THE EMISSION SPECTRUM OF THE PD^+ MOLECULE

N. A. NARASIMHAM AND M. N. DIXIT

Spectroscopy Division, Atomic Energy Establishment, Trombay, 414 A, Cadell Road, Bombay-28

INTRODUCTION

THE spectrum of the PD^+ molecule was not known prior to the present investigation though the emission spectrum of PH^+ was reported nearly ten years ago.[1] PH^+ has an electronic structure similar to the hydrides of the carbon group and, as expected, has a band system (3567–4228 Å) corresponding to the $^2\Delta - {}^2\Pi$ transitions in the CH-type molecules.[2] The spectrum of the isotopic molecule, PD^+ has now been obtained in a microwave discharge through phosphorus vapour, deuterium and helium gas. The new emission bands lie at 3683 Å, 3826 Å and 4086 Å. An analysis of their vibrational and rotational structure shows that they are the 1–0, 0–0 and 0–1 bands of PD^+ involving the $^2\Delta - {}^2\Pi$ transition. Results of these studies are presented in this article.

EXPERIMENTAL

PH^+ was obtained earlier[1] from a hollow cathode discharge through helium containing a little of phosphorus vapour and hydrogen. It was found necessary to maintain a constant flow of helium at 2–3 mm. pressure through the discharge tube. The same method of excitation could not be tried to excite the spectrum of the corresponding phosphorus deuteride because of the limited quantity of deuterium gas available. For this purpose, therefore, sealed-in quartz discharge tubes, containing traces of phosphorus vapour, deuterium and about 3 mm. of helium gas, were prepared in the manner described by Tomkins and Fred.[3] These sealed-in tubes, on excitation with a microwave (2450 mc./s.) discharge, gave new emission bands attributable to PD^+.

ANALYSIS OF NEW BANDS

(a) Vibrational Structure The bands obtained in the present studies are similar to the emission bands of PH^+ which are shown in juxtaposition in Fig. 1 (*a*). Each band contains two sub-bands with $^sR_{21}$, R_1 and R_2, Q_2 heads. These band heads could be arranged into a Deslandres vibrational scheme as shown in Table I. R_1 and Q_2 heads of the 3826 Å band show shifts of 136 cm.$^{-1}$ from corresponding heads of the 0–0 band of PH^+ at 3854 Å. The isotope shift calculated for the 0–0 band of PD^+ agrees very well with this value. The other two bands at 3683 Å and 4086 Å have shifts expected of the 1–0 and 0–1 bands of PD^+. The isotope shifts thus provide an unambiguous vibrational assignment of the three bands as shown in the Deslandres Table I and further prove that the emitter of the bands is the PD^+ molecule.

TABLE I

Deslandres vibrational scheme of the band heads (in cm.$^{-1}$) of PD^+

v' \ v''		0	$\Delta G''(\frac{1}{2})$	1
0	$^sR_{21}$	26125	1663	24462
	R_1	26077	1667	24410
	R_2	25830	1664	24166
	Q_2	25792	1668	24124
$\Delta G'(\frac{1}{2})$	..	1015	..	..
	..	1026	..	..
	..	1017	..	..
	..	1013	..	..
1	$^sR_{21}$	27140	..	..
	R_1	27103	..	..
	R_2	26847	..	..
	Q_2	26805	..	..

(*b*) *Rotational Structure.*—The 3826 Å band which is strongest of the three bands has been photographed on a 6·6 m concave grating spectrograph at a dispersion of 0·55 Å/mm. and is shown in (*b*) and (*c*) of Fig. 1. The two bands involving $^2\Delta_{3/2} - {}^2\Pi_{3/2}$ and $^2\Delta_{3/2} - {}^2\Pi_{1/2}$ transitions are shown separately. Each of the sub-bands contains 12 branches which form close pairs of Λ-doublets. As expected, the Λ-doubling in the $^2\Pi_{3/2}$ state is found to be much smaller at low J values than in the $^2\Pi_{1/2}$ state as a result of which Λ-doubling in the branches of $^2\Delta_{3/2} - {}^2\Pi_{3/2}$ is perceptible only at high J values. Detailed analysis of the rotational structure of the two sub-bands has shown that the $^2\Delta$ state is regular with small spin-splitting (case *b*) while the $^2\Pi$ state is regular with large spin-splitting (case *a*). The rotational constants and the $\Delta G(\frac{1}{2})$ values of the $^2\Delta$ and $^2\Pi$ states are given in Table II.

Predissociation of rotational levels with $N \geqslant 13$ of $v' = 0$ of the $^2\Delta$ state of PH^+ was earlier observed.[1] In the case of PD^+, this would

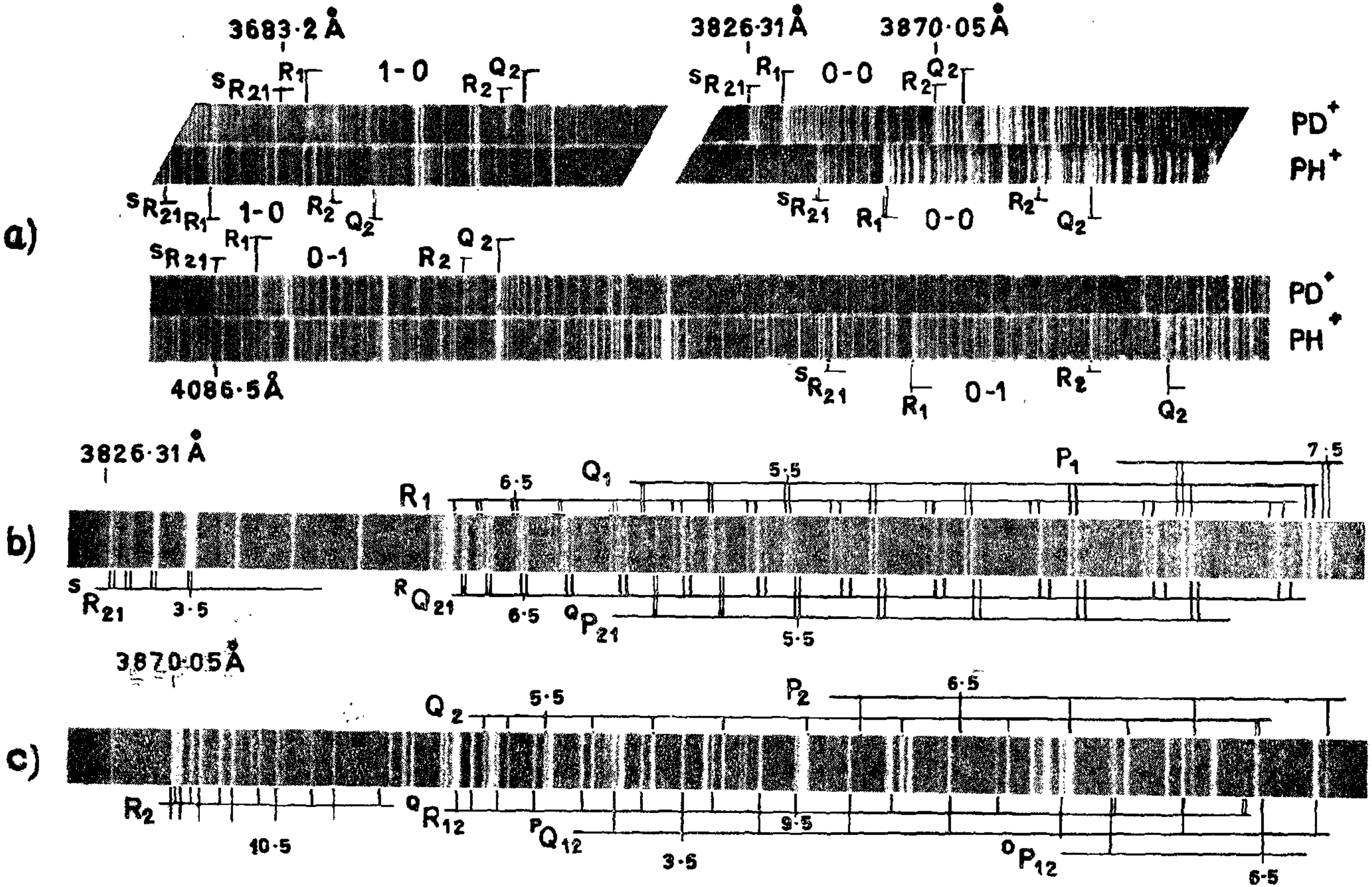

FIG. 1. Emission bands of PH^+ and PD^+

TABLE II
Vibrational and rotational constants (in cm.$^{-1}$) of $^2\Delta$ and $^2\Pi$ states of PD$^+$

State	$\Delta G(\frac{1}{2})$	B_0	r_0(Å)	D_0	A_0	γ	p
$^2\Delta$	1017	3·635 (3·635)	$1{\cdot}565_9$	0·0001713 (0·0001673)	1·35	0·09	..
$^2\Pi$	1666	$4{\cdot}350_5$ ($4{\cdot}345_2$)	$1{\cdot}431_3$	0·000116 (0·000111)	295·83	..	0·08

Values in parentheses are calculated ones from B_0 and D_0 of PH^+.

correspond to N $\geqslant$ 17 levels of $v' = 4$. The rotational lines involving N $\geqslant$ 17 levels of $v' = 0$ are either extremely weak or not observed in the 0–0 band of PD^+.

1. Narasimham, N. A., *Can J. Phys.*, 1957, **35**, 901.
2. Mulliken, R. S, *Rev. Modern Phys.*, 1932, **4**, 1.
Tomkins, F. S. and Fred, M., *J. Opt. Soc. Am.*, 1957, **47**, 1087.

FOETAL RESORPTION IN BARBITAL SODIUM TREATED PREGNANT RATS

A. V. CHAMPAKAMALINI AND M. APPASWAMY RAO
Department of Zoology, Manasa Gangotri, Mysore-6, India

INTRODUCTION

BARBITURATES are extensively used as sedative, hypnotic, anæsthetic and anticonvulsant drugs. They are known to reduce the adrenocortical secretions and inhibit the pituitary hormone production.[1,2] It is well established that normal pregnancy necessitates a balanced proportion of ovarian and adrenocortical hormones, which are under the control of anterior pituitary.[3-5] As there is paucity of information regarding the effect of barbiturates on pregnancy,[6] the present investigation was undertaken to study the effect of Barbital Sodium on pregnancy in albino rats.

EXPERIMENTAL

Adult female rats (180–220 gm.) of Wistar strain were mated with fertile males on the day of prœstrus. Rats showing sperms in their vaginal smear on the following morning were selected for the experiment and that day was designated as day 0 of pregnancy. The rats were kept in individual cages at a room temperature of 27 ± 1° C. and maintained on CFTRI chow with water *ad lib*. On day 8 of pregnancy they were laparotomized under ether anæsthesia in sterile condition to note the number of implantation sites. 20 mg. of Barbital Sodium (M & B) in 1 ml. of distilled water per 100 gm. body weight was administered subcutaneously from day 8 to 19 and autopsied on day 20 of pregnancy. The controls received 1 ml. of distilled water per 100 gm. body weight per day. Body weight and vaginal smear were recorded daily. The fœtuses, uteri, ovaries, adrenals and thymus were weighed. The tissues were fixed in Bouin's fluid, sectioned at 10 μ thick and stained with Harris' hæmatoxylin-eosin.

RESULTS AND DISCUSSION

The results indicate that out of 12 pregnant rats treated with Barbital Sodium, 8 show complete resorption of the embryos at autopsy and their uteri resemble those of the non-pregnant rats, despite they possess implantations on the day of laparotomy (Table I, Figs. 1 and 3). In these rats continuous vaginal bleeding has been observed from day 9 to 11 of pregnancy followed by estrus and prolonged diestrus. Out of the remaining 4 treated rats only 1 shows partial resorption (Fig. 4) and the rest 3 possess live fœtuses whose weights are considerably less than those of the controls (Fig. 5). All the controls have normal pregnancy without any significant fœtal resorption (Table I, Fig. 2), wherein the per cent fœtal survival is 92·7, while in the treated it is only 36. Though there is no significant change in the ovarian weight between the controls and the drug-treated rats, histological studies of the ovaries reveal that in the treated rats the corpora lutea are small with many developing follicles, while in the controls the corpora lutea are large.

Barbiturates are known to inhibit the release of pituitary hormones and reduce the adrenocortical secretions,[1,2] and probably their action is mediated through the hypothalamus.[7] It is well known that hypophysectomy, ovariectomy or adrenalectomy during early phase of pregnancy causes fœtal resorption in rats.[4-8] In the present experiment the fœtal resorption in Barbital Sodium-treated rats may be