ROTATIONAL ANALYSIS OF THE $^1\Pi - X\,^1\Sigma$ SYSTEM OF AsN

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Received August 29, 1969

Abstract

The $^1\Pi$-X $^1\Sigma$ bands of AsN were excited by means of radio-frequency discharge through nitrogen and helium and traces of arsenic. The 0–0 band (2784·25 Å) and the 0–1 band (2868·74 Å) were photographed in the third order of a 6·6 meter concave grating spectrograph at a dispersion of 0·38 Å/mm. and analysed for their rotational structure. Perturbations observed in the $^1\Pi$ state were studied in detail.

Introduction

Spinks (1934) obtained in emission, nearly thirty red degraded bands, from a transformer discharge through metallic arsenic and a few mm. of nitrogen. These bands were attributed to AsN. Of these, only ten bands, which were relatively free from overlap of the second positive bands of N_2, could be fitted into the following expression:

$$\nu_{\text{head}} = 35905\cdot 9 + (863\cdot 02\, v' - 8\cdot 2\, v'^2) - (1062\cdot 6\, v'' - 5\cdot 36\, v''^2).$$

An arrangement of the bands in a Deslandres vibrational scheme showed that some of them deviated considerably from expected positions. The 2–0 band, for instance, occurred at 33·12 cm.$^{-1}$ farther from the one calculated from the above expression. Perturbation was attributed to be the cause of such a displacement.

Spinks also attempted to analyse the rotational structure of the 0–0, 0–1, 1–0, 1–2 and 2–0 bands but was not successful. However, drawing an analogy with the PN bands, he suggested the electronic structure to be of $^1\Pi - {}^1\Sigma$ type.

It was thought necessary to make a detailed analysis of the rotational structure of the bands and they were therefore photographed at a dispersion and resolution higher than that obtained earlier. While our studies of the

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AsN bands were in progress, the publication of Jean D'Incan and B. Femelat (1967) appeared, where they reported only a partial analysis of the 0–0 and 0–1 bands. However, in our investigations, it has been possible to make a satisfactory analysis of the rotational structure of 0–0 and 0–1 bands, including the perturbations. These are dealt with in the present paper.

Very recently, a red degraded band at 3432 Å was recorded by the same authors, Jean D'Incan and B. Femelat (1968), who attributed it to a $^1\Sigma$–X $^1\Sigma$ transition.

EXPERIMENTAL

The emission spectrum of AsN was excited by a radio-frequency (2–6 Mc/s) discharge through nitrogen and helium at 2 mm. pressure and traces of arsenic. The discharge tube was of quartz and was 40 cm. long and 1 cm. in diameter. A quartz window was fused on one end while the other end was closed. Metallic arsenic was vapourised into the discharge tube. During the vapourisation, the discharge tube was kept at 600° C. The 0–0 band at 2784·25 Å and the 0–1 band at 2868·74 Å were photographed in the third order of the 6·6 meter concave grating spectrograph at a dispersion of 0·38 Å/mm. and shown in Fig. 1. Atomic lines of thorium excited by a microwave (2450 Mc/s) discharge in a sealed tube containing thorium iodide were used as standards (Zalubas, 1960).

ROTATIONAL ANALYSIS AND DISCUSSION

Rotational Structure of the 0–0 *and* 0–1 *Bands*

The rotational structure of the two bands shows three branches P, Q and R. The Q branch is the most intense and readily recognisable. The P branch is much weaker. The rotational lines do not show any splitting even at high J values. All these observations indicate the transition to be of $^1\Pi$–$^1\Sigma$ type. Considerable difficulty however has been experienced in picking up the branches in the normal way because of severe perturbations in the branches of both the bands.

As mentioned above, the intense lines in both the 0–0 and 0–1 bands are straight away taken to be Q branch lines. The successive differences of the Q branch lines were then plotted against a running number of J. From the following relation,

$$Q(J+1) - Q(J) = 2(B_v' - B_v'') + 2(B_v' - B_v'')J,$$

it is known that the gradient is equal to the intercept, $2(B_v' - B_v'')$. This served as a great help in a preliminary assignment of the J values for the

TABLE I

Vacuum wave numbers and line assignments of the 0–0 (2784·25 Å) and 0–1 (2868·74 Å) bands of the $^1\Pi$–$X^1\Sigma$ system of AsN

J	0–0 Band P	0–0 Band Q	0–0 Band R	0–1 Band P	0–1 Band Q	0–1 Band R
7	..	..	..	..	..	34847·71
8	..	..	..	..	..	48·01
9	35885·24	35895·89	35905·72*	34827·73	34838·36	48·24*
10	82·98	93·75	05·72*	25·56	36·49	48·24*
11	80·56	92·68	05·72*	23·47	35·18	48·24*
12	78·07	91·03	05·48	21·16	33·87	48·24*
13	75·99	89·58	05·26	18·86	32·49	48·01
14	73·32	88·01	04·46	16·47	31·17	47·71
15	70·68	86·26	03·89	13·91	29·44	47·32
16	67·90	84·48	03·03	11·24	27·73	46·23
17	65·08	82·45	02·16	08·42	25·90	45·44
18	61·96	80·32	00·97	05·50	23·89	44·44
19	58·78	77·89	00·69	02·33	21·60	44·44
20	54·70	75·03	898·77	798·43	18·86	42·79
21	51·85	73·14	97·19	96·03	17·43	41·43
22	47·85	69·91	95·49	92·12	14·44	40·02
23	44·05	66·96	93·78	88·51	11·68	38·36
24	39·73	63·99	91·78	84·88	09·14	37·02
25	36·07	60·13	91·78	81·20	05·20	36·49
26	32·13	58·98	88·26	77·15	04·10	33·89
27	28·85	55·75	87·78	74·28	01·24	33·35
28	35823·41	35852·65	35885·39	34769·27	34798·43	34831·17
29	20·03	49·51	82·98	66·11	95·51	28·98
30	14·98	46·31	80·56	61·09	92·57	26·76
31	10·31	43·11	78·07	56·69	89·54	24·62
32	05·78	39·73	75·69	52·34	86·45	22·44
33	01·13	36·30	73·32	48·11	83·26	20·22
34	796·64	32·91	70·68	43·78	79·99	17·89
35	91·96	29·21	67·90	39·42	76·66	15·52
36	87·11	25·46	65·08	34·97	73·24	13·02
37	82·33	21·64	62·27	30·43	69·72	10·40
38	77·41	17·79	..	25·81	66·11	07·74
39	72·26	13·49	..	21·06	62·39	04·83
40	67·38	09·64	..	16·27	58·61	01·86
41	61·97	05·37	..	11·26	54·66	..
42	56·50	01·13	..	06·06	50·72	..
43	50·69	796·64	..	00·47	46·36	..
44	..	91·45	..	..	41·81	..
45	..	86·08	..	..	..	..

* Band head.

Q branch lines. The P and R branch lines were later assigned (as shown in Table I) from a comparison of the usual combination relations, R (J) — Q (J), Q (J + 1) — P (J + 1), etc. Equivalent sets of corresponding combination relations obtained in the 0–0 and 0–1 bands are shown in Table II. The almost close agreement of the combination differences confirms that the bands have a common initial vibrational level.

TABLE II

Combination differences, in cm.$^{-1}$, of the $v' = 0$ level of the $^1\Pi$ state of AsN

J	$\Delta_1F(J)$ R (J)—Q (J)		Q (J+1) —P (J+1)		Δ_2F (J) R (J)—P (J)	
	0–0 band	0–1 band	0–0 band	0–1 band	0–0 band	0–1 band
8	..	..	10·65	10·63	..	..
9	9·83	9·88	10·77	10·93	20·48	20·51
10	12·74	11·75	12·12	11·71	22·74	22·68
11	13·04	13·06	12·96	12·71	25·16	24·77
12	14·45	14·37	13·59	13·63	27·41	27·08
13	15·68	15·52	14·69	14·70	29·27	29·15
14	16·45	16·54	15·58	15·53	31·14	31·24
15	17·63	17·88	16·58	16·49	33·21	33·41
16	18·55	18·50	17·37	17·48	35·13	34·99
17	19·71	19·54	18·36	18·39	37·08	37·02
18	20·65	20·55	19·11	19·27	39·01	38·94
19	22·80	22·84	20·33	20·43	41·91	42·11
20	23·74	23·93	21·29	21·40	44·07	44·36
21	24·05	24·00	22·06	22·32	45·34	45·40
22	25·58	25·58	22·91	23·17	47·64	47·90
23	26·82	26·68	24·26	24·26	49·73	49·85
24	27·79	27·88	24·06	24·00	52·05	52·14
25	31·65	31·29	26·85	26·95	55·71	55·29
26	29·48	29·77	26·90	26·96	56·13	56·72
27	32·03	32·11	29·24	29·16	58·93	59·07
28	32·74	32·74	29·48	29·40	61·98	61·90
29	33·47	33·47	31·33	31·48	62·95	62·87
30	34·25	34·19	32·80	32·85	65·58	65·67
31	34·96	35·08	33·95	34·11	67·66	67·93
32	35·96	35·99	35·17	35·15	69·91	70·10
33	37·02	36·96	36·27	36·24	72·19	72·11
34	37·77	37·90	37·25	37·21	74·04	74·11
35	38·69	38·86	38·35	38·27	75·94	76·10
36	39·62	39·78	39·31	39·29	77·97	78·05
37	40·63	40·68	40·38	40·30	79·94	79·97
38	..	41·63	41·23	41·33	..	81·93
39	..	42·44	42·26	42·34	..	83·77
40	..	43·25	43·40	43·40	..	85·59
41	..	..	44·63	44·66	..	..
42	..	..	45·95	45·89	..	..

Perturbations

A detailed examination of the rotational structure of the 0–0 and 0–1 bands revealed that the P, Q and R branch lines with $J \leqslant 30$ were shifted considerably from their expected positions. A plot of the Q branch lines against $J(J+1)$ shown in Fig. 2, for example, clearly indicated a deviation

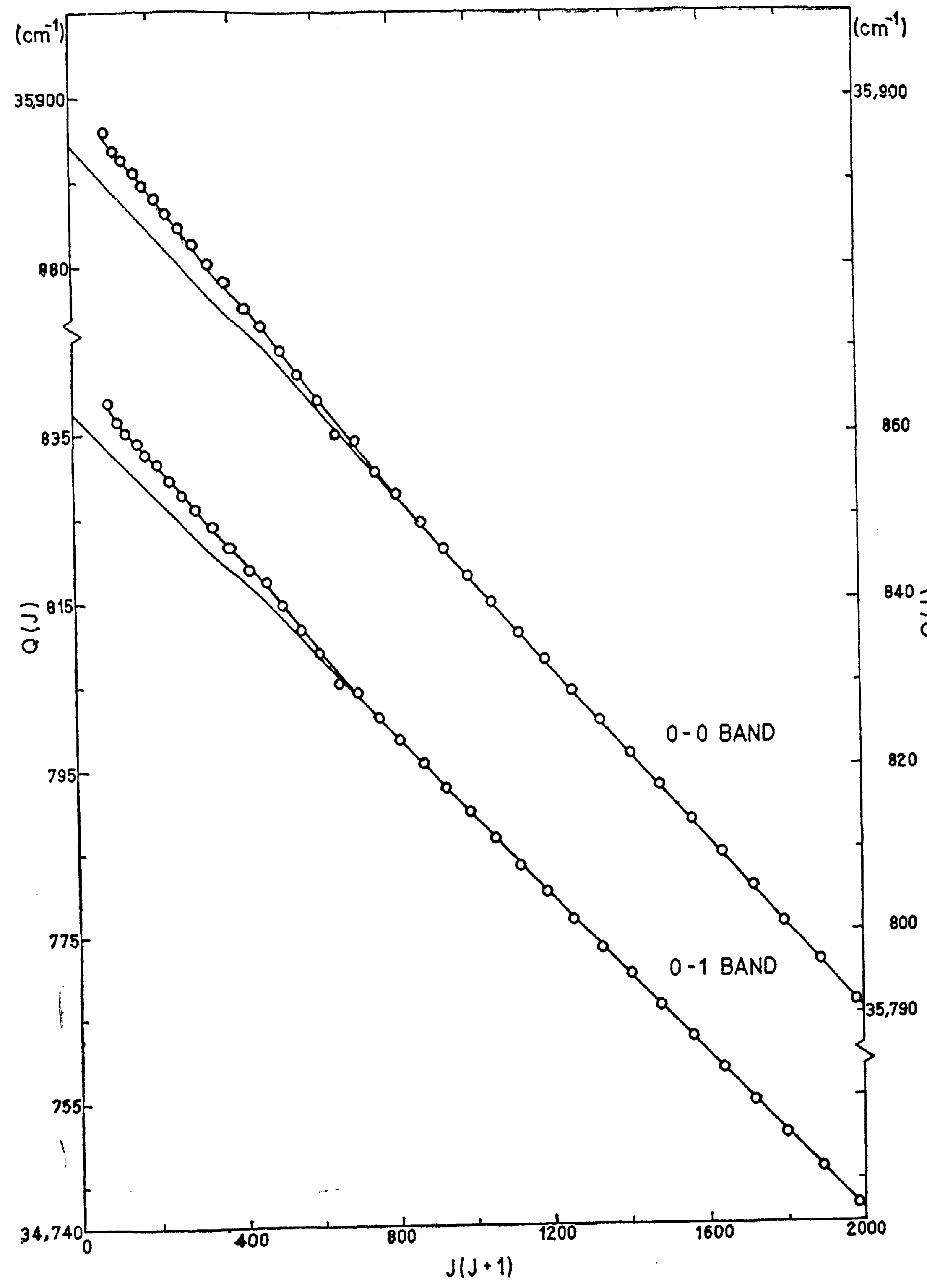

FIG. 2. A plot of $Q(J) = \nu_0 + (B_v' - B_v'')\,J(J+1)$ against $J(J+1)$.

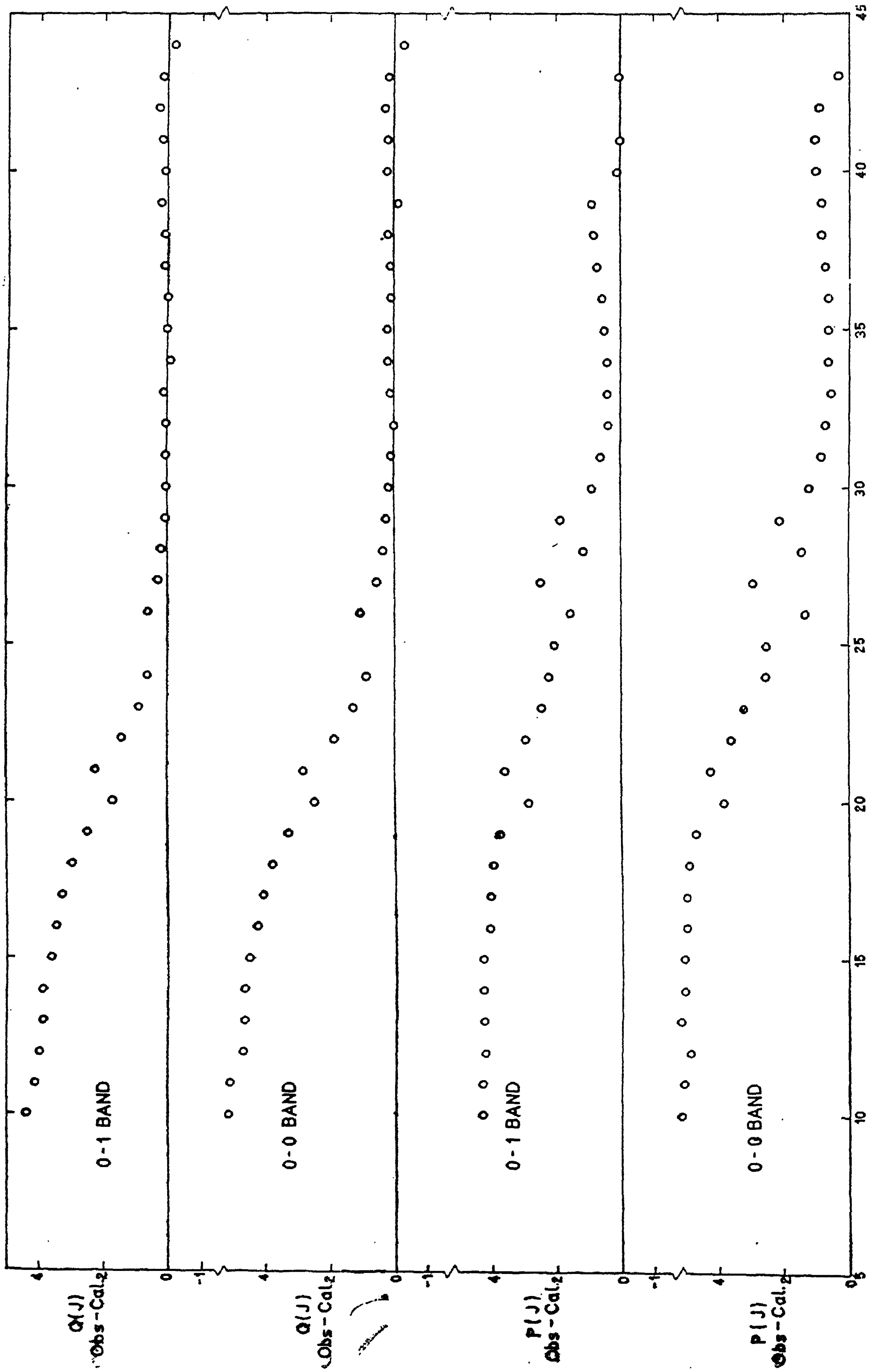

FIG. 3. (Obs.-Cal.) Values of P and Q branch lines of 0–0 and 0–1 bands of AsN.

of all rotational lines with $J \leqslant 30$. These deviations increased towards the head of each band. Similar behaviour was noticed in the P and R branches. This means, that all the three branches of the $^1\Pi$–$^1\Sigma$ transition suffer perturbations.

Though the combination relations,

$$\Delta_1 F(J) = R(J) - Q(J) \simeq Q(J+1) - P(J+1)$$

were expected to be approximately equal in the case of negligible Λ-doubling of the initial $^1\Pi$ state of molecule like AsN, the values of $\Delta_1F(J)$ differed very significantly for J values upto and including $J = 30$. This means that only these rotational lines that involved transitions upto and including $J = 30$ were perturbed. However, for values of J beyond 30, these relations showed only a small combination defect thereby indicating no perturbation of the lines with J greater than 30. These observations indicated that perturbation of the rotational levels with $J \leqslant 30$ of the initial $^1\Pi$ state could bring about such variations in the two sets of $\Delta_1F(J)$ values. These are manifested as large differences between the observed and calculated values for the P, Q and R branches. The deviations observed in all the three branches (in both the 0–0 and 0–1 bands) were very much larger than the combination defects observed for rotational lines with $J > 30$. Among the three branches, the P and R lines showed larger deviations than the Q lines. In Fig. 3 are shown the differences between the observed and calculated values of P and Q branches.

This situation could perhaps be better visualised in a qualitative way in the energy level diagram of Fig. 4 where the perturbed levels of $^1\Pi$ state were shown alongside the levels corresponding to the perturbing state. Since both the components were affected, such a perturbing state would be a degenerate one.

The rotational lines P (20) and R (18), P (21) and R (19), P (27) and R (25), P (29) and R (27) show deviations in the same direction by about the same magnitude (Fig. 1) as one would expect since the P and R lines arise from the same Λ-component (*see* for example Fig. 4). The Q branch lines, particularly those at Q (20), Q (21) and Q (25), also show perturbations. It is not quite clear how these perturbations are related to the above P and R lines, though Q (20) has some bearing to P (21) and R (19) lines.

Though perturbations were observed for a number of rotational levels of both the 0–0 and 0–1 bands, only a few extra lines were observed which could not be identified with certainty. It was not therefore possible to determine the B value of the perturbing state.

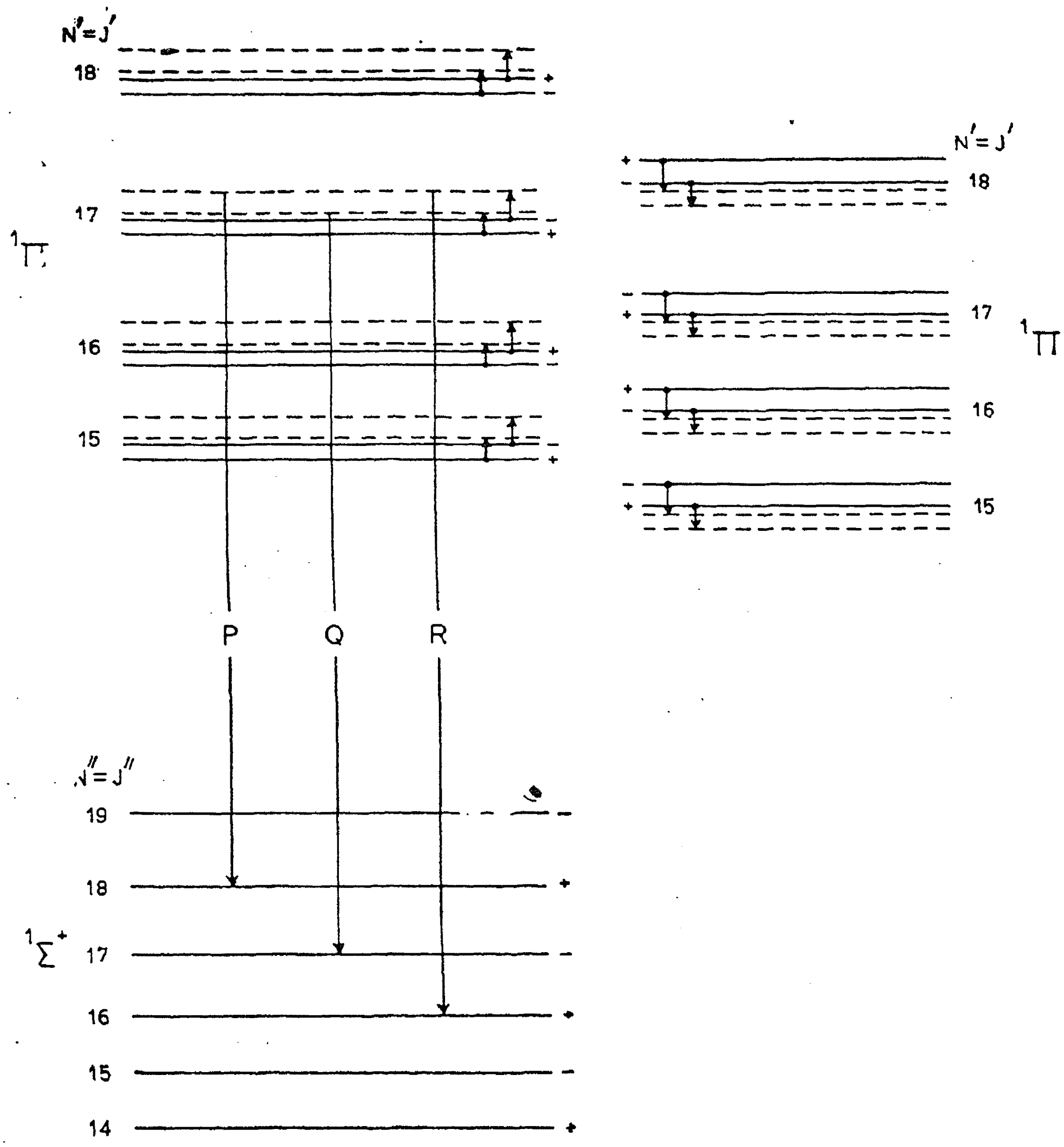

FIG. 4. Perturbations in $^1\Pi$ state with $^1\Pi$ state of AsN.

Owing to severe perturbations in the 0–0 and 0–1 bands, it was not possible to determine their band origins using all the observed rotational lines in the P, Q and R branches. They were therefore determined from the unperturbed lines of the Q branches. The relation

$$Q(J) = \nu_0 + (B_v' - B_v'') J (J + 1)$$

was used for the evaluation of the band origins.

The rotational constants of both the states were also determined using mostly the unperturbed lines and the corresponding $\Delta_1 F(J)$ values. The final set of vibrational and rotational constants are given in Table III.

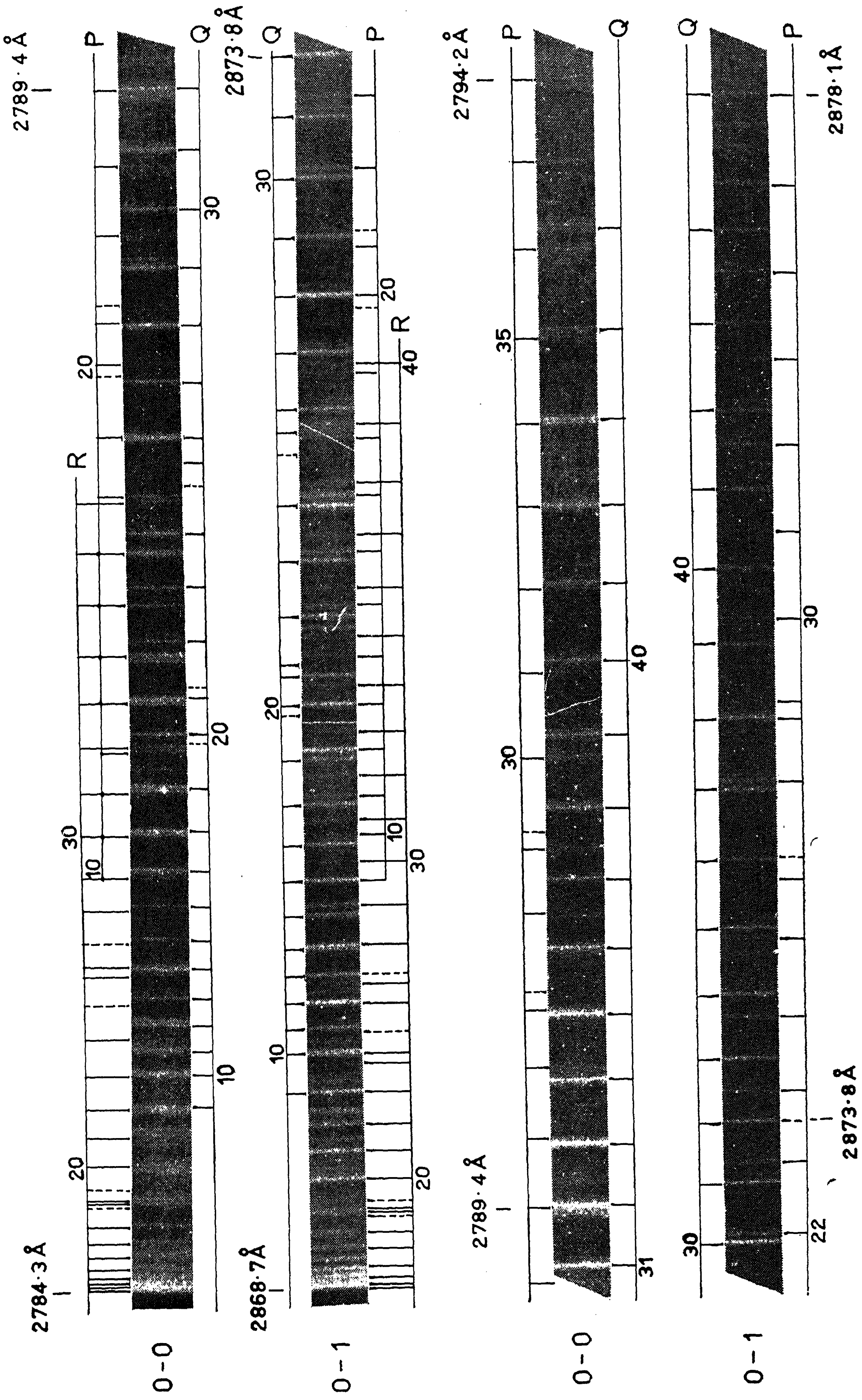

FIG. 1. Rotational structure of 0–0 and 0–1 bands of $^1\Pi$–$^1\Sigma$ system of AsN.

TABLE III

Vibrational and rotational constants of $X\,^1\Sigma$ and $^1\Pi$ states of AsN, in cm.$^{-1}$

(*a*) $X\,^1\Sigma$ state:

B_0''	0·5880
D_0''	$0{\cdot}31\times10^{-8}$
B_1''	0·5873
D_1''	$0{\cdot}31\times10^{-8}$
B_e''	0·5884
α''	$0{\cdot}7\times10^{-3}$
r_e''	1·558 Å
$\Delta G''(\frac{1}{2})$	1056·8

(*b*) $^1\Pi$ state

B_0'	0·5395
D_0'	$0{\cdot}3\times10^{-8}$
r_0'	1·627 Å

(*c*) Band origins

0–0 band	35894·2 cm.$^{-1}$
0–1 band	34837·4 cm.$^{-1}$

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