is passed through a monochromator to eliminate the light of the laser pulse diffused by the walls of the cell. The excitation and the observation are made near the band head in order to obtain the greatest fluorescence intensity (Fig. 2). The boxcar gate duration is 1 ns, the scanning aperture delay range is 500 ns, the scan time is 10^3 s. Each lifetime has been extrapolated to zero H_2 (or D_2) pressure with measurements at less than 10^{-2} torr. Figure 3 represents the laser pulse and the fluorescence signal obtained with the same apparatus and drawn with the same time scale. After the laser pulse (Fig. 3a) the emitted light decreases exponentially (Fig. 3b, c). The time spread of the photomultiplier is much shorter than the measured lifetime and the exponential part of the recorded current follows exactly that of the fluorescent light.

The lifetimes given in table II are very near each other. However, the $\Pi_{1/2}$ ($v' = 1$) state of CdH and $\Pi_{1/2}$ ($v' = 0$) state of CdD have longer lifetimes. Important variations of the lifetimes may be induced by rotational perturbations [8] and in the case of the $^2\Pi_{1/2}$ ($v' = 1$) state of CdH a few rotational states about $J' = 15.5$ are perturbed by the $B^2\Sigma^+$ state [6]. Nevertheless in our experiment the intensities of the $^2\Pi_{1/2}$ perturbed rotational states are weak compared to the total intensity of the band.

FIG. 3. — Signals obtained with the apparatus of figure 1 for : the dye laser pulse at 4 491 Å (a), the CdH fluorescence at 4 791 Å, 5×10^{-2} torr H_2 , in normal scale (b) and in logarithmic scale (c).

TABLE I

Band heads of CdD, A ²Π → X ²Σ⁺ transition. Wavelength in Å

$v' \backslash v''$	$\underline{\Pi_{1/2}}$						$\underline{\Pi_{3/2}}$				
	0	1	2	3	4	5	0	1	2	3	4
0	4 500	4 710	4 924				4 300	4 509	4 708	4 886	
1	4 265	4 473	4 664	4 857	5 038	5 200	4 100	4 268	4 438	4 618	4 783

TABLE II

Lifetimes of CdH and CdD A ²Π states

		CdH		CdD	
		$\underline{\Pi_{1/2}}$	$\underline{\Pi_{3/2}}$	$\underline{\Pi_{1/2}}$	$\underline{\Pi_{3/2}}$
$v' = 0$	Excitation				
	$v'' = 0 \rightarrow v' = 0$	4 509 Å	4 313 Å	4 500 Å	4 300 Å
	Detection				
	$v'' = 0 \rightarrow v'' = 1$	4 791 Å	4 571 Å	4 710 Å	4 509 Å
$v' = 1$	τ (ns)	70 ± 6	70 ± 6	85 ± 8	68 ± 7
	Excitation				
	$v'' = 0 \rightarrow v' = 1$	4 198 Å	4 026 Å	4 265 Å	4 100 Å
	Detection				
	$v'' = 1 \rightarrow v'' = 1$	4 437 Å	4 247 Å	4 473 Å	4 268 Å
	τ (ns)	77 ± 7	72 ± 7	66 ± 6	67 ± 6

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