

Rotational analysis of $A^1\Pi-X^1\Sigma^+$ bands of As^{14}N and As^{15}N : perturbation studies in the $A^1\Pi$ state

P SARASWATHY and G KRISHNAMURTY

Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

MS received 14 December 1987; revised 29 August 1988

Abstract. The ultraviolet bands of $A^1\Pi-X^1\Sigma^+$ system of As^{14}N and its isotopic species As^{15}N were excited in a quartz tube containing specpure nitrogen and traces of AsCl_3 vapour, using a microwave discharge (2450 MHz). Bands of As^{15}N were obtained using $^{15}\text{N}_2$ enriched to 95.5%. Rotational structure of several bands of As^{14}N and As^{15}N photographed under high dispersion (0.14 Å/mm) was reanalysed. Detailed studies of the observed perturbations in the levels of $v' = 0$ to 4 led to the identification of two $^3\Sigma^-$ and a $C^1\Sigma^-$ states. Molecular parameters T_e , ω_e , $\omega_e x_e$, B_e and α_e were determined for all the electronic states studied. Vibrational assignments of the perturbing levels were made using the isotope shift studies.

Keywords. Perturbations; configuration; molecular constants; rotational analysis; vibrational assignments.

PACS No. 33-20

1. Introduction

The ultraviolet band system of AsN molecule lying in the region 2400–3400 Å was reported nearly five decades ago (Spinks 1934). Thirty red degraded bands were obtained in emission in a transformer discharge through metallic arsenic and a few torr of nitrogen. Vibrational analysis of ten bands of this system lying in the 2600–3100 Å region which were relatively free from the overlap of the second positive bands of N_2 enabled Spinks (1934) to represent the band heads by the following expression:

$$\begin{aligned} v_{\text{head}} = & 35905.9 + (863.02v' - 8.24v'^2) \\ & - (1062.6v'' - 5.36v''^2). \end{aligned} \quad (1)$$

From the vibrational analysis, it was concluded that the level $v' = 2$ of the upper state deviated from the expected position by 33.12 cm^{-1} which was attributed to perturbation. Spinks (1934) also attempted to carry out the rotational analysis of 0–0, 0–1, 1–0, 1–2 and 2–0 bands but was not successful due to strong perturbations. However, the band system was assigned to the electronic transition, $^1\Pi-^1\Sigma^+$ in analogy with PN molecule wherein a similar band system was observed by Curry *et al* (1933) in the ultraviolet region.

A partial rotational analysis of two bands 0–0 and 0–1 was attempted by D'Incan and Femeiat (1967) who excited the bands of AsN in a high frequency (27 MHz) discharge containing a mixture of nitrogen and arsenic vapour. The rotational structure analysis of the above mentioned bands was incomplete due to severe

perturbations. During the course of these investigations D'Incan and Femelat (1968) observed one red shaded band at 3432 Å which was attributed to an electronic transition $^1\Sigma^- - ^1\Sigma$. The lower state of this transition was shown to be the ground state of AsN.

Dixit *et al* (1970) carried out the rotational analysis of the 0–0 and 0–1 bands excited in radio-frequency (2–6 MHz) discharge through nitrogen, helium (2 torr) and traces of arsenic metal vapour. Although the rotational structure was photographed at a fairly good dispersion (0.38 Å/mm), the analysis was incomplete due to lack of sufficient intensity. Detailed rotational analysis of six ultraviolet bands involving $v' = 0$ and 1 of the upper state was first carried out by Jones (1970) who established that the bands arise from the transition $^1\Pi - X^1\Sigma^+$. These studies were further extended by Femelat and Jones (1974) to $v' = 2$ and 3 levels of $^1\Pi$ state and the *P*, *Q* and *R* branches successfully sorted out. Their analysis showed that all the levels starting from $v' = 0$ to 3 were severely perturbed although the nature of the perturbing states could not be established. The isotopic shifts of these bands were studied by Krishnamurty and Thomas (1976) by exciting the bands of As ^{14}N and the isotopic species As ^{15}N in a microwave discharge using a mixture of AsCl $_3$ and pure $^{14}\text{N}_2$ for As ^{14}N and $^{15}\text{N}_2$ enriched to 95.5% for As ^{15}N molecules. These studies confirmed the vibrational assignments of the bands of $^1\Pi - X^1\Sigma^+$ system.

Although the ultraviolet bands of AsN are known for a long time, deperturbation studies to explain some of the numerous perturbations were attempted only recently by Perdigon and Femelat (1982). Their studies led to the identification of an electronic state $a^3\Pi^*$ causing perturbations in the $A^1\Pi$ state. From the high resolution spectral studies of $A^1\Pi - X^1\Sigma^+$ bands of As ^{14}N and As ^{15}N , it was shown that the band at 3432 Å which was earlier assigned to the transition $^1\Sigma - X^1\Sigma^+$ (D'Incan and Femelat 1968) was the 0–0 band of the $b^3\Pi_0 - X^1\Sigma^+$ system. The effective spin-orbit constant, *A*, for $b^3\Pi$ state was reported as 420 cm $^{-1}$ from their studies. Recently Ohanessian *et al* (1985) reported the theoretical study of the AsN spectrum, based on large configuration interaction (CI) and non-empirical pseudopotentials. These studies confirmed that $^1\Sigma^-$, $^3\Sigma^-$ and $^3\Pi$ are the perturbers of $A^1\Pi$ state.

The motivation in undertaking these studies is to reinvestigate the rotational structure of the bands to understand the observed perturbations in the $A^1\Pi$ state. While the present studies were in progress, Perdigon and Femelat (1982) published their results on the $b^3\Pi$ and $A^1\Pi$ states on AsN arising from the ($\sigma\pi$) configuration.

2. Experimental

The electronic emission bands of AsN molecule were excited in microwave (2450 MHz) discharge in a quartz tube using a mixture of AsCl $_3$ and pure nitrogen. The bands of isotopic species As ^{15}N were obtained using specpure nitrogen isotope $^{15}\text{N}_2$, enriched to 95.5%. Preliminary studies were carried out at a dispersion of 2.3 Å/mm using a 3.4 metre Ebert Jarrell-Ash grating spectrograph with a grating of 1200 grooves/mm and

* In analogy with the nomenclature used for ten valence electron molecules, $a^3\Pi$, henceforth is referred to as $b^3\Pi$ throughout this paper.

blazed at 3300 Å. Rotational structure of the bands of As¹⁴N as well as As¹⁵N was photographed on a 10.6 metre Ebert grating spectrograph using 1200 grooves/mm grating blazed at one micron in the fourth order at a dispersion 0.14 Å/mm in the wavelength region of 2500–3100 Å. The spectra were recorded on Kodak 103 a-0 emulsion. The first and second orders were eliminated by the emulsion and the third order was cut off using a nickel sulphate filter. Iron-neon hollow cathode lines were used as wavelength standards. The plates were measured using a Jarrell-Ash photoelectric comparator. The accuracy of the sharp rotational lines was $\pm 0.08 \text{ cm}^{-1}$.

3. Results and discussion

3.1 Vibrational structure

The ultraviolet bands of As¹⁴N and As¹⁵N obtained in emission are shown in figure 1. The band system consists of well-defined sequences and is relatively free from the overlap of the impurity bands such as AsO, As₂ etc with the exception of $\Delta v = +3$ and $+2$ sequences of N₂ second positive bands. It may be mentioned here that the presence of the isotopic bands due to ¹⁵N₂ and the absence of bands due to ¹⁴N¹⁵N species clearly show that the nitrogen isotope retained its 95.5% abundance without getting diluted.

Isotope shift studies by Krishnamurty and Thomas (1976) showed that the observed band heads could be represented by the expression:

$$\begin{aligned} \nu_{v'v''} = & 36005.30 + [870.53(v' + \frac{1}{2}) - 8.06(v' + \frac{1}{2})^2] \\ & - [1068.12(v'' + \frac{1}{2}) - 5.35(v'' + \frac{1}{2})^2]. \end{aligned} \quad (2)$$

Results of these studies show that while the calculated positions of the band heads agree well with the observed ones, bands involving $v' = 2$ level of $A^1\Pi$ state deviate from the expected positions by about 33 cm^{-1} . In other words it appears from the gross structure studies that the only vibrational level of $A^1\Pi$ which is severely perturbed to the extent of 33 cm^{-1} is $v' = 2$ while $v' = 0, 1$ and 3 levels are not perturbed. Rotational structure analyses of these bands show that the above conclusion is dubious. On the contrary the high resolution studies presented in the following section show that all the known vibrational levels $v' = 0-4$ of $A^1\Pi$ are perturbed.

3.2 Rotational structure and analysis

The rotational structure of the bands of AsN is very complex in contrast to the structure of a similar band system in the isovalent molecules such as SiO (Field *et al* 1976). The resolution employed in the present studies was good enough to resolve not only the rotational structure completely but was found to be useful in sorting out some of the extra lines which appeared at the places of severe perturbations. Seventeen bands namely 0-0, 0-1, 0-2, 0-3, 1-0, 1-2, 1-3, 1-4, 2-0, 2-1, 2-2, 2-3, 2-4, 3-0, 3-1, 3-2, 3-3 and 3-5 of As¹⁴N and As¹⁵N and two more bands 4-1 and 4-2 of As¹⁴N were analysed. These bands arise from the electronic transition $^1\Pi-^1\Sigma^+$ which is expected to consist of three branches *P*, *Q* and *R* where *Q* branch is the most intense and *R* is the head forming branch. The rotational structure of two bands namely 0-0 and 0-1 of As¹⁵N is shown in figure 2. It may be seen from the figure that the regular pattern of all

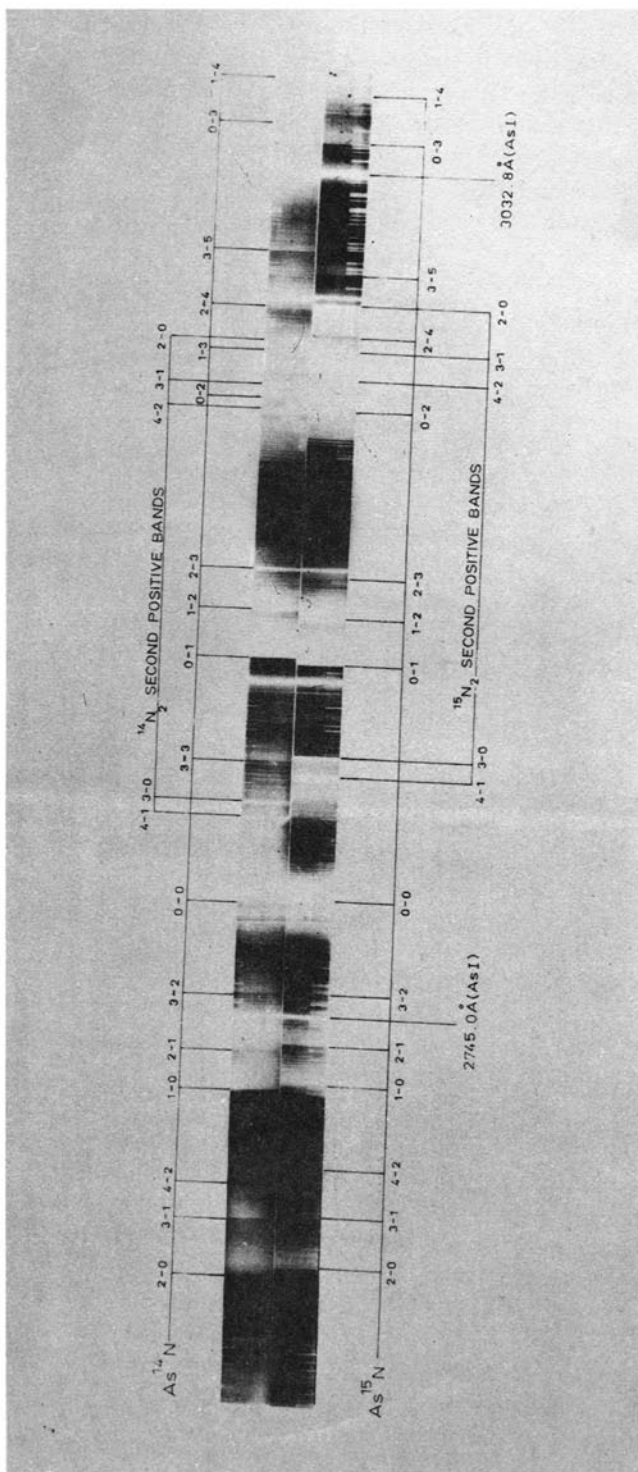


Figure 1. The $A^1\Pi-X^1\Sigma^+$ band system of $As^{14}N$ and $As^{15}N$.

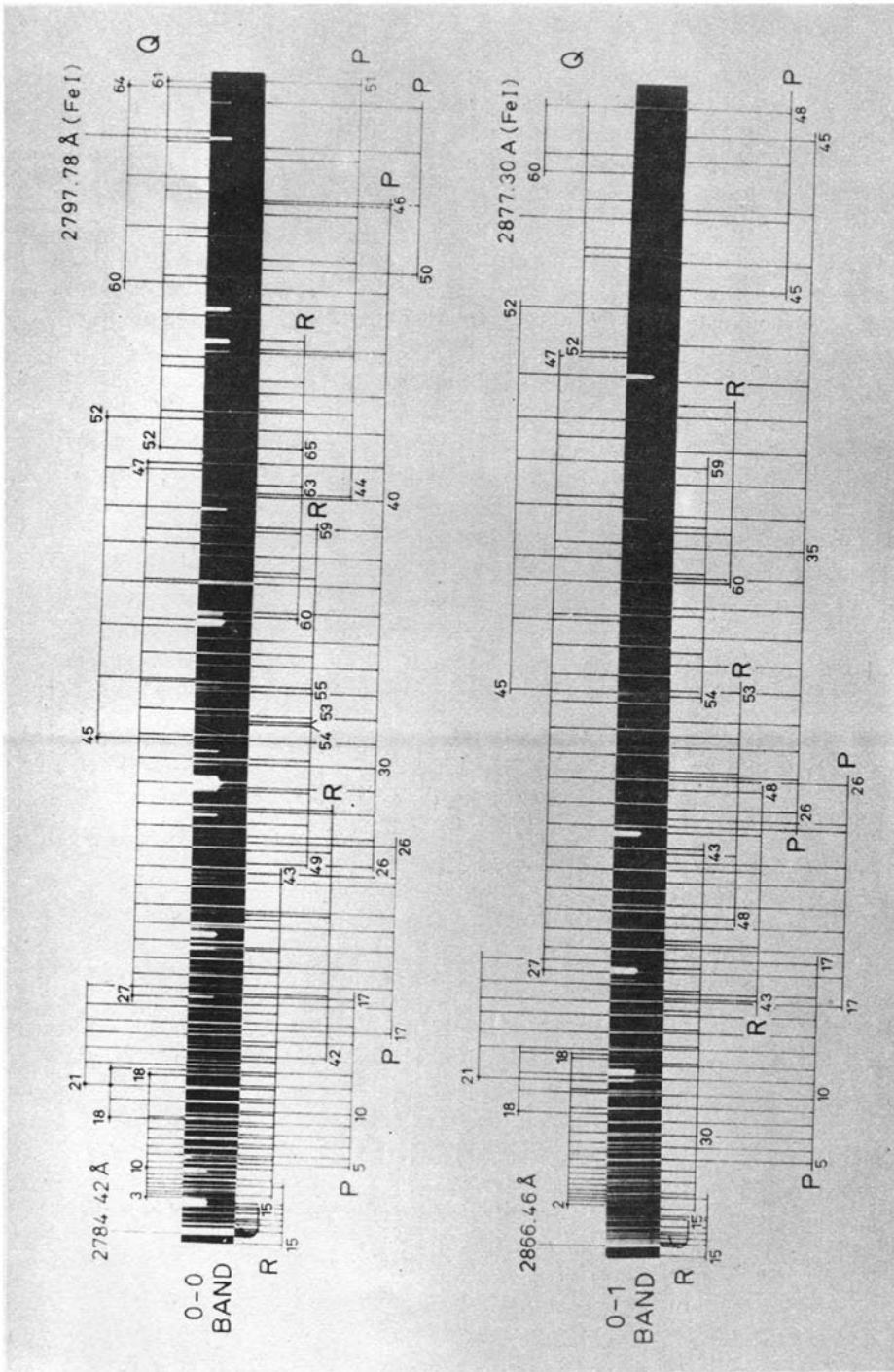


Figure 2. Rotational structure of 0-0 and 0-1 bands of As¹⁵N.

the three branches is badly disturbed due to severe perturbations. Although the electronic transition involved is a simple type, considerable difficulty was experienced in picking up the branches.

The rotational assignments, especially where the branch lines were severely perturbed, were made unambiguously using the following relation (Herzberg 1950) choosing the bands having a common upper level:

$$\begin{aligned} R_{v'v_1''}(J) - R_{v'v_2''}(J) &= Q_{v'v_1''}(J) - Q_{v'v_2''}(J) = P_{v'v_1''}(J) - P_{v'v_2''}(J) \\ &= G''(v_2'') - G''(v_1'') - (B_{v_1''} - B_{v_2''})J(J+1). \end{aligned} \quad (3)$$

A straight line graph was obtained by plotting the above combination differences against $J(J+1)$. Besides providing a sensitive check on the correctness of the rotational analysis, intercepts of these plots provided accurate values of the vibrational quanta of the ground state of As^{14}N and As^{15}N molecules.

The vibrational constants thus obtained and the rotational constants obtained from the ground state combination differences agreed well with those of Perdigon and Femelat (1982). Incidentally it may be mentioned here that despite severe perturbations in the levels of $A^1\Pi$ state, the ground state combination differences, $\Delta_2 F''(J)$, remained unaffected since they involved R and P branches arising from the same Λ -component of the $A^1\Pi$ state.

The line listing of the P , Q and R branches of all the analysed bands of As^{14}N and As^{15}N is not presented here and they are available from the authors on request.

Perturbations in the $A^1\Pi$ levels were found to be so complex that it was not possible to evaluate the molecular constants of the $A^1\Pi$ state making use of the combination differences derived from the P , Q and R branches. However, the following attempts were made to understand the observed spectral features.

3.3 Shifts in the vibrational levels of $A^1\Pi$ state

Vibrational term values, T_v , of the $A^1\Pi$ state relative to $v'' = 0$ of the ground state were computed by adding the appropriate ground state vibrational term values $G''(v)$ given by the following expression to the band origins obtained from the rotational analysis.

$$G''(v) = 1068.71\rho(v'' + \frac{1}{2}) - 5.45\rho^2(v'' + \frac{1}{2})^2, \quad (4)$$

where $\rho = 1$ for As^{14}N and 0.9715956 for As^{15}N . The T_v values thus obtained for $v' = 0-4$ of As^{14}N and $v' = 0-3$ of As^{15}N are listed in table 1 along with the calculated positions of the levels. The (obs-cal) values in the table show that $v' = 3$ level of As^{14}N exhibits maximum deviation of 28.61 cm^{-1} contrary to the earlier observations of Spinks (1934) and Krishnamurty and Thomas (1976) who reported that $v' = 2$ level deviated by about 33 cm^{-1} and the levels $v' = 0, 1$ and 3 hardly showed any significant deviation. The calculated T_v values were obtained using the molecular constants of $A^1\Pi$ reported by Perdigon and Femelat (1982).

3.4 Isotope shifts in the observed bands

It was mentioned already that the isotope shifts studies in the bands of $A^1\Pi-X^1\Sigma^+$ system were reported by Krishnamurty and Thomas (1976) based on the band head (R)

Table 1. Shifts observed (in cm^{-1}) in the vibrational levels of $A^1\Pi$ state.

V	T_0 Observed	T_0 Calculated	Obs-cal
As¹⁴N			
0	35900.14	35899.24	0.90
1	36754.54	36758.06	- 3.52
2	37611.22	37606.64	4.58
3	38416.43	38445.04	- 28.61
4	39288.97	39273.24	15.73
As¹⁵N			
0	35898.32	35902.07	- 3.75
1	36723.03	36736.77	- 13.74
2	37569.79	37561.85	7.94
3	38371.37	38377.31	- 5.94

measurements. In the present work these isotopic shifts were recalculated using the band origins obtained from the rotational analysis. The observed and the calculated band origins and the observed and calculated isotopic shifts are presented in table 2. Although the observed and calculated isotope shifts do not agree due to perturbations in the $A^1\Pi$ state, the minimum shift in the 0-0 band shows the correctness of the vibrational assignments.

3.5 Perturbations in the $A^1\Pi$ state

In analogy with the isovalent molecules the three ten valence electron configurations of AsN may be written as:

- I. $7\sigma^2 8\sigma^2 9\sigma^2 3\pi^4$ $X^1\Sigma^+$.
- II. $7\sigma^2 8\sigma^2 9\sigma 3\pi^4 4\pi$ $b^3\Pi, A^1\Pi$.
- III. $7\sigma^2 8\sigma^2 9\sigma^2 3\pi^3 4\pi$ $a^3\Sigma^+, d^3\Delta, e^3\Sigma^-, C^1\Sigma^-, D^1\Delta, E^1\Sigma^+$.

The observed perturbations in the $A^1\Pi$ state are too complex to provide a satisfactory interpretation unlike the isovalent molecules, CO, CS, SiO, SiS etc. and analogous molecule PN where the observed perturbing states were identified with the configuration III mentioned above. Perdigon and Femelat (1982) explained some of the features by developing Hamiltonian matrix models. However, there are several features which still remain unexplained.

Careful examination of Gero's plots (Perdigon and Femelat 1982) shows that all the observed vibrational levels of $A^1\Pi$ of As¹⁴N and As¹⁵N were mostly perturbed by $^3\Sigma^-$ and $^1\Sigma^-$ states. In addition, a series of extra levels were identified in the $v' = 0, 2, 3$ and 4 of As¹⁴N and $v' = 1$ level of As¹⁵N, the exact nature of the perturbing states causing these extra levels is still to be established. Results of the deperturbation studies enabled Perdigon and Femelat (1982) to conclude that some of the higher vibrational levels of $b^3\Pi$ state arising from the $(\sigma\pi)$ configuration appear due to the strong mixing of the $A^1\Pi$ state with other perturbing states via spin-orbit interactions. These are some of the perturbations identified. Besides these many other perturbations are yet to be identified. Some aspects of these interactions are discussed here.

Table 2. Band origins and isotope shifts (in cm^{-1}) of $A^1\Pi-X^1\Sigma^+$ bands of AsN.

$V'-V''$	As^{14}N		As^{15}N		Isotope shifts	
	$\nu(\text{obs})$	$\nu(\text{cal})$	$\nu(\text{obs})$	$\nu(\text{cal})$	obs	cal
0-0	35900.14	35899.24	35898.32	35902.07	-1.82	2.83
0-1	34842.33	34841.43	34870.25	34874.00	27.92	32.57
0-2	33795.41	33794.52	33852.46	33856.21	57.05	61.69
0-3	32759.40	32758.50	32844.95	32848.70	85.55	90.20
1-0	36754.54	36758.06	36723.03	36736.77	-31.51	-21.29
1-2	34651.40	34653.33	34677.17	34690.91	25.77	37.58
1-3	33613.80	33617.32	33669.66	33683.40	55.86	66.08
1-4	32588.70	32592.21	32672.43	32686.17	83.73	93.96
2-0	37611.22	37606.64	37569.79	37561.85	-41.43	-44.79
2-1	36553.41	36548.83	36541.72	36533.78	-11.69	-15.05
2-3	34470.48	34465.90	34516.42	34508.48	45.94	42.58
2-4	33445.37	33440.79	33519.19	33511.25	73.82	70.46
3-0	38416.43	38445.04	38371.37	38377.31	-45.06	-67.73
3-1	37358.62	37387.23	37343.30	37349.24	-15.32	-37.99
3-2	36311.67	36340.31	36325.51	36331.45	13.84	-8.86
3-3	35275.66	35304.30	35318.00	35323.94	42.34	19.64
3-5	33236.34	33264.98	33333.82	33339.76	97.48	74.58

3.6 $^3\Sigma^- \sim A^1\Pi$ interactions

It is well known that the dominant interaction in the vibrational levels of $A^1\Pi$ state in the isovalent molecules, CO, CS, SiO, SiS, PN etc. is due to the $e^3\Sigma^-$ state arising from the configuration III mentioned above. The characteristic feature of this interaction is that there are two perturbations in the P and R branches at J_1 and J_3 values and one perturbation in the Q branch at J_2 , the three J values being $J_1 < J_2 < J_3$. However, it is interesting to note that the $^3\Sigma^- \sim A^1\Pi$ interactions identified in the present studies cannot be attributed to only one $^3\Sigma^-$ state. For example in the $v' = 0$ level of As^{14}N , perturbations characteristic of $^3\Sigma^- \sim A^1\Pi$ interactions occur at four places. If we assume that all the four interactions are due to only one $^3\Sigma^-$ state, then the vibrational quanta, ΔG , obtained from the successive differences of the term values suggest that very high vibrational levels of $^3\Sigma^-$ are involved in causing perturbations in the levels of $A^1\Pi$ state. Further, the magnitude of the isotope shifts observed is not compatible with those expected for levels involving higher vibrational numbering.

In order to estimate the magnitude of the deviations of the rotational levels of the $A^1\Pi$ from their expected positions, the rotational term values $T_v(J)$ of the levels belonging to the various vibrational levels of the upper state were obtained relative to $J = 0, v'' = 0$ of $X^1\Sigma^+$ state by adding the appropriate lower state rotational term values to the P, Q and R branch lines. The $T_v(J)$ values thus obtained for the $v' = 0$ to 4 levels of As^{14}N and $v' = 0$ to 3 levels of As^{15}N were fitted to an expression using a linear least square fit computer program

$$T_v(J) = T_v + B_v J(J+1) - D_v J^2(J+1)^2. \quad (5)$$

T_v , B_v and D_v values for $A^1\Pi$ and the extra levels were obtained. The term values T_v (relative to $J = 0, v = 0$ of $X^1\Sigma^+$ state) of $^3\Sigma^-$ state perturbing the levels $A^1\Pi$ state were evaluated using the relation:

$$T_v(^3\Sigma^-) - T_v(A^1\Pi) = [B_v(A^1\Pi) - B_v(^3\Sigma^-)]J_0(J_0 + 1). \quad (6)$$

In the above expression, the rotational constant B_v of the perturbing state, $^3\Sigma^-$ was obtained from the Gero's plots, J_1/J_3 and slope methods as discussed in detail by Field *et al* (1976) in the case of SiO. J_0 is the interpolated value of J at which the levels of $A^1\Pi$ and $^3\Sigma^-$ states would be exactly degenerate and are valid only for the perturbation in the Q branch. The values of T_v , B_v and J_0 values are presented in table 3 under the column $^3\Sigma^-$ (observed) in juxtaposition with the T_v values of $A^1\Pi$.

It was mentioned earlier that all these observed perturbations cannot be due to one $^3\Sigma^-$ state. On the other hand it was found that all the T_v values (third column of table 3) can be separated into two series belonging to two different $^3\Sigma^-$ states, which are designated as $f^3\Sigma^-$ and $e^3\Sigma^-$. The two electron configurations which can give rise to two $^3\Sigma^-$ states may be described as:

$$7\sigma^2 8\sigma 9\sigma 3\pi^4 4\pi^2 \dots ^1\Sigma^+, ^1\Sigma^-, ^1\Delta, ^3\Sigma^-(2), ^3\Delta, ^5\Sigma^-,$$

$$7\sigma^2 8\sigma^2 9\sigma^2 3\pi^2 4\pi^2 \dots ^1\Sigma^+(3), ^1\Sigma^-, ^1\Delta(2), ^1\Gamma, ^3\Sigma^+(2), ^3\Sigma^-(2), ^3\Delta(2), ^5\Sigma^+,$$

Table 3. Observed T_v and B_v values of $^3\Sigma^-$ levels perturbing the vibrational levels of $A^1\Pi$ and their classification into $f^3\Sigma^-$ and $e^3\Sigma^-$ states.

$A^1\Pi$		$^3\Sigma^-$ (obs)			$f^3\Sigma^-$ (cal)		$e^3\Sigma^-$ (cal)	
v	T_v	T_v	B_v	J_0	T_v	v	T_v	v
As¹⁴N								
0	35900.14	35978	0.345	22.4	35977	1	—	—
		36281	0.344	49.7	—	—	36284	3
		36627	0.350	68.1	36615	2	—	—
1	36754.54	36857	0.316	22.5	—	—	36863	4
		37206	0.328	47.5	37237	3	—	—
		37392	0.334	61.9	—	—	37423	5
2	37611.22	37978	0.287	43.0	—	—	37964	6
3	38416.43	38584	0.324	29.7	—	—	38486	7
		38828	0.335	51.5	—	—	38989	8
		39009	0.31	61.5	39004	6	—	—
4	39288.97	39340	0.31	20.0	—	—	39473	9
		39495	0.33	39.4	39565	7	—	—
As¹⁵N								
0	35898.32	35947	0.38	17.5	35947	1	—	—
		36180	0.36	46.0	—	—	36225	3
		36580	0.31	67.0	36570	2	—	—
1	36723.03	36784	0.39	17.0	—	—	36790	4
		37037	0.32	45.0	37175	3	—	—
		37341	0.345	60.0	—	—	37341	5
2	37569.79	37815	0.305	39.5	—	—	37863	6

which involve simultaneous excitation of two electrons. These are expected to lie at higher energies relative to the lower valence states. It is, therefore, unlikely that the two $^3\Sigma^-$ states causing perturbations in the $A^1\Pi$ state arise from either of these configurations, unless there is some sort of configuration mixing with the valence configurations. It is difficult to reach at a definite conclusion about the origin of two $^3\Sigma^-$ states in the absence of any ab initio calculations. Making use of these values for As^{14}N and As^{15}N , molecular constants T_v , ω_e , $\omega_e x_e$, B_e and α_e values were evaluated following the same procedure adopted in the case of PN (Saraswathy and Krishnamurthy 1987). The constants thus obtained were used to calculate the T_v values presented in table 3, under $f^3\Sigma^-$ and $e^3\Sigma^-$ column.

3.7 $b^3\Pi \sim A^1\Pi$ interactions

Studies by Perdigon and Femelat (1982) show that the levels of $b^3\Pi$ which are involved in the perturbation with $A^1\Pi$ state, appear as a result of interaction with a third state. For example in the $v = 0$ level of As^{14}N an extra level having a T_v value of 35812 cm^{-1} and $B_v = 0.4107\text{ cm}^{-1}$ perturbs the $^3\Pi_0$ component ($v = 8$) at $J = 18$. Similarly in $v = 1$ of As^{15}N , an extended series of levels are observed due to the interaction of $v = 9$ of $b^3\Pi_1$ having $T_v = 36806\text{ cm}^{-1}$ with an extra level. Thus the $b^3\Pi \sim A^1\Pi$ appears to be a three-level interaction process not reported so far in any of the isovalent molecules. Constants of $b^3\Pi$ states were reported by Perdigon and Femelat (1982) from the rotational analysis of the 0-0 band lying at 3432 \AA of $b^3\Pi_0 - X^1\Sigma^+$ system. Using these constants the T_v values (which lie in proximity of $A^1\Pi$ levels) of the three components $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ are listed in table 4 along with the expected B_v values. The T_v and B_v values computed for extra levels are also listed in table 4.

3.8 $C^1\Sigma^- \sim A^1\Pi$ interactions

In addition to the above interactions, there is a class of perturbations wherein only f -parity levels are affected. These were identified as $^1\Sigma^- \sim ^1\Pi$ interactions by Perdigon and Femelat (1982). In the present studies efforts were made to correlate some of these interactions to one $^1\Sigma^-$ state referred as $C^1\Sigma^-$ in analogy with the isovalent molecules.

Molecular constants T_v , ω_e , B_e and α_e were evaluated making use of the As^{14}N and As^{15}N data in a similar way as in the case of $^3\Sigma^-$ states. These constants along with the vibrational assignments of the $C^1\Sigma^-$ levels causing perturbations in $A^1\Pi$ levels are listed in table 5. Comparison of the calculated T_v values with the observed values shows the validity of the derived constants.

Molecular constants of $X^1\Sigma^+$, $C^1\Sigma^-$, $b^3\Pi$, $e^3\Sigma^-$, $f^3\Sigma^-$ and $A^1\Pi$ states are listed in table 6.

4. Conclusion

The rotational structure analysis of several bands of As^{14}N and As^{15}N and the detailed examination of the observed perturbations in the vibrational levels of $A^1\Pi$ state shows that the perturbations appear to be predominantly due to $b^3\Pi$, $C^1\Sigma^-$, $e^3\Sigma^-$ and $f^3\Sigma^-$ states. The complexity of the rotational structure and the shifts in the vibrational levels of the $A^1\Pi$ state may be attributed not only due to the interactions of

Table 4. Term values (T_v) and rotational constants (B_v) (in cm^{-1}) of $A^1\Pi$, $b^3\Pi$ and extra levels.

$A^1\Pi$		$b^3\Pi$			Extra level		
v	T_v	B_v	v	T_v	B_v	T_v	B_v
As ¹⁴ N							
0	35900.14	0.4948	8	35805(³ Π_0) 36225(³ Π_1) 36645(³ Π_2)	0.4527	35812	0.4107
1	36754.54	0.5185	9	36578(³ Π_0) 36998(³ Π_1) 37418(³ Π_2)	0.4466	36846	0.4199
2	37611.22	0.4921	10	37337(³ Π_0) 37757(³ Π_1) 38177(³ Π_2)	0.4404	37569 37629	0.376 0.435
3	38416.43	0.4794	11	38082(³ Π_0) 38502(³ Π_1) 38922(³ Π_0)	0.4343	38485 38645	0.45 —
4	39288.97	0.4593	12	38813(³ Π_0) 39233(³ Π_1) 39653(³ Π_2)	0.4283	39243	0.392
As ¹⁵ N							
0	35898.32	0.4673	8	35631(³ Π_0) 36051(³ Π_1) 36471(³ Π_2)	0.4287		
1	36723.03	0.4737	9	36386(³ Π_0) 36806(³ Π_1) 37226(³ Π_2)	0.4231	36793	0.432
2	37569	0.4627	10	37127(³ Π_0) 37547(³ Π_1) 37967(³ Π_2)	0.4175		
3	38371	0.4606	11	37855(³ Π_0) 38275(³ Π_1) 38695(³ Π_2)	0.4119		

Table 5. Observed and calculated T_v values of $^1\Sigma^-$ levels perturbing the vibrational levels of $A^1\Pi$ of As¹⁴N.

$A^1\Pi$		$^1\Sigma^-(\text{obs})$		$C^1\Sigma^-(\text{cal})$		
v	T_v	J_0	T_v	B_v	v	T_v
0	35900.14	9.7	35913	0.372	15	35940
		61.9	36400	0.368	16	36421
1	36754.54	41.7	36997	0.362	17	36925
2	37611.22	49.0	37937	0.353	19	37909
3	38416.43	53.5	38849	0.342	20	38861
4	39288.97	30.3	39402	0.337	22	39325

Table 6. Molecular constants (in cm^{-1}) of some of the low lying valence states of As^{14}N .

State	T_e	ω_e	$\omega_e x_e$	B_e	$\alpha_e \times 10^3$	$D_e \times 10^6$ *	$\gamma_e(\text{\AA})$
$A^1\Pi$	35999	869	5.1	0.5006	6.8	0.66	1.690
$f^3\Sigma^-$	34990	670	8.0	0.37	5.0	0.45	1.965
$e^3\Sigma^-$	34108	656	9.7	0.365	5.4	0.45	1.979
$b^3\Pi$	29632	897	6.9	0.5045	6.1	0.64	1.683
$C^1\Sigma^-$	26950	640	4.0	0.425	4.6	0.75	1.834
$X^1\Sigma^+$	0	1068.71	5.45	0.54566	3.659	0.52	1.618

* Values calculated using Kratzer's relation (Herzberg 1950).

the $A^1\Pi$ with each of the perturbing state but also due to the mutual interaction among the perturbing states. Unlike the isovalent ten-valence electron molecules, CO, CS, SiO, SiS, GeO, PN, there seems to be two $^3\Sigma^-$ states causing perturbations in the levels of $A^1\Pi$ state. It is interesting to note that the vibrational levels of the $e^3\Sigma^-$ and $f^3\Sigma^-$ states causing perturbations in the $A^1\Pi$ state involve low v values since their T_e values lie nearer to the $A^1\Pi$ state while in the case of the isoelectronic molecule GeO (Lagerqvist and Renhorn 1982) higher vibrational levels of $e^3\Sigma^-$ state were found to be responsible for the perturbations in the $A^1\Pi$ state. More detailed deperturbations studies and configuration interaction calculations are needed to unravel the observed perturbations.

Acknowledgements

We wish to thank Dr S L N G Krishnamachari for his interest in the work. We are highly indebted to Drs P Perdigon and B Femelat, Universite Claude Bernard (Lyon I), Villeurbanne, France for their valuable suggestions at various stages of the work. We are also extremely thankful to Professor W E Jones, Dalhousie University, Halifax, Canada for valuable discussions and continued interest in the work.

References

- Curry J, Herzberg L and Herzberg G 1933 *Z. Phys.* **86** 348
D'Incan J and Femelat B 1967 *C.R. Acad. Sci.* **264** 1261
D'Incan J and Femelat B 1968 *C.R. Acad. Sci.* **267** 796
Dixit M N, Krishnamurty G and Narasimham N A 1970 *Proc. Indian Acad. Sci.* **A71** 23
Femelat B and Jones W E 1974 *J. Mol. Spectrosc.* **49** 388
Field R W, Lagerqvist A and Renhorn I 1976 *Phys. Scr.* **14** 298
Herzberg G 1950 *Molecular spectra and molecular structure 1: Spectra of diatomic molecules* (New York: Van Nostrand)
Jones W E 1970 *J. Mol. Spectrosc.* **34** 320
Krishnamurty G and Thomas O 1976 *J. Pure Appl. Phys.* **14** 236
Lagerqvist A and Renborn I 1982 *Phys. Scr.* **25** 241
Ohanessian G, Durand G, Volatron F, Halwick P and Malrieu J P 1985 *Chem. Phys. Lett.* **115** 545
Perdigon P and Femelat B 1982 *J. Phys.* **B15** 2165
Saraswathy P and Krishnamurty G 1987 *Pramana - J. Phys.* **29** 53
Spinks J W J 1934 *Z. Phys.* **88** 511