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ON THE SYNTHESIS OF CdH (OR CdD) FROM Cd 5 3P AND H2 (OR D2)

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Résumé. — On excite le niveau 5 3P du cadmium par bombardement électronique ou par voie optique, et on observe la variation de sa durée de vie ou de l'intensité de la lumière qu'il émet quand on ajoute H2 ou D2. On montre ainsi qu'il y a à la fois des transferts d'excitation entre les niveaux du triplet et une désexcitation conduisant à la synthèse de l'hydrure. La section efficace de désexcitation de 5 3P1, beaucoup plus grande que celle des métastables 5 3P0,2 est égale à (33 ± 5) Å² et (16 ± 3) Å² pour H2 et D2 respectivement.

Abstract. — The cadmium level 5 3P is excited by electron impact or by Cd resonance light, and the variations of its lifetime or of the emitted light are measured as either H2 or D2 is added. We show the existence of excitation transfers between the components of the triplet state and of a quenching which lead to the production of the hydride. The quenching cross-section from the 5 3P1 state is found to be much greater than that from the metastable 5 3P0,2 states and equal to (33 ± 5) Å² and (16 ± 3) Å² for H2 and D2 respectively.

1. Introduction. — The spectra of alkaline-earth hydrides have been recorded for a long time in mixtures of hydrogen and metal vapours in discharges or arcs. As most electronic states may be excited by visible light, selective dye laser excitation will allow us to make diagnostics about their synthesis [1] and spectroscopic measurements without Doppler effect [2]. In this paper, as a first approach towards such studies, we describe classical experiments about the synthesis of CdH (or CdD) from the 5 3p state of Cd reacting with H2 (or D2).

The synthesis of CdH, CdD, ZnH, have been obtained [3, 4, 5] by optical excitation of the metal to the first 3P1 state, in a few 10⁻¹ torr H2. This first 3p state includes metastable states and by electron impact it may be the most populated excited state of the metal. We consider the reaction :

\[ M^* + H_2 \rightarrow MH + H + \Delta E \]

\[ E_M^* - D_0^0(H_2) = - D_0^0(MH) + \Delta E \]  

(1)

\[ E_M^* \] is the excitation energy of the metal M in the first triplet state [6]. \( D_0^0(H_2) \) and \( D_0^0(MH) \) are the dissociation energies of H2 and the hydride respectively, from the ground state \( v = 0 \) [7].

According to the values of \( \Delta E \), three different cases may occur, for the alkaline earth hydrides :

— Hg : the energy of Hg* is high enough to dissociate H2. HgH has been obtained in the excited state [4, 8].

— Cd, Zn, Mg, Be : the reaction (1) is exothermic. The hydride may appear in the ground state by the reaction (1).

— Ca, Ba, Sr : the reaction (1) is endothermic, with a great energy defect compared to \( kT \). The reaction (1) is not possible from the first excited state of the metal.

From these conservation considerations it appears easier to obtain the Cd, Zn, Mg and Be hydrides than the Ca, Ba and Sr ones. Moreover, the first series requires a temperature lower than the second one to attain a reasonable vapour pressure. We have chosen the synthesis of CdH as an example because it requires the lowest temperature. Moreover the lifetime of the first excited Cd 3P1 state is the most convenient for these experiments.

The Cd 5 3P state is excited by slow electrons or by Cd resonance light. We observe the 5 3P1 → 5 1S0 line, 3 261 Å, and measure the variation of its intensity and of the P1 lifetime when H2 or D2 is added. The comparison of these various results allows us to evaluate the importance of transfers between the triplet states and to measure the quenching cross-section of 5 3P1 by H2 or D2, which is very likely the cross-section for the exchange reaction (1) providing CdH or CdD.

2. Experimental set-up. — The gas is excited in a pentode allowing the measurement of lifetimes by the phase-shift technique [9]. The cell is in an oven heated by thermocoax. The cadmium is in a tail which is the...
coldest part of the cell. Its temperature as measured with a thermocouple determines the vapour pressure in the cell [10]. A continuous flow of gas (H$_2$, D$_2$, N$_2$, He) can circulate through the pentode. The pressure is given by a Pirani gauge calibrated against a Macleod gauge. As the observed region is not at the same temperature as the gauge, the pressure will be the same everywhere on condition that the mean free path of the molecules is smaller than the diameter of the tubes of the pumping system [11]. From total cross-section values [12] we deduce that it is actually the case if the pressure is greater than 10$^{-2}$ torr. The density of molecules is inversely proportional to each local temperature.

The light issued from the inter-electrodes space is focused on the slit of a Jobin-Yvon HRS 1 monochromator. We use an E.M.I. 9558 QB photomultiplier.

In order to measure the temperature in the observed region, we add a small quantity of N$_2$ to the gas in the cell. We observe the B $^2\Sigma_u^+ \rightleftharpoons \chi ^2\Sigma_g^+$, 0 $\rightarrow$ 0, R branch of N$_2^+$ whose lines can be easily separated. The maximum intensity occurs for the R$_{9,10}$ lines which corresponds to a temperature of (700 $\pm$ 50) K, as $B = 2.0$. The head of the R branch has lines which coincide with those of the tail of the P branch [13]. The calculated relative populations at 700 K show that the effect of this overlap is negligible for R greater than 5 and the calculated intensities agree with the experimental intensities in all the band. The temperature measured is the same in the various conditions of our experiments.

Figure 1 shows the variation of the intensity of the Cd resonance line with the accelerating voltage. When a substraction of 1.5 V due to contact potentials [12] is made, our low pressure curve 1a resembles the curve obtained by Zapesochnyi and Shevara [14]. The energy spread of the electrons is sufficiently small (about 1/3 eV) to provide a selective excitation of the 5 $^3P$ level of Cd: the maximum intensity occurs at 1 V above the threshold of 4 V, whereas the threshold value for the upper levels is 6 V. Figure 1b shows that the energy of the electrons is reduced when 1 torr of H$_2$ is added and that their energy spread is increased: electrons of about 4 eV may excite H$_2$ to v = 1 and lose 1/2 eV [15] and the electrons of more than 8 eV may excite the dissociative 2 $^3\Sigma_u^+$ level of H$_2$ [16]. When He is added up to 1 torr instead of H$_2$, no change of the curve 1a is obtained: He has no level to be excited in the considered energy range.

3. Description of the measurements. — 3.1 Lifetime. — In the phase-shift experiment, the anode current is 50 $\mu$A and the excitation frequency is 100 kHz. We used the known lifetimes of N$_2$ C$^3\Pi_u$, He 4 $^3S$ and He 3 $^3P$ to calibrate the phase measu-
The measured lifetime of $5^3\text{P}_1$ with a tail temperature $T = 200 \, ^\circ\text{C}$ is $\tau = 2.0 \times 10^{-6} \, \text{s}$. It is slightly shorter than the values given by other authors [17]. For $T = 300 \, ^\circ\text{C}$ its lifetime increases to $2.5 \times 10^{-6} \, \text{s}$ due to the radiation trapping. The variation of the lifetime with the $\text{H}_2$, $\text{D}_2$, and $\text{He}$ pressures is given in figure 2a, 2b. The maximum applied voltage is 7 eV to avoid cascades in $\text{Cd}$ and dissociation of $\text{H}_2$.

3.2 INTENSITY AFTER ELECTRONIC EXCITATION. — The excitation is done in the pentode. In order to reduce the error due to the spread in energy of the electrons by collisions with the gas, the observation region is chosen to be as close as possible to the first grid, and the accelerating voltage is adjusted for each pressure in order to obtain the maximum intensity of light. The current is kept constant, equal to 50 µA. The variation of the intensity $I$ of the $\text{Cd} \, 3 \, 260 \, \text{Å}$ line is recorded with the $\text{H}_2$, $\text{D}_2$, and $\text{He}$ pressures (Fig. 3). $I_0$ is the intensity for zero foreign gas pressure.

3.3 INTENSITY AFTER OPTICAL EXCITATION. — The excitation lamp is a quartz cell containing $\text{Cd}$ and a buffer gas, excited by a magnetron. In order to obtain the same conditions for the relaxation of the excited states, the observation region is the pentode inter-electrode space and the cathode is heated as for the electronic excitation experiments. The fluorescent light is detected in the same way as the intensity of the light emitted after electronic excitation (Fig. 4).

4. Results. — When He is added, we observe a small increase of the intensity and of the lifetime at a temperature which allows multiple scattering. The He gas may act as a buffer which reduces the collisions of $\text{Cd} \, 5 \, 3\text{P}_1$ with the walls.

— When $\text{N}_2$ is added, the intensity by optical excitation does not vary. The transfers $P_1 \rightarrow P_{0,2}$ do not occur as the vibrational energy is too high ($\omega_v = 2300 \, \text{cm}^{-1}$) and the rotational energy difference between consecutive levels is too small ($B_v = 2 \, \text{cm}^{-1}$). However, the intensity by electronic excitation increases with the $\text{N}_2$ pressure. For the reason as above the $P_2 \rightarrow P_1$ transfer is unlikely to occur. The observed effect may be due to excitation transfers from the $\text{N}_2$ metastable $A \, 3\Sigma^+_u$ state to the $\text{Cd} \, 6 \, 3\text{S}_1$ state, as they have the same excitation energy.

— When $\text{H}_2$ or $\text{D}_2$ is added, the intensity by optical excitation decreases and the corresponding quenching cross-section $\sigma$ may be obtained:

$$
\text{for } \text{H}_2: \sigma = (20 \pm 4) \, \text{Å}^2 \\
\text{for } \text{D}_2: \sigma = (9 \pm 2) \, \text{Å}^2.
$$

By electronic excitation the lifetime and the intensity increase for small pressure and decrease for higher pressures: the $3\text{P}_1$ level is both populated by transfers from the metastable $3\text{P}_{0,2}$ and depopulated by quenching according to the reaction (1). In figure 5 we have gathered the variation of $1/\tau$, $1/I_d$, $1/I_{\text{opt}}$ with the $\text{H}_2$
pressure, taken from figures 2a, 3 and 4. A very similar set of curves is obtained with D₂ but the slopes of the straight parts of the curves are approximately 3.1, 3.7 and 3.1 times smaller for 1/τ, 1/τₑ and 1/τₒpt respectively.

In order to obtain theoretical curves which fit the experimental ones, we describe the variation of the population \( \frac{dp_0}{dt} \) of the \(^3\)P₂, \(^3\)P₁ and \(^3\)P₀ levels by the coupled equations:

\[
\begin{align*}
\frac{dp_0}{dt} &= \left( \frac{dp_0}{dt} \right)^0 - \left[ \frac{1}{\tau_0} + kN(\sigma_0 + \sigma_{0-1} + \sigma_{0-2}) \right] p_0 + kN(\sigma_{1-0} p_1 + \sigma_{2-0} p_2) \\
\frac{dp_1}{dt} &= \left( \frac{dp_1}{dt} \right)^0 - \left[ \frac{1}{\tau_1} + kN(\sigma_1 + \sigma_{1-0} + \sigma_{1-2}) \right] p_1 + kN(\sigma_{0-1} p_0 + \sigma_{2-1} p_2) \\
\frac{dp_2}{dt} &= \left( \frac{dp_2}{dt} \right)^0 - \left[ \frac{1}{\tau_2} + kN(\sigma_2 + \sigma_{2-0} + \sigma_{2-1}) \right] p_2 + kN(\sigma_{0-2} p_0 + \sigma_{1-2} p_1)
\end{align*}
\]

where:

\( \left( \frac{dp_i}{dt} \right)^0 \) is proportional to the excitation cross-section of the level \( i \). As the Cd \(^5\)P states have a good L-S coupling [17], these cross-sections by electron impact are proportional to the multiplicity of each fine level. By optical excitation \( \left( \frac{dp_0}{dt} \right)^0 \) and \( \left( \frac{dp_2}{dt} \right)^0 \) are equal to zero.

\( \sigma_{ij} \) transfer cross-section from level \( i \) to level \( j \).

\( \sigma_i \) quenching cross-section for level \( i \).

\( N \) density of molecules.

\( \tau_i \) lifetime of level \( i \) at zero pressure for the foreign gas.

We adopt an exponential decay law although the destruction of the metastable atoms is due to the collisions with the walls [10], and

\[ k = 2 \left( \frac{\tau_0}{2\pi RT} \frac{1}{M_{H,D}} \frac{1}{M_{Cd}} \right)^{1/2} \]

With a continuous excitation, when stationary populations are attained, the resolution of the system (2) allows one to obtain \( p_1 \) against \( N \). With a modulated excitation \( (1 + \cos \omega t) \), one obtains

\[ p_1 = \tilde{p}_1(1 + \cos (\omega t + \varphi_1)) \]

from (2), i.e. \( \tau_1(N) = \frac{\Delta}{\omega} \).

The intensity \( I \) of the observed light is proportional to \( p_1/\tau_1 \), where \( \tau_1 \) is the radiative lifetime 2.0 μs, and \( p_1 \) the population of \(^3\)P₁ at a given pressure.

A first approach may be made considering the two metastables together and a system of only two equations. The populations and lifetime of \(^3\)P₁ may be expressed relatively simply:

\[ \begin{align*}
 p_1 \text{ calc.} &= \frac{0.5 c + b}{ac - bd} \\
 p_1 \text{ opt.} &= \frac{0.5 c}{ac - bd} \\
 \tau_1(N) &= \left( \frac{a+c}{0.5 c+b} \right) \left( \frac{5(c+b)}{ac-bd-\omega^2} + \frac{0.5(a+c)}{\omega^2} \right)
\end{align*} \]

The values obtained with these formulae (3) for \( 1/Iₑt \), \( 1/Iₒpt \) at high pressures are equal to \( \sigma_1 Nk/1.5 \) and \( \sigma_1 Nk/0.5 \) respectively if \( \sigma_0 \) and \( \sigma_2 \) are equal to zero. This is the greatest possible ratio between them. Figure 5 shows that this is nearly the case for the experiment, which would give \( \sigma_1 \approx 40 \, \text{Å}^2 \), \( \sigma_0 \approx \sigma_2 \approx 0 \).

The values of the transfer cross-sections and of the metastable lifetime must be adjusted to obtain the right shape of the curves, for instance at pressures.
lower than $10^{-1}$ torr. For the transfer cross-sections $P_1 > P_0$ (for which $\Delta E \approx kT$), we take the detailed balance [11] into account. In table I we give the values of the reaction and transfer cross-sections used with the system of three eq. (2) to obtain the curves of figure 6.

An obvious cause of uncertainty at low pressure is that the lifetime of the metastable state cannot be sufficiently similar in the experiments giving $T_1$, $T_2$, and $T_3$, because of necessary changes in the geometry of the observed region. What remains important at this stage of the work is that $\sigma_1$ must be much greater than $\sigma_0$ and $\sigma_2$ and its order of magnitude may be considered as correct:

$$\sigma_1(5\,^3P_1, H_2) = (33 \pm 6) \text{ Å}^2 \text{ at } 700 \text{ K}$$
$$\sigma_1(5\,^3P_1, D_2) = (16 \pm 3) \text{ Å}^2 \text{ at } 700 \text{ K}.$$

The energy separations between consecutive rotational states in $H_2$ or $D_2$ (Table III) are nearly equal to the energy separations in the $Cd\,^5\,^3P$ state (Table I) and transfers may occur. Such transfers have already been observed in the $4\,^3P_{0,1}$ ground state of Se ($\Delta E = 544 \text{ cm}^{-1}$) with $H_2$ [18], and their cross-sections have been measured (19 Å²). This value and our result have the same order of magnitude.

In reference [5] relative yields of CdH and CdD produced in reactions of Cd $^5\,^3P$ with $H_2$ or $D_2$ have been measured by resonance flash photolysis and found equal to $1 : 0.34$, in good agreement with our result assuming that the quenching of Cd provides only the synthesis of CdH or CdD.

In several cases $\Delta E$ is negative (Table II), and the reaction (1) can occur only if a contribution of the thermal energy is provided. At the temperature of the experiment, i.e. $T = 700 \text{ K}$ where $kT = 490 \text{ cm}^{-1}$, and at low current, only $v = 0$ is populated in the ground state of $H_2$. While the energies of translation and rotation can aid the reaction (1), the vibrational energies cannot do so. We plan to carry out similar experiments with Zn where the fine structure is much less than $kT$ and where $\Delta E(1) > kT$ for both $H_2$ and $D_2$, so as to establish:

### Table I

| $\sigma_{ii}$ and transfer $\sigma_{i \rightarrow j}$ cross-sections in Å² used to obtain the curves of figure 6 |
|---|---|---|---|
| $\lambda$ | 0 | 1 | 2 |
| 0 | 5.5 | 11 | 0 |
| 1 | 11 | 33 | 0 |
| 2 | 5.5 | 16.5 | 5.5 |

### Table II

| $E^*$: energy of the $5\,^3P_{0,1,2}$ states of Cd |
| $\Delta E(1) (H_2)$, $\Delta E(1) (D_2)$: exothermicity of the reaction (1) |
|---|---|---|
| $D^0_0(H_2) = 4.476 \text{ eV}$; $D^0_0(D_2) = 4.553 \text{ eV}$ |
| $D^0(CdH) = 0.376 \text{ eV}$; $D^0(CdD) = 0.704 \text{ eV}$ |

<table>
<thead>
<tr>
<th>$E^*$</th>
<th>$\Delta E(1) (H_2)$</th>
<th>$\Delta E(1) (D_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5,^3P_0$</td>
<td>30 118</td>
<td>30 660</td>
</tr>
<tr>
<td>30 $p$</td>
<td>31 830</td>
<td>31 660</td>
</tr>
<tr>
<td>31 830</td>
<td>30 118</td>
<td>30 660</td>
</tr>
</tbody>
</table>

### Table III

Energy difference $\Delta E$ between successive rotational states in $H_2$ and $D_2$ and relative populations at 700 K. The ortho and para species are separated.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\Delta E \text{ cm}^{-1}$</th>
<th>$p%$</th>
<th>$\Delta E \text{ cm}^{-1}$</th>
<th>$p%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>356</td>
<td>0.06</td>
<td>179</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>829</td>
<td>0.14</td>
<td>417</td>
<td>0.27</td>
</tr>
<tr>
<td>4</td>
<td>1 185</td>
<td>0.05</td>
<td>654</td>
<td>0.08</td>
</tr>
<tr>
<td>6</td>
<td>0.00</td>
<td>895</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.00</td>
<td>910</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

In reference [5] relative yields of CdH and CdD produced in reactions of Cd $^5\,^3P$ with $H_2$ or $D_2$ have been measured by resonance flash photolysis and found equal to $1 : 0.34$, in good agreement with our result assuming that the quenching of Cd provides only the synthesis of CdH or CdD.
if the variation of the reaction cross-section obtained when we add either H₂ or D₂ is due to the signs of ΔE (1) or to the mass difference;

- if the reaction cross-section difference between P₁ and P₀,₂ is due to the value of ΔE (1) or to a selection rule depending on the mechanism of the reaction.

5. Appearance of the hydride. — In the pentode, the electrons are accelerated by no more than 6 V to excite the 5 ³P state of Cd without excitation of upper levels and without dissociation of H₂. The hydride is then obtained in the ground state by the reaction (1) from 5 ³P. A subsequent electron impact excites the hydride. The lifetime of the free radical thus obtained is limited by the collisions with the electrodes as the probability for dissociation on metal seems to be high [20]. The concentration is however sufficiently high to permit one to observe the A ²Π₁/₂,₃/₂ → X ²Σ bands [21] easily. As the internuclear distances rₑ are very close in the A ²Π and the X ²Σ states [21], the most intense band must be the 0-0 band if the molecule is in its ground state v'' = 0. This is indeed the case in our spectra and it must be so, even if no relaxation takes place, as ΔE (1) is not sufficient to obtain the hydride in a vibrationally excited state. In figure 7 we represent the CdH and CdD, A ²Π₃/₂ → X ²Σ(0-0) bands obtained with 10⁻¹ torr of H₂ and D₂ respectively. In figure 8 we give the variation of the intensity of the 0-0 band head for CdH and CdD with the H₂ or D₂ pressures. A maximum is obtained at a pressure where the intensity of the Cd resonance line has been divided by three. Bender [3] had also observed a maximum quantity of hydride at about 5 x 10⁻¹ torr, by optical excitation of Cd. If the quantity of hydride does not tend asymptotically to a limit corresponding to the quenching of all the 5 ³P states, but decreases for high H₂ pressures, this effect may be due to a quenching of the hydride excited state or to the reversal of the synthesis reaction if H accumulates.

An attempt has been made to measure the lifetime of the A ²Π₁/₂,₃/₂ states of CdH and CdD by the phase-shift technique. In order to obtain adequate intensities of the hydride bands, the temperature of the tail is 260 °C where the Cd pressure is equal to the H₂ pressure, i.e. 10⁻² torr. The electronic current is a few mA. With such a current it has not been possible to work with a peak voltage lower than 12 V. The hydride may then be obtained from the 5 ³P state of Cd and also from higher Cd states which can provide the hydride directly in an excited state. For that reason our measurements give only an upper limit for the lifetimes, which is about 200 ns. The excitation frequency is 100 kHz. We use the C ³Π₀ level of N₂ as reference with τ = 45 ns [9].

The experiments described in this last section are made difficult by the fact that the same electron beam is used to provide the synthesis and to excite the hydride. These two functions may be separated by using a dye laser to excite the hydride. Such experiments are in progress and would allow us to develop experiments presented in this paper as a first approach.

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References