Electronic Spectra of Diatomic Oxides of Group 5A Elements

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## 1. Introduction

A comparative study of the spectral terms of an isoelectronic sequence of atoms and ions has been found to be of great help in the elucidation of term sequences in other atoms and ions.[1] Atoms lying in the same group of the periodic table exhibit many spectral similarities and regularities and the successful use of these regularities in the development of the theory of atomic structure prompted a corresponding attempt in the spectra of molecules. This is not easily possible even today because the spectral studies of molecular ions are few and far between so that not many isoelectronic molecular systems are available for such a comparative study. This limitation on the available data had made the comparative study of spectra of similar molecules (for example, molecules consisting of atoms from the same group of the periodic table) of added importance. It has been found that the spectral features of such a group of molecules show a gradual change in going from one molecule to another and in fact the apparent lack of such regularities in the observed data do point to significant errors of analysis or identification (see Nair and Rai[2] and Rai et al.[22]). In the present review we present a detailed and critical analysis of the spectroscopic information available regarding the diatomic oxides of group 5A elements.

For the lighter molecules (NO, PO, and AsO) of this group many, if not all, of the electronic states arising from the low lying electronic configurations are known and are well characterized but for the heavier molecules SbO and BiO, this is far from true. For these latter molecules very few electronic states are known and the number of well-characterized states is still fewer. Most of this information has become available only in the last few years. The known states in different molecules of this group are shown in Figure 1.

2. Ground State

The ground state of diatomic molecules are characterized in different ways. According to the separated-
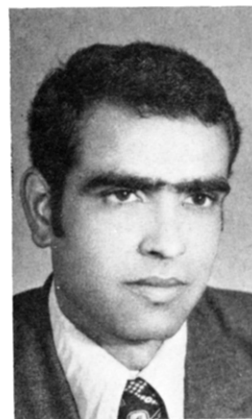
S. B. Rai, currently a staff member in the Laser and Spectroscopy Laboratory of the Department of Physics, Banaras Hindu University, obtained his Ph.D. in 1974. Born in 1949, he obtained his postgraduate education at the Banaras Hindu University. He has been engaged in the study of high-resolution spectra of diatomic molecules for almost 10 years and has made significant contributions to the spectra of PO, SbO, SiCl, CuCl, etc. He is currently engaged in setting up a laser fluorescence setup for the study of diatomic spectra.

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atom viewpoint the molecular ground state arises from the combination of two atomic ground states viz., ^{4}S (ground state of N, P, As, Sb, or Bi) and ^{3}P (ground state of atomic oxygen). The coupling of the corre-
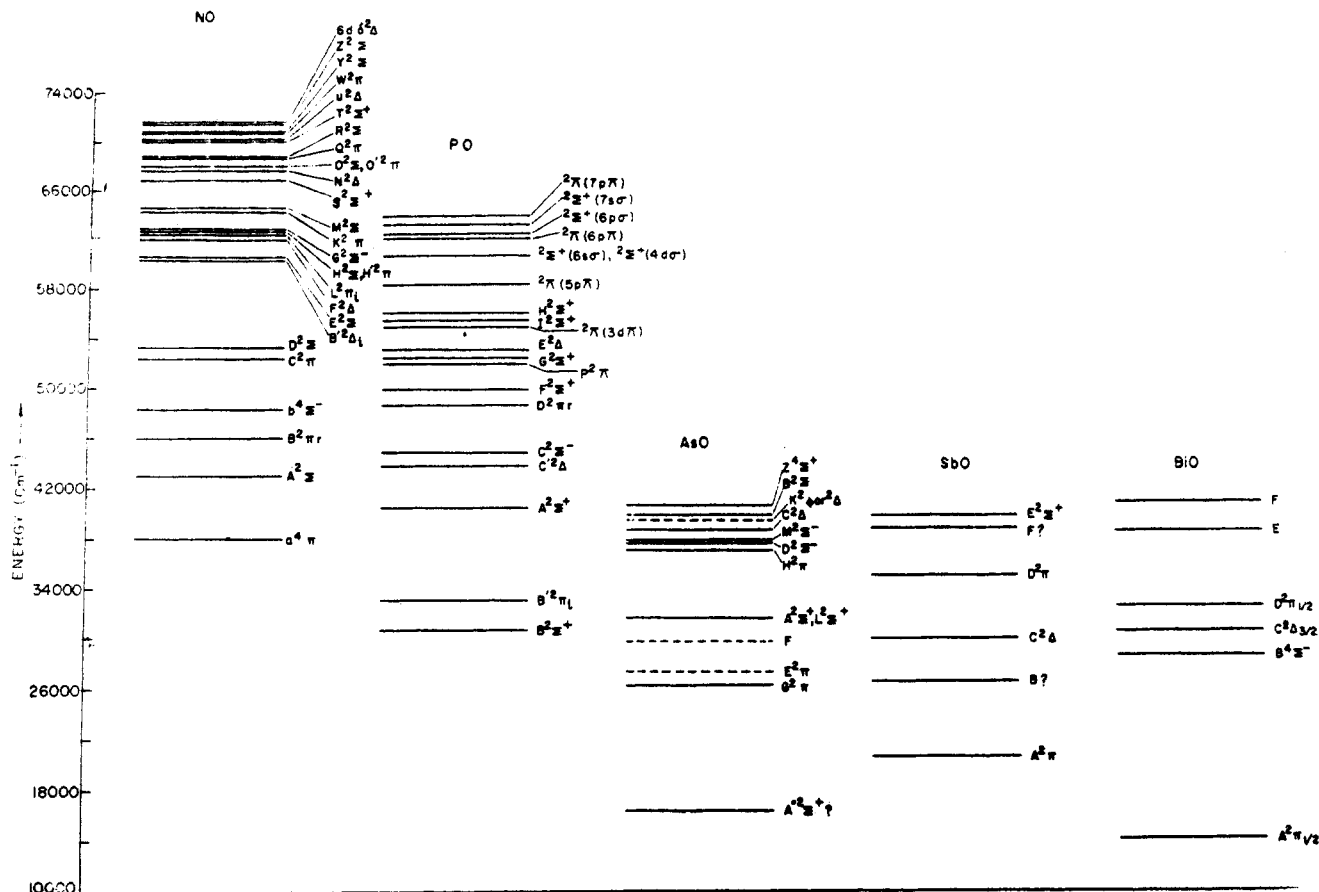
Figure 1. Energy states known in the oxides of N, P, As, Sb, and Bi.

sponding orbital and spin angular momenta according to the usual rules indicates that doublet, quartet, and sextet states of the type Λ (= 0) and Λ (= 1) would be possible for the molecule. Considerations of spin pairing and comparison with other cases indicate that of these six states the $^2\Pi$ state would be the lowest lying stable state. $^2\Sigma$, $^6\Sigma$, and $^6\Pi$ states arising from this combination will be totally repulsive while the states $^4\Sigma$ and $^4\Pi$ may be either repulsive or may have a shallow minimum.

The ground-state configuration of these molecules can be written as

$$KK..... \ (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi)...^2\Pi.. \qquad (I)$$
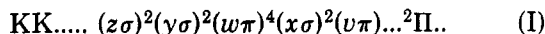
where KK..... refer to the electrons that occupy the completely filled atomic orbitals in the two atoms. The $(z\sigma)$ and $(y\sigma)$ are respectively the bonding and the antibonding combinations $(ns\sigma_X + 2s\sigma_O)$ and $(ns\sigma_X - 2s\sigma_O)$ of the ns_X orbital of the group VA atom ($n = 2, 3, 4, 5,$ and 6 for N, P, As, Sb, and Bi) and the 2s orbital of oxygen. The $(x\sigma)$ orbital is the bonding combination $(np\sigma_X + 2p\sigma_O)$ while the $(w\pi)$ and $(v\pi)$ orbitals represent the bonding and the antibonding combination $(np\pi_X - 2p\pi_O)$ and $(np\pi_X + 2p\pi_O)$, respectively, of the π orbitals. The antibonding combination $(np\sigma_X - 2p\sigma_O)$ would represent a fairly low lying virtual molecular orbital. While the electron configuration in all these molecules will be qualitatively very similar the energy ordering of the molecular orbitals as well as their bonding or antibonding character, and the relative contributions of the various atomic orbitals would change in going from the lighter to the heavier molecules of this group. All the experimental and theoretical
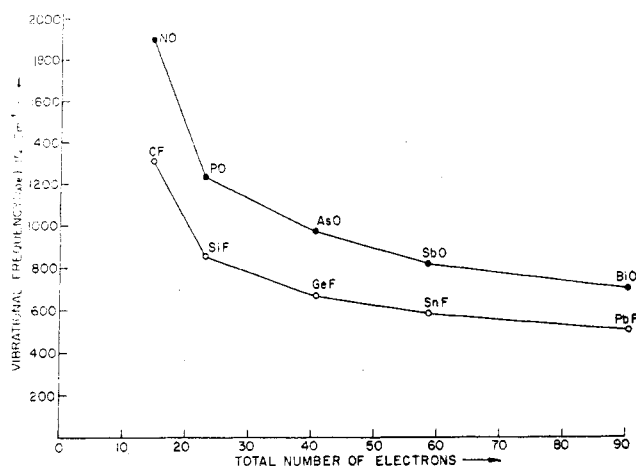

Figure 2. Variation of ω_e with total number of electrons.

evidence to date is consistent with the $(v\pi)$ orbital being the highest occupied molecular orbital in the ground state leading to a $^2\Pi_r$ state as the ground state in all cases. Of course, as we go toward the heavier molecules of this sequence the coupling changes to case c and the two components of the $^2\Pi_r$ state behave almost as independent states having $\Omega = {}^1/_2$ and $\Omega = {}^3/_2$ with the former lying lower.

The diatomic oxides of group 5A atoms are isoelectronic with the diatomic halides of group 4A elements. To bring home the similarities in energy levels and spectroscopic properties of isoelectronic sequences we have plotted in Figures 2 and 3 the values of the ω_e and the spin orbit interaction parameter A, respectively, for the ground state of the two groups of molecules. The striking resemblance between the curves for the two
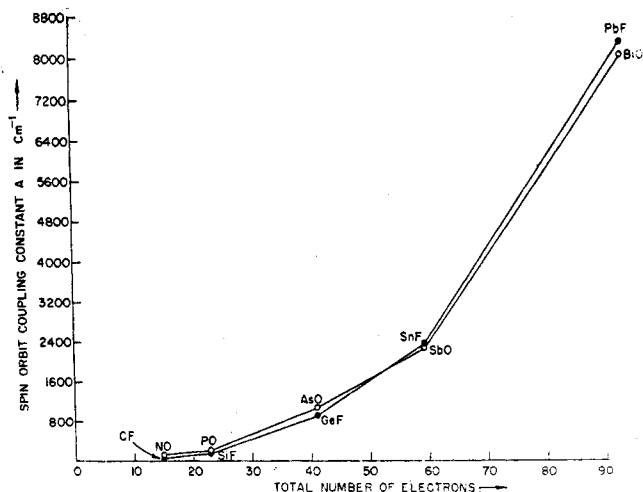
Figure 3. Variation of spin orbit coupling constant A with total number of electrons.
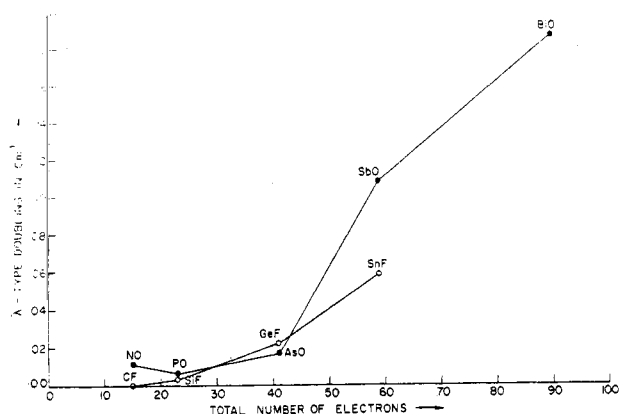

Figure 4. Variation of λ-type doubling with total number of electrons.

Figure 5. Variation of r_e with total number of electrons.

sequences emphasizes the utility of comparing results for isoelectronic sequences in the case of molecules. The transition from case a to case c in going from lighter to the heavier members of the two sequences is apparent from Figure 3.

The strength of the interaction between the orbital angular momentum and the nuclear rotation, as well as the strength of the attractive force between the two atoms, shows a fairly regular variation with the total number of electrons. Figure 4, which shows the variation of the λ-type doubling parameters, clearly indicates that there should be a substantial λ doubling in the ground state of SbO molecule whereas the experimental data prior to our own work (Rai et al.[22,23]) did not give any trace of this doubling. This had resulted in a wrong estimate of the equilibrium internulcear distance of the ground state by the previous workers as can be clearly seen from Figure 5 which shows that the earlier r_e value does not lie on a smooth curve as does our value.

3. Excited States

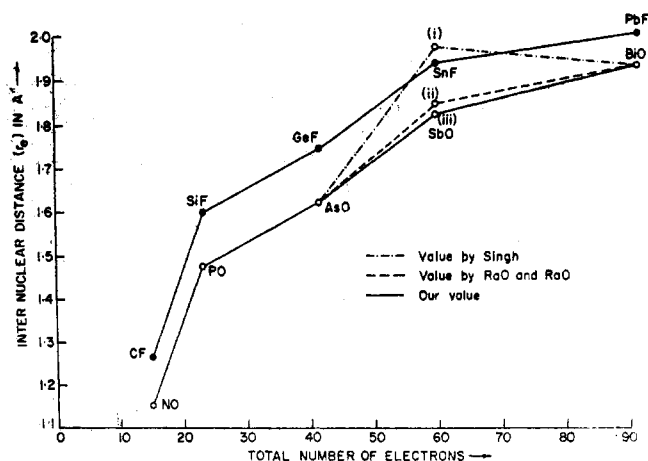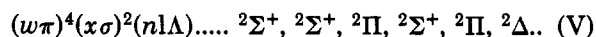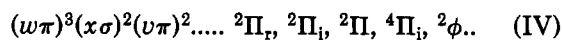The low lying excited states for these molecules arise from the following electron configurations
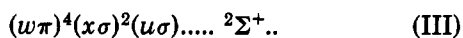
$$(w\pi)^4(x\sigma)(v\pi)^2 \ldots\ldots \ {}^2\Sigma^+, \ {}^2\Sigma^-, \ {}^4\Sigma^-, \ 2\Delta.. \quad \text{(II)}$$

$$(w\pi)^4(x\sigma)^2(u\sigma)\ldots\ldots \ {}^2\Sigma^+.. \quad \text{(III)}$$

$$(w\pi)^3(x\sigma)^2(v\pi)^2\ldots\ldots \ {}^2\Pi_r, \ {}^2\Pi_i, \ {}^2\Pi, \ {}^4\Pi_i, \ {}^2\phi.. \quad \text{(IV)}$$

$$(w\pi)^4(x\sigma)^2(nl\Lambda)\ldots\ldots \ {}^2\Sigma^+, \ {}^2\Sigma^+, \ {}^2\Pi, \ {}^2\Sigma^+, \ {}^2\Pi, \ {}^2\Delta.. \quad \text{(V)}$$

The different excited states involved in different transitions are usually classified and assigned to different configurations by making use of the observed vibrational frequencies and internulcear distances of the various molecular orbitals. Thus, since $(x\sigma)$ orbital is only weakly bonding (sometimes even nonbonding), a state arising by the promotion of an electron from this orbital to a strongly antibonding $v\pi$ orbital is likely to be accompanied by a decrease in the magnitude of the vibrational frequency and an increase in the equilibrium internuclear distance. Thus states arising from configuration II would have small values of ω_e and larger vaues of r_e as compared to the ground state. Both $u\sigma$-$(np\sigma_X - 2p\sigma_O)$ and $v\pi(np\pi_X + 2p\pi_O)$ orbitals have antibonding character in these molecules with the former being slightly more antibonding and hence the ${}^2\Sigma^+$ state arising from configuration III would have only slightly different ω_e and r_e values as compared to the ground state.

Configuration IV involves the promotion of an electron from a strongly bonding $(w\pi)$ orbital to a strongly antibonding $(v\pi)$ orbital and is likely to involve a substantially large decrease in ω_e and a similar large increase in r_e. In configuration V the orbital $(nl\Lambda)$ refers to a Rydberg orbital and since the Rydberg orbital because of its large size has very little effect on the molecular core, the states arising from this configuration would have great similarity with the ground state of the ion. In general, the Rydberg states involve very high excitation energy and give rise to bands mostly in the ultraviolet or vacuum ultraviolet regions. The Rydberg molecular states form convergent series very similar to the Rydberg series in atoms and their study leads to precise determination of molecular ionization potential. A large number of Rydberg states are known in the spectrum of both NO and PO and these, at least in the case of NO, are quite well studied. On the other hand only a few Rydberg states are known for the heavier molecules of this group, e.g., AsO, SbO, and BiO, and even these are not well characterized. The electronic states and spectrum of NO have been discussed in great detail by Miescher,[3] Kaufman and Edlen,[4] Miescher and Alberti,[5] and Miescher and Huber[6] in several reviews and we will refer to those when needed to emphasize a point in the discussion for the other molecules.

The first excited state in PO is $B^2\Sigma^+$ state (perturbations in the B–X system have been interpreted to

show the existence of a $^4\Pi$ and $^4\Sigma^-$ state at lower energies than $B^2\Sigma^+$) which is the upper state of the well-known β band system[7,8,9,10,11] and is also involved as the lower state in several other band systems.[12,13] Rotational analysis of these systems yields for this state a r_e value which is quite close to the r_e value for the ground state of the PO^+ ion indicating that this state is of the Rydberg type. The vibrational frequency ω_e for this state is however much smaller than the corresponding value in the ground state of PO^+. This is a fact that is in disagreement with the expected behavior of a Rydberg type state. Theoretical LCAO–MO–SCF calculations on this state performed by Ackerman et al.[14] also indicate that this state should be considered as a non-Rydberg or a valence state. Their calculation also showed that this state is due to antibonding combination of orbitals $3p\sigma_P$ and $2p\sigma_O$. The state $B^2\Sigma^+$ is a fairly stable state with a deep potential minima and 11 vibrational levels are experimentally observed. (Recently Ghosh et al.[15] have reported a band involving $v = 24$ of this state.) The higher vibrational levels with $v \geq 6$ show the existence of rotational perturbations that have been ascribed to the interactions with different vibrational levels of various states, e.g., $A^2\Sigma^+$, $b^4\Sigma^-$, $b'^2\pi_i$, and a $^4\pi$. The $\omega_e(B)/\omega_e(X)$ ratio for the $B^2\Sigma^+$ state in PO is 0.94.

A laser fluorescence study of the $B - X^2\Pi_{1/2}$ system has been reported recently by Clyne and Heaven.[78] They have measured the lifetime of the zeroth level of the $B^2\Sigma^+$ state as 250 ± 10 ns.

A low-lying $^2\Sigma^+$ state, namely the $A''^2\Sigma^+$ state, has been reported in AsO.[16] The $\omega_e(B)/\omega_e(X)$ for this state is 0.89 which is similar to the corresponding value in PO, indicating that this state of AsO is the analogue of the $B^2\Sigma^+$ state of PO. This conclusion however is less than confirmed as the chemiluminescence source, in which this state has been observed for the first time, yields very poor spectra making the analysis somewhat suspect.[17] The extensive work by Anderson and Callomon[18] on the spectra of AsO did not succeed in observing this state. A second low lying excited $^2\Sigma^+$ state in AsO is the $B^2\Sigma^+$ state which is of the Rydberg type and we will discuss it later on.

A low-lying $^2\Sigma^+$ state giving rise to the B–X band system in SbO was reported many years ago by Sengupta.[19] The available rotational analyses of the (0,0) band of this system[20,21,53,74,75] are most probably incorrect as the constants do not agree with the recent work on the C–X and D–X systems.[22,23] Many vibrational levels up to $v = 9$ are known in the B state and the $\omega_e(B)/\omega_e(X) = 0.71$. The superposition of sequence bands and the presence of isotopes makes the rotational structure in this system very complex. Rotational structure in the (0,0) and (1,0) bands of the $^2\Sigma^+ - ^2\Pi_{3/2}$ component has recently been reanalyzed[76] and this is confirmed that the B state is a $^2\Sigma^+$ state. Bands of the $^2\Sigma^+ - ^2\Pi_{1/2}$ component of this system are heavily overlapped by structure of some unknown band system. A $^4\Sigma^-$ state has been reported to lie very close to the $B^2\Sigma^+$ state in molecules of this group as well as in isoelectronic molecules of the type GeF, SiF,.... It is possible that the overlapping observed in the $^2\Sigma^+ - ^2\Pi_{1/2}$ component of the B–X system is due to $^4\Sigma^- - ^2\Pi$ transition. A band system due to SbO^+ has recently been reported[73] in the same region as the B–X system of
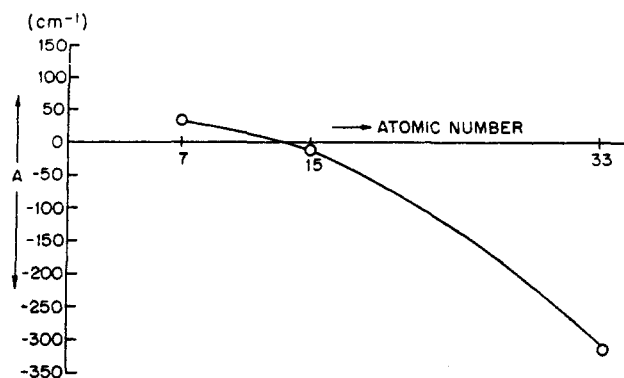

Figure 6. Variation of A with atomic number in the lowest $^2\Pi$ state of NO, PO, and AsO.

SbO. Rotational analysis of this system has been carried out by Tripathi et al.[77]

In the early work on the B–X system of BiO, Bridge and Howell[24] and Babu and Rao[25] concluded that the B state is a $^2\Sigma^+$ state. However, the recent work by Barrow et al.[26] has confirmed that the upper state of this system is a $^4\Sigma^-$ state rather than a $^2\Sigma^+$ state. The only $^2\Sigma^+$ state known in BiO is the $E^2\Sigma^+$ state which is of Rydberg type in nature and lies at a very high energy. The $^2\Sigma^+$ state arising from configuration II is expected to lie quite close in energy to the $^4\Sigma^-$ state and, thus, can not be identified with the above $^2\Sigma^+$ state. Only one component $^4\Sigma_{1/2}^-$ of the $^4\Sigma^-$ state is known in BiO. All the vibrational levels of even this component with $v \geq 6$ are predissociated by a repulsive state (most probably a $^2\Sigma$ state) dissociating into ground-state atoms.

The next higher excited state in these molecules is $B'^2\Pi_i$ in PO, $A'^2\Pi_i$ in AsO, $A^2\Pi$ in SbO, and $A^2\Pi$ in BiO; all of these are analogous to $B'^2\Pi_r$ state of NO. This state dissociates in all cases into normal state of oxygen ^3P and the first excited state ^2D of the other atom and is one of the $^2\Pi$ states arising from configuration IV. The vibrational frequency in this valence state is quite small in comparison to the value in the ground state. The same holds good for the constant A and the λ-type doubling constant. A very large number of vibrational levels (27 in PO, 13 in AsO, 9 in SbO, and 11 in BiO) are observed; they are involved in a large number of red-shaded bands in transition to the ground state. These vibrational levels have energy values quite close to the different vibrational levels of several Rydberg and non-Rydberg states resulting in a large number of perturbations.

A very interesting feature of these states is observed if the spin orbit interaction parameter A is plotted against the atomic number of the group 5A element (see Figure 6). Thus, while the $B^2\pi_r$ state in NO is a regular doublet, the $B'^2\pi$ and $A'^2\pi$ states in PO and AsO, respectively, are inverted. The spin orbit splitting in the corresponding states in SbO and BiO is not known. Further, a rapid increase in the spin orbit coupling constant A with the vibrational quantum number v is observed in this state in all these molecules for which relevant data are available. Thus in NO ($B^2\pi_r$) for $v = 0$, A is 31.32 cm^{-1} while for $v = 25$ it becomes 77 cm^{-1}.[27] In PO ($B'^2\pi_i$) for $v = 0$, A is -13.6 cm^{-1} while for $v = 23$, A is $+ 30$ cm^{-1}.[28,29] In AsO ($A'^2\pi_i$) this variation has been expressed as

$$A_v = -316.08 + 2.93(v + \tfrac{1}{2}) + 0.111(v + \tfrac{1}{2})^2$$

Roche and Lefebvre-Brion[30] have offered an explanation for these observations on the basis of self-consistent-field molecular-orbital calculations. They find that, the antibonding π orbital (referred to as $v\pi$ in the configurations given earlier) is largely concentrated on the phosphorus atom in the $B'^2\Pi_i$ state in PO and makes a large negative contribution to the spin orbit coupling constant A causing the latter to become negative. A similar thing holds good for AsO also. However, this orbital in NO is more evenly distributed over the two constituent atoms and makes very little contribution to A.

An interesting feature of the $B'^2\Pi_i$ state in PO is the near equality of the ω_e and B_e values for this state with the corresponding values for the $D'^2\Pi_r$ state. This D' state was observed to be involved in two band systems namely D'-B and D'-X[31,32] giving rise to bands in the visible and the ultraviolet region, respectively. Earlier studies[31,32] were able to detect only one vibrational level (identified as the $v = 0$ level), which was shown to perturb a non-Rydberg $D^2\Pi_r$ state. More recent and extensive studies by Coquart et al.[33] and by Ghosh et al.[15] have resulted in the discovery of many new vibrational levels in this state. Studies of the isotope shift in bands arising from the level identified earlier[31,32] as the $v = 0$ level of the $D'^2\Pi_r$ show that this level has $v = 24$ and is in fact identical with the expected $v = 24$ level of the $B'^2\Pi_i$ state. The molecular orbital calculations by Roche and Lefebvre-Brion[30] referred to earlier had also indicated this identity. Only two vibrational levels $v = 0$ and 1 of this state ($B'^2\Pi_i$) are found free from perturbations. Levels with intermediate values of v are perturbed by the vibrational levels of the $B^2\Sigma^+$ and the $A^2\Sigma^+$ states whereas levels with larger values of v are perturbed by the various levels of the $D^2\Pi_r$ state. Recently Cornet et al.[34] rephotographed the B'-X system of PO in absorption, and have succeeded in recording a larger number of bands (including those previously assigned to the D'-X system). They concluded from this study that the vibrational numbering in the B' state made by Verma[28] should be increased by 2 units.

The existence of the $A'^2\Pi_i$ state in AsO came to light from perturbations observed in the higher vibrational levels of the $A^2\Sigma^+$ state.[35] Four successive vibrational levels of this $A'(^2\Pi_i)$ state were detected and it was found that these belong to the $^2\Pi_{3/2}$ component of a new state $G^2\Pi_i$ (this same state was later assigned as $A'^2\Pi_i$). Somewhat later, Mrozowski and Santaram[36] observed the A'-X transition and more recently bands involving higher vibrational levels of this A' state were reported by Goure and d'Incan[37-39] and by Kushwaha et al.[16] These workers concluded that the A' state is a $^2\Pi_i$ state with $A = -309$ cm^{-1} and showed that the vibrational frequency of this A' state is very similar to the value reported earlier by Morgan and Callomon[35] for the $G^2\Pi_i$ state. The identity of the two states was confirmed by Anderson and Callomon[18] who analyzed the rotational structure in a large number of bands of the A'-X system. The extrapolated values of the rotational constant B for the 9th, 10th, 11th, and 12th vibrational levels of the A' state were found to be identical with the values of the rotational constant for the four vibrational levels of the G state reported earlier.[35] They also confirmed

that it is the $^2\Pi_{1/2}$ component of the A' state which is perturbing the $A^2\Sigma^+$, not the $^2\Pi_{3/2}$ component as reported by earlier workers.[35]

The rotational structure in any band involving the $A^2\Pi$ state in SbO has not yet been analyzed and even the proposed vibrational analysis of this system does not seem perfect. Sengupta's[19] analysis indicates that the $A^2\Pi$ state is a regular $^2\Pi$ state with spin orbit coupling constant $A = 133$ cm^{-1}. Lakshman[20] observed only one component of this state but the later studies by Shimauchi[40] indicate that this analysis is suspect. The variation of the parameter A among the corresponding $^2\Pi$ states of this group of molecules does indicate that this state in SbO should have a large negative A value but all the known $^2\Pi$ states of SbO are regular. Comparison of the ratios $\omega_e(A)/\omega_e(X)$ and $T_e(A)/T_e(X)$ for SbO with NO, PO, and AsO however indicates that it is the $A^2\Pi$ state of SbO which is the analogue of the $^2\Pi$ states referred to earlier in PO and AsO. This controversy can not be clarified at this stage unless further work on the A-X system of SbO becomes available.

The situation in BiO is similar, in that only one component of the $^2\Pi$ state; i.e., $^2\Pi_{1/2}$ ($v = 2...9$) is known. Barrow et al.[26] have assigned the state as a $^2\Pi_r$ having a small spin orbit coupling constant and with a small λ doubling. The many weak rotational perturbations observed in the bands involving the sixth and seventh levels of this state have been interpreted as being due to interaction with the higher vibrational levels of the $^2\Pi_{3/2}$ component of the ground state. It seems plausible that even if this characterization as a $^2\Pi_r$ state is correct, we must have a close $^2\Pi_i$ state in this molecule also.

The next higher excited state known in PO is the $A^2\Sigma^+$ and is the lowest known Rydberg state for this molecule. The analogous states known in AsO, SbO, and BiO are $B^2\Sigma^+$, $E^2\Sigma^+$, and $E^2\Sigma^+$, respectively, and all of these are analogous to the $A^2\Sigma^+$ state in NO. This state is involved in many extensive and intense band systems involving the ground as well as the other excited states. Thus in PO, in addition to the well-known γ system ($A^2\Sigma^+ - X^2\Pi$ transition),[43,46] the $A^2\Sigma^+$ state also combines with many excited Rydberg as well as non-Rydberg states[12,13,41,42] giving rise to strong and extensive band systems in the visible and the infrared regions of the spectrum. The ω_e and B_e values for this state in all the molecules are considerably greater than the corresponding ground-state values and are close to the values for the corresponding ionic ground state (see Table I). The spin splitting constant γ has a very small magnitude for this state in all these molecules. It has been observed that nearly all the vibrational levels of this state, both in PO and AsO, are rotationally perturbed either by a stable or a repulsive state. The perturbations are of both heterogeneous and homogeneous type. Only one level with $v = 0$ is known for this state in BiO while four levels ($v = 0-3$) are known in SbO. Some peculiar features of this state for the various molecules of this group are enumerated below.

The A-X system in PO is very intense and develops well both in emission and in absorption (Rao,[43] Coquart et al.,[44,45] Dixit and Narsimham[46]). Thirteen vibrational levels are observed in the A state and bands involving all of them show rotational perturbations. The nature of the different perturbing states has been determined

TABLE I. A Comparison of Molecular Constants of the Rydberg States of NO, PO, and AsO with the Ground State of Their Ions

molecules	w_e, cm^{-1}	B_e, cm^{-1}	r_e, Å	γ, cm^{-1}
NO ($A^2\Sigma^+$)	2374.31	1.9965	1.0634	0.0027
NO$^+$ ($X^1\Sigma^+$)	2376.42	1.9973	1.0632	
PO ($A^2\Sigma^+$)	1390.94	0.7801	1.4313	0.0013
PO$^+$ ($X^1\Sigma^+$)	1405.0			
AsO ($B^2\Sigma^+$)	1098.3	0.5128	1.5764	+0.0042
AsO$^+$ ($X^1\Sigma^+$)	1091.32	0.5199	1.5680	
SbO ($E^2\Sigma^+$)	849.0			
SbO$^+$ ($X^1\Sigma^+$)	941.94	0.32513 (B_1)	1.8074	

TABLE II. Rotational Perturbations in the $A^2\Sigma^+$ State of PO

vibrational levels	nature of perturbing states[a]	nature of perturbing states[b]
$v = 0, N = 10$	$b^4\Sigma^-, N = 9$	$b^4\Sigma^-, v = 7, N = 9$
$v = 0, N = 17$	$b^4\Sigma^-, N = 18$	$b^4\Sigma^-, v = 7, N = 18$
$v = 0, N = 55$	$B'^2\Pi_i, v = 12, N = 55$	?
$v = 1, N = 30$	$b^4\Sigma^-, N = 29$	$b^4\Sigma^-, v = 9, N = 29$
$v = 1, N = 36$	$b^4\Sigma^-, N = 37$	$b^4\Sigma^-, v = 9, N = 37$
$v = 2, N = 19$	$B'^2\Pi_i, v = 15, N = 19$	?
$v = 2, N = 39$	$b^4\Sigma^-, N = 38$	$b^4\Sigma^-, v = 11, N = 38$
$v = 2, N = 45$	$b^4\Sigma^-, N = 46$	$b^4\Sigma^-, v = 11, N = 46$
$v = 3, N = 10$	?	$C'^2\Sigma^-, v = 0, N = 9$
$v = 3, N = 13$	$B'^2\Pi_i, v = 17, N = 12$	?
$v = 3, N = 14$	$B'^2\Pi_i, v = 17, N = 14$	?
$v = 3, N = 17$	$B'^2\Pi_i, v = 17, N = 18$	$C'^2\Sigma^-, v = 0, N = 18$
$v = 3, N = 44, 45$	$B'^2\Pi_i, v = 18, N = 44, 45$	?
$v = 4, N = 32$	?	$C^2\Sigma^-, v = 1, N = 31$
$v = 4, N = 38$	?	?
$v = 4, N = 39$	?	$C^2\Sigma^-, v = 1, N = 40$
$v = 4, N = 41, 42$	?	?
$v = 5, N = 33$	$B'^2\Pi_i, v = 22, N = 33$	?
$v = 5, N = 43$	?	$C^2\Sigma^-, v = 2, N = 42$
$v = 5, N = 49$	?	$C^2\Sigma^-, v = 2, N = 50$

[a] Reference 41. [b] Reference 45.

by detailed studies of these perturbations but there are several aspects that are not yet well settled and require further work. A summary of the observed perturbations is given in Table II. Vibrational perturbations also have been observed in $v = 3, 4$, and 5 levels of this state. Several intensity anomalies have been observed in different vibrational levels of this state.

Though Connelly[47] has reported, in absorption, bands involving vibrational levels up to $v = 5$ in the $B^2\Sigma^+$ state of AsO molecule, Callomon and Morgan[35] could observe only one level $v = 0$ in emission. The bands involving $v' > 0$ are slightly diffuse even in absorption indicating a weak predissociation in levels with $v' > 0$. The predissociation has been interpreted as being due to interaction with the unstable $^4\Sigma^+$ state dissociating into the ground-state atoms. In the case of the $E^2\Sigma^+$ state of BiO molecule all the vibrational levels with $v' > 0$ are predissociated again by a repulsive state dissociating into the ground-state atoms (Bridge and Howell[24]).

The Rydberg state $E^2\Sigma^+$ of SbO molecule has not yet been rotationally analyzed but a reasonably complete vibrational analysis of the E–X system has been proposed by Shimauchi.[40] She could observe vibrational levels up to $v' = 5$ in this state in both absorption and emission. All the bands in the E–X system involving $v' = 2$ of this state are slightly shifted from their expected positions to the higher energy side and have very small intensity indicating a vibrational perturbation in this level.

The next excited state in PO is the $C'^2\Delta$ and a similar $^2\Delta$ state is known in AsO, SbO, and BiO (in all cases

TABLE III. Variation of Molecular Constants in the NR$^2\Delta$ State

states	T_e, cm^{-1}	$r_e'(^2\Delta)/r_e''$ (ground state), $X^2\Pi$	$w_e'(^2\Delta)/w_e''(^2\Pi)$	A, cm^{-1}, ($^2\Delta$)
$B'^2\Delta$ (NO)	60 364.2	1.13	0.64	-2.40
$C'^2\Delta$ (PO)	43 742.7	1.07	0.67	0
$C^2\Delta$ (AsO)	38 662.0	1.09	0.68	48
$C^2\Delta$ (SbO)	30 031	1.08	0.70	568
$C^2\Delta$ (BiO)	30 700	1.09	0.67	
$T_0, {}^2\Delta_{3/2}$				

it is labeled as $C^2\Delta$). The corresponding state in NO is the $B'^2\Delta$ state arising from configuration $(w\pi)^4$-$(x\sigma)(v\pi)^2$. The $T_e(^2\Pi)$, $r_e(^2\Delta)/r_e(X\,^2\Pi)$, $w_e(^2\Delta)/w_e(X^2\Pi)$ values in the five molecules NO, PO, AsO, SbO, and BiO are given in Table III. The small value of the ratio $A(C^2\Delta)/A(X^2\Pi)$ can be understood, if we note that the C state arises from the configuration $(x\sigma)(v\pi)^2$ where a $(v\pi)^2$ group of electrons gives rise to a $^1\Delta$ state and the doubling comes in due to spin $= {}^1/_2$ of the $(x\sigma)$ electron. The doubling, therefore involves a spin–other orbit interaction in place of the usual spin orbit interaction where both the spin and the orbital angular momenta belong to the same electron.

Five vibrational levels ($v = 0$–4) are known in the $C'^2\Delta$ state of PO (levels with $v = 14$–18 have also been reported from perturbations observed in the $E^2\Delta$ state).[33,48–50,51a,b,80] The extremely small doublet splitting observed in this state had led to an erroneous identi-

fication of this as $^2\Sigma^-$ [48,49] state arising from the same configuration. The later experimental work by Coquart et al.[33] and by Prudhomme et al.[51a] as well as theoretical work by Ackerman et al.[14] has however confirmed that this state is a $^2\Delta$ (case b) state and the $^2\Sigma^-$ state expected from this configuration is to be identified with the $C^2\Sigma^-$ state which differs in energy from this state by 1091 cm^{-1}. All the known vibrational levels of this state show effects of localized perturbations of both heterogeneous as well as homogeneous types.

The spin–orbit coupling constant A in the $C^2\Delta$ state of AsO is only 50 cm^{-1} and therefore, at higher J it behaves as a state intermediate between Hund's case a and case b. Vibrational levels up to $v = 4$ are known in the $C^2\Delta_{5/2}$ component of this state but in $^2\Delta_{3/2}$ component only the lowest $v = 0$ level is observed.[18,37,52] The nonappearance of higher levels in the $^2\Delta_{3/2}$ component of this state has been explained by Goure et al.[37-39] as being due to predissociation. The bands involving the vibrational levels $v = 0, 1, 2,$ and 3 of the $C^2\Delta_{5/2}$ state show many rotational perturbations. The perturbations observed in the bands with $v = 0, 1,$ and 2 have been identified as of heterogeneous type whereas in the $v = 3$ level only homogeneous perturbations are detected. The perturbations have been explained as due to the successive vibrational levels of an unknown state K which may be either $^2\Delta_r$ or $^2\phi_i$. The molecular constants for this new state have also been reported.[18,37]

The $C^2\Delta$ state in SbO is a pure case a state with a spin orbit splitting of 568 cm^{-1}. Vibrational levels up to $v = 12$ in $^2\Delta_{5/2}$ and up to $v = 11$ in $^2\Delta_{3/2}$ are known. A vibrational perturbation has been reported in the $v = 3$ level of the $^2\Delta_{5/2}$ component of this state. Rotational structure in only two bands (2,0) and (3,0) of the $C^2\Delta_{3/2} - X^2\Pi_{1/2}$ subsystem have so far been analyzed.[23,53] An interesting feature of the more recent analysis[23] is the observation that in this subsystem the $2\Delta B$ value and the λ-doubling constant in the ground state are nearly equal. The λ doublets are, therefore, not observable as the λ component of one particular member but overlap on the next higher member of the same branch. The λ doubling in the C state is found to be very small.

Only one vibrational level is known in the $C^2\Delta$ state of BiO which is most probably the $v = 0$ level of the $^2\Delta_{3/2}$ component. It has been suggested that the higher vibrational levels of this component as well as all levels of the $^2\Delta_{5/2}$ component are predissociated by a repulsive state dissociating into the ground-state atoms. The C state is likely to be a pure case a state with very small λ doubling.

The next state in the order of increasing energy is $C^2\Sigma^-$ in PO and $D^2\Sigma^-$ in AsO. This is the analogue of the $G^2\Sigma^-$ state in NO. No $^2\Sigma^-$ state is known in BiO and SbO molecules. The $^2\Sigma^-$ states are also correlated with the same electron configuration, i.e., $(w\pi)^4(x\sigma)(v\pi)^2$. Transitions from this state to the ground state are observed giving rise to bands in the ultraviolet region. The negative parity of this $^2\Sigma^-$ state has been confirmed on the basis of the combination defect observed in the transition $C - X^2\Pi_{1/2}$ which has a sign opposite to that expected for a $^2\Sigma^+ - ^2\Pi_{1/2}$ transition. The spin splitting in the $^2\Sigma^-$ state is very small. Small perturbations have been reported in the $v = 0$ and $v = 1$ levels of this state in AsO and have been analyzed as being caused by the

$H^2\Pi$ [18,35] state. Prudhomme et al.[51a] and Coquart et al.[45] have reported similar perturbations in the $v = 0, 1,$ and 2 levels of this state in PO.

Lofthus and Miescher[54] have explained the negative sign of the λ doubling in the ground $^2\Pi_{1/2}$ state of the NO molecule as being primarily due to the influence of this $^2\Sigma^-$ state. If such interaction does exist, the λ doubling in the ground state can be written as

$$\Delta\nu_{dc} = \frac{2ABl(l + 1)}{\nu(\Sigma^-,\Pi)}$$

Using this relation they calculated the λ-doubling constant for the ground state of NO and obtained a value of 0.0115 cm^{-1} which is in close agreement with the experimental value 0.0115 cm^{-1}. Application of the same relation leads to the values 0.013 cm^{-1} and 0.048 cm^{-1} for the ground states of PO and AsO, respectively, as compared to the experimental values of 0.007 and 0.017 cm^{-1}, respectively. It was suggested by Anderson and Callomon[18] that we must consider in the above calculation the interaction of the $X^2\Pi$ state with not only the $^2\Sigma^-$ state but also the close lying $A^2\Sigma^+$ state. The total λ-doubling separation can thus be written as

$$\Delta\nu_{dc} = \frac{2ABl(l + 1)}{\nu(\Sigma^+,\Pi)} + \frac{2ABl(l + 1)}{\nu(\Sigma^-,\Pi)}$$

The calculated value of $\Delta\nu_{dc}$ comes out to be 0.012 cm^{-1} for AsO (observed 0.013 cm^{-1}); 0.007 cm^{-1} for PO (observed 0.007 cm^{-1}) and 0.0092 cm^{-1} for NO (observed 0.0115 cm^{-1}).

Six vibrational levels ($v = 0-5$) are known in the $C^2\Sigma^-$ state of PO of which the three lowest levels show the effects of perturbation by the $A^2\Sigma^+$ state. The vibrational numbering has recently been modified by Prudhomme et al.[51a] In AsO, eight vibrational levels ($v = 0-7$) are known and, the first two levels show the effect of weak perturbations of both heterogeneous and homogeneous type. The heterogeneous perturbations have been explained as being due to the $H^2\Pi$ state whereas the homogeneous ones are attributed to an unknown $^2\Sigma^-$ state which is not totally repulsive.[18]

No $^2\Sigma^-$ state is known in SbO and BiO molecule but a comparison of T_e and ω_e values for the $^2\Sigma^-$ state in NO, PO, and AsO indicates that this state in the SbO molecule should lie about 31 000 cm^{-1} above the ground state with an ω_e value of 650 cm^{-1}. For BiO the expected energy above the ground state is $\sim$26 000 cm^{-1} and the estimated vibrational frequency is $\sim$460 cm^{-1}.

The next state in PO is the $D^2\Pi_r$ state analogous to the $C^2\Pi_r$ state of NO. This is the first Rydberg state of the $^2\Pi$ type known in PO molecule and arises from the $4p\pi$ component of the 4p complex. The state arising from $4p\sigma$ component of the 4p complex is the $G^2\Sigma^+$ state. These two states have nearly equal energy ($\sim$3892 cm^{-1} apart). The separation between the similar states of the 3p complex of NO ($C^2\Pi_r$ and $D^2\Sigma^+$) is only 958 cm^{-1}. The comparatively large separation in the case of PO has been explained by Jungen[56] and by Lefebvre-Brion and Moser[57] as being due to the repulsive interaction between the $G^2\Sigma^+(4p\sigma)$ state and the $B^2\Sigma^+$ state which in reality arises from a $3p\pi$ orbital. Since the $^2\Sigma^+$ and the $^2\Pi$ states in both the molecules

TABLE IV. Estimated Molecular Constants for the $b^4\Sigma^-$ and the $a^4\Pi_i$ States of PO

states	T_e, cm^{-1}	w_e, cm^{-1}	$w_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	ref
$^4\Sigma^-$	34837	889	6.62	0.644	0.006	59 60
$^4\Pi_i$	27550	800	7.26	0.5982	0.0066	10

are quite close to one another an interaction of the pure precession type is expected to occur (Lagerqvist and Miescher[58]).

The $D^2\Pi$ state in PO is involved in band systems lying in the visible ($D^2\Pi_r$–$B^2\Sigma^+$ transition) and the ultraviolet ($D^2\Pi_r$–$X^2\Pi_r$ transition) regions. The spin orbit splitting in this state is only 26 cm^{-1} indicating that the state is intermediate between Hund's case a and case b coupling. Only one vibrational level with $v = 0$ has been observed in this state, the higher vibrational levels are presumably predissociated. Recently Ghosh et al.[15] have observed three more vibrational levels of this state viz., $v = 1, 2,$ and 3 in the absorption spectrum but the bands involving these levels show a diffuse structure indicating the effect of predissociation. The predissociation has been interpreted as being due to the repulsive part of the $^4\Pi_i$ state arising from the ground atomic states. The $N = 34$ rotational level of the $v = 0$ vibrational level of this state is highly perturbed by the corresponding rotational level of the $v = 24$ level of the $B'^2\Pi_i$ state. Higher vibrational levels of this state observed in absorption also show anomalous values of A due to these perturbations. No Rydberg states of the $^2\Pi$ type are known in AsO, SbO, and BiO molecules.

4. Other Known States in PO

4.1. Non-Rydberg States

There are two more non-Rydberg states known in PO namely $F^2\Sigma^+$ and $P^2\Pi_r$. In addition the existence of a $^4\Sigma^-$ state and another a $^4\Pi_i$ state has been guessed from the observed perturbations in the $A^2\Sigma^+$ and the $B^2\Sigma^+$ states, as well as the predissociation of the $D^2\Pi_r$ and the $B'^2\Pi_i$ states. No transitions to or from any of these states are yet known. From the detailed analyses of the observed perturbations in the $A^2\Sigma^+$ and $B^2\Sigma^+$ states (Verma and Jois,[41] Verma and Singhal,[59] Ngo et al.,[13] and Coquart et al.[60]) it has been concluded that the $b^4\Sigma^-$ state is a stable state arising from the configuration $(w\pi)^4(x\sigma)(v\pi)^2$. The theoretical study of PO by Roche and Lefebvre-Brion[30] also supports this conclusion. This is the lowest possible $^4\Sigma^-$ state in PO and the final molecular constants for this state as reported by Coquart et al.[60] are given in Table IV.

The existence of a $^4\Pi_i$ state in PO similar to the $^4\Pi_i$ state of NO had been proposed by Couet et al.,[31] Verma et al.,[12] and by Roche and Levebvre-Brion[30] as the state responsible for the predissociations observed in the $D^2\Pi_r$ and $B'^2\Pi_i$ states. The predissociation limits derived from these observations are very close to the dissociation limit of the ground state indicating that the $^4\Pi_i$ state also dissociates into ground-state atoms and has a shallow minimum. The dissociation energy of PO derived from these predissociations is 49536 cm^{-1} (a more recent value is 49090 cm^{-1}),[61] which is in good agreement with the mass spectrometric value of 49712

$\pm$ 700 cm^{-1} reported by Drowart et al.[62] The detailed theoretical investigation of PO by Roche and Lefebvre-Brion[30] showed that the $^4\Pi_i$ state dissociating into ground-state atoms would lie nearly 12000 cm^{-1} below the $^4\Sigma^-$ state and they predicted its T_e values as $\sim$25000 cm^{-1}. In a more recent study[11] of the observed rotational perturbations in the higher vibrational levels of the $B^2\Sigma^+$ state it has been found necessary to assume that the perturbations in the $v = 8$ level of the $B^2\Sigma^+$ state are caused by a vibrational level of the $^4\Pi_i$ state with large v value. On the basis of the molecular constants for this state (in PO) estimated in analogy with the corresponding values of NO, it is concluded that these perturbations are due to the $v = 16$ level of the $^4\Pi_i$ state. An approximate potential energy curve for this state has been given by Verma et al.[12] and the molecular constants are summarized in Table IV.

The vibrational and rotational constants for the $F^2\Sigma^+$ state are very similar to the corresponding values for the $C'^2\Delta$ state. The different vibrational levels of this state are very strongly perturbed and no regularity in the vibrational separation is apparent. The vibrational assignments made by Ngo et al.[13] have been confirmed from the study of vibrational isotopic shift. The $F^2\Sigma^+$ state is involved in several transitions, e.g., $F^2\Sigma^+$ – $X^2\Pi$, $F^2\Sigma^+$–$A^2\Sigma^+$, and $F^2\Sigma^+$–$B^2\Sigma^+$ [12,13,42] giving rise to bands in the ultraviolet, infrared, and visible regions of the spectrum, respectively. It is intriguing that bands involving a few vibrational levels show anomalous intensity behavior which has been ascribed to a weak predissociation and to coincidences in energy of these levels with levels of the A, G, H, and I states. Thus $v = 3$ level of this state has nearly the same energy as the $v = 9$ level of the $A^2\Sigma^+$ state and the $v = 0$ level of the $G^2\Sigma^+$ state and a mixing of the corresponding wave functions is probably responsible for the bands involving $v = 3$ of the $F^2\Sigma^+$ state to appear with much larger intensity. Similarly the $v = 5$ level of the $F^2\Sigma^+$ state is coincident with $G(v = 1)$ and $A(v = 10)$ levels and shows the effect of a homogeneous perturbation in the bands involving this level. The spin splitting constant γ in this state has been found to be quite large.

Another non-Rydberg $^2\Pi_r$ state has recently been reported by Ghosh and Verma[61] in $P^{16}O$ and Prudhomme and Coquart[79] in $P^{18}O$ as being involved in a transition to the ground state giving rise to bands in the vacuum ultraviolet region. The ω_e and B_e values for this state are found to be very small in comparison to those for other states of this molecule. A large number of vibrational levels are observed in this state but due to large perturbations, their assignments are not yet conclusive. Ghosh and Verma[61] have concluded that this state belongs to configuration $(w\pi)^3(x\sigma)^2(v\pi)^2$. The spin orbit coupling constant in this state is estimated as $\sim$200 cm^{-1}. Except for the bands involving the levels $v + 5$, $v + 8$, and $v + 9$ of this state in $P^{16}O$ the F_2 component is not observed in the rotational structure of any other bands. The bands with ($v + 12$) and ($v + 13$) of this state do not appear whereas bands with ($v + 14$) and ($v + 15$) are quite diffuse indicating the existence of localized predissociations. The rotational structure in almost all the six observed bands involving this state is perturbed. The perturbations are mostly of the homogeneous type and the perturbing state is a Rydberg state. However, in $P^{18}O$ bands involving both

the components of the $P^2\Pi$ state up to $v + 9$ (except $v + 3$) could be observed.

4.2. Rydberg States

The highest occupied $(v\pi)$ orbital in these molecules is a strongly antibonding orbital and promotion of an electron from this antibonding orbital to a very extended Rydberg orbital $nl\Lambda$ is almost equivalent to the removal of an antibonding $(v\pi)$ electron from the molecule resulting in a stronger bond. Hence much larger values of ω_e and B_e are expected for Rydberg states than for the ground state. Just like in the case of atoms the Rydberg states in molecules also form a converging series, the study of which leads to an accurate value of the ionization potential and the quantum defect.

In the case of NO a large number of Rydberg states belonging to the $ns\sigma$, the $np\sigma,\pi$, and the $nd\sigma,\pi,\delta$ complexes are known and one expects similar states in PO molecule also. All such states involving a common value of n lie quite close to each other and nearly all their vibrational levels show effects of perturbations. These observed perturbations have been explained as being largely due to the non-Rydberg states described earlier but sometimes mixing of various Rydberg states is responsible for these perturbations. These perturbations are exemplified by drastic changes in coupling conditions and by anomalously large values for A or γ in some states.

A. States Belonging to the ns Complex

The first Rydberg state belonging to this complex is the $A^2\Sigma^+$ state arising from the excitation of an electron from the $v\pi$ orbital to the $4s\sigma$ Rydberg orbital. We have already discussed this state earlier. The next higher energy Rydberg state belonging to this complex is the $I^2\Sigma^+$ state associated with the orbital $5s\sigma$. As expected for Rydberg type states, the ω_e and r_e values for the $I^2\Sigma^+$ state are quite close to the values for the $A^2\Sigma^+$ state. This state is known to combine radiatively with the $A^2\Sigma^+$,[42] $B^2\Sigma^+$,[12,13] and $X^2\Pi$[13] states and to give rise to band systems in the visible, infrared, and ultraviolet region, respectively. Only three vibrational levels viz., $v = 0$, 1, and 2 are known in this state. Bands involving all of these levels show evidence of extensive homogeneous and heterogeneous perturbations. In all cases the rotational structure is broken off at higher values of N probably due to predissociations caused by the repulsive $A'^2\Sigma^+$ state[12] dissociating into ground-state atoms. The heterogeneous perturbations are caused by a close lying $^2\Pi$ state and reach their maximum strength at the same value of N in all the three successive vibrational levels of the $I^2\Sigma^+$ state. This is an indication that the perturbing $^2\Pi$ state should also have nearly the same values of ω_e and B_e as the $I^2\Sigma^+$ state, and it is strongly suggested that the $^2\Pi$ state is also a Rydberg state.

Recently Ghosh and Verma[63] have reported two other members of this series viz., $6s\sigma(^2\Sigma^+)$ and $7s\sigma(^2\Sigma^+)$ in transitions to the ground state giving rise to bands in the vacuum ultraviolet region at 1645 Å and 1581 Å, respectively. Only the (0,0) bands of the two systems could be observed. In the $6s\sigma(^2\Sigma^+)-X^2\Pi$ transition the $6s\sigma(^2\Sigma^+)-X^2\Pi_{3/2}$ component of the (0,0) band is completely overlapped by the (2,0) band of the E–X system. The rotational structure in these bands is very weak and

no extensive analysis could be made.

B. States Belonging to the np Complex

The known Rydberg states belonging to the np complex are $D^2\Pi_r(4p\pi)$, $G^2\Sigma^+(4p\sigma)$; $^2\Pi(5p\pi)$; $^2\Sigma(6p\sigma)$, $^2\Pi(6p\pi)$; and $^2\Pi(7p\pi)$. The $^2\Sigma^+$ state corresponding to $5p\sigma$ and $7p\sigma$ are not yet known. These states combine with the ground state giving rise to band systems in the ultraviolet and vacuum ultraviolet regions. The D and G states also combine with the B state to give bands in the visible region. In general the two states arising from a particular np orbital lie very close to one another with the σ component having slightly higher energy than the π component. The separation between the two components decreases as n increases. The closeness of the $^2\Sigma^+$ and $^2\Pi$ components is responsible for a relationship of pure precession between the two and the spin splitting in the $^2\Sigma^+$ state becomes almost equal to the λ doubling in the $^2\Pi$ state.

The $D^2\Pi_r$ state of this molecule has already been discussed in detail above and no further consideration is given. Four vibrational levels with $v = 0$, 1, 2, and 3 are known for the $G^2\Sigma^+$ state.[12,13,41] The bands involving $v = 0$, 2, and 3 of G state are red shaded, whereas the bands involving $v = 1$ are violet degraded. This abrupt change in the shading has been explained as being due to a strong perturbation by the $F^2\Sigma^+$ state.[12] Irregular intensity variations and abrupt changes in the separation between corresponding lines of the main and satellite branches have also been observed. Because of these perturbations the curve between B_v and v shows an abnormal shape.

A band observed at 1720 Å in the absorption spectrum of PO has been assigned as the (0,0) band of the $5p\pi(^2\Pi)-X(^2\pi)$ transition. The rotational structure indicates the presence of homogeneous perturbations. No band which could be ascribed to the other component namely $5p\sigma(^2\Sigma^+)$ of the 5p complex could be observed. Ghosh and Verma[63] have reported the (0,0) band of the $6p\pi(^2\Pi)-X(^2\Pi)$, $6p\sigma(^2\Sigma^+)-X(^2\Pi)$, and $7p\pi(^2\Pi)-X(^2\Pi)$ transitions. The rotational structures in all these bands are weak in intensity. In the (0,0) band of the $6p\pi(^2\Pi)-X(^2\Pi)$ system the rotational structure near the head shows an unresolved broad structure. The structure in the (0,0) band of the $7p\pi(^2\Pi)-X(^2\Pi)$ transition is again weak and no rotational analysis could be performed and so the assignment is still tentative.

C. States Belonging to the nd Complex

Only two members, viz., with $n = 3$ and 4 of the nd complex are known in PO. The states arising from the 3d complex are $3d\delta(E^2\Delta)$, $3d\pi(^2\Pi)$, and $3d\sigma(H^2\Sigma^+)$. The $3d\delta(E^2\Delta)$ state lies below the $(3d\pi)^2\Pi$ and $(3d\sigma)H^2\Sigma^+$ states as is the case in the corresponding 3d complex in NO, however, the order of $3d\sigma(H^2\Sigma^+)$ and $3d\pi(^2\Pi)$ in PO is opposite to that obtained in NO with the $^2\Pi$ state at a lower energy than the $^2\Sigma^+$ state. According to Mulliken[64] the σ, π, and the δ components of a 3d complex should lie in the order of increasing energy. This thing is in opposition to what is observed in PO. Ghosh and Verma[63] have calculated the quantum defects for these orbitals and found a negative value for the $3d\sigma$ component in contrast to a positive value for the $3d\pi$ component. A similar result was obtained in the case of the σ and π components in 3d complex of NO molecule also (Huber and Miescher[65]). This has

been explained by Jungen[66] as occurring due to penetration effect which is of different origin in various Λ components.

The $3d\delta(E^2\Delta)$ state belongs to Hund's case b and shows the effects of predissociation in that levels with $v > 2$ are not observed. This state combines radiatively with the ground state only giving rise to bands in the ultraviolet region.[7,67,68,80] All bands show evidence of perturbations with the strength of perturbation increasing as we go from $v = 0$ to $v = 2$. It has not yet been possible to decide whether the perturbations are of heterogeneous or homogeneous type. According to Coquart et al.[67] all the perturbations observed here are of the homogeneous type with $C'^2\Delta$ as the perturbing state. However, according to Ghosh and Verma[63] a homogeneous perturbation between a Rydberg and a non-Rydberg state should be very strong and most probably the perturbations are of the heterogeneous type, the perturbing state being a new valence state of the $^2\Pi$ type ($p^2\Pi$). However even these authors agree that the perturbations in the $v = 0$ level seem to be of the homogeneous type.

The $^2\Pi$ state arising from the electronic excitation $v\pi \rightarrow 3d\pi$ expected to lie in between the $3d\delta(^2\Delta)$ and $3d\sigma(^2\Sigma^+)$ states had remained unknown till recently. Ghosh and Verma[63] have however interpreted two new bands observed at 55224 cm^{-1} and 55461 cm^{-1} and showing a rotational structure compatible with a $^2\Pi$–$X^2\Pi$ transition as the (0,0) bands of the subsystems $3d\pi(^2\Pi_{1/2})$–$X(^2\Pi_{1/2})$ and $3d\pi(^2\Pi_{3/2})$–$X(^2\Pi_{3/2})$. They also observed the (1,0) band of this transition which yields a ω_0 value for the $3d\pi(^2\Pi)$ state as 1500 cm^{-1}. Prudhomme and Coquart[79] have observed recently a band at 59798 cm^{-1} in the spectrum of $P^{18}O$ which they have assigned as $(3d\pi)^2\Pi(v = 3) \rightarrow X^2\Pi(v = 0)$. No bands involving $v' = 0$, 1, and 2 are observed in this work and this is attributed to possible predissociations. The bands in both $P^{16}O$ and $P^{18}O$ show severe perturbations some of which are attributed to the $P^2\Pi$ state. The $H^2\Sigma^+$ state arising from the excitation $v\pi \rightarrow 3d\pi$ is known to combine with the $X^2\Pi$ as well as the $B^2\Sigma^+$ state giving rise to bands in the ultraviolet region.[12,13] Only two vibrational levels, viz. $v = 0$ and 1, are known both of which show a large number of localized perturbations. The rotational structure in these bands is cut off at $N = 26$ for bands with $v' = 0$ and at $N = 19$ for bands with $v = 1$.

Two new bands at 60845 and 60622 cm^{-1} have been observed in the absorption spectrum by Ghosh and Verma[63] who have tentatively assigned them as the two (0,0) subbands of the transition $4d\sigma(^2\Sigma^+)$–$X(^2\Pi)$. No other state belonging to the 4d complex is so far known in $P^{16}O$. Prudhomme and Coquart[79] have observed two weak bands in $P^{18}O$ at 59435 cm^{-1} and 59206 cm^{-1} which they have assigned as the (0,0) band of the $4d\delta$–$X^2\Pi$ transition. Further they have also noted a band at 58210 cm^{-1} due to an unassigned $^2\Pi$–$^2\Pi$ transition. It is obvious that this region of spectrum of PO (both the isotopic molecules) deserves further study. The electronic energy T_e of different members of a series of Rydberg levels can be expressed as

$$T_e = I_0 - \frac{R}{(n - \delta)^2}$$

where, I_0 is the ionization potential, R is the Rydberg

TABLE V. Quantum Defects and Dissociation Products of the Various Rydberg States of PO[a]

states	electron configuration	quantum defect		dissociation product
		PO	P	
$A^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 4s\sigma$	1.989	2.17	$3s^2 3p^2 4s + {}^3P$
$I^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 5s\sigma$	1.985	2.17	$3s^2 3p^2 5s + {}^3P$
$^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 6s\sigma$	1.984	2.17	$3s^2 3p^2 6s + {}^3P$
$^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 7s\sigma$	1.984	2.17	$3s^2 3p^2 7s + {}^3P$
$D^2\Pi_r$	$(w\pi)^4(x\sigma)^2 4p\pi$	1.598	1.75	$3s^2 3p^2 4p + {}^3P$
$G^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 4p\sigma$	1.306	1.75	$3s^2 3p^2 4p + {}^3P$
$^2\Pi$	$(w\pi)^4(x\sigma)^2 5p\pi$	1.576	1.75	$3s^2 3p^2 5p + {}^3P$
$^2\Pi$	$(w\pi)^4(x\sigma)^2 6p\pi$	1.582	1.75	$3s^2 3p^2 6p + {}^3P$
$^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 6p\sigma$	1.405	1.75	$3s^2 3p^2 6p + {}^3P$
$^2\Pi$	$(w\pi)^4(x\sigma)^2 7p\pi$	1.632	1.75	$3s^2 3p^2 7p + {}^3P$
$E^2\Delta$	$(w\pi)^4(x\sigma)^3 3d\delta$	0.243	0.36	$3s^2 3p^2 3d + {}^3P$
$^2\Pi$	$(w\pi)^4(x\sigma)^3 3d\pi$	0.050	0.36	$3s^2 3p^2 3d + {}^3P$
$H^2\Sigma^+$	$(w\pi)^4(x\sigma)^3 3d\sigma$	-0.087	0.36	$3s^2 3p^3 3d + {}^3P$
$^2\Sigma^+$	$(w\pi)^4(x\sigma)^2 4d\sigma$	0.005	0.36	$3s^2 3p^2 4d + {}^3P$
$^2\Delta$	$(w\pi)^4(x\sigma)^2 4d\delta$	0.38	0.36	$3s^2 3p^2 4d + {}^3P$

[a] Data from Ghosh and Verma, *J. Mol. Spectrosc.* **1978**, *72*, 200 and Prudhomme and Coquart, *ibid.* **1979**, *74*, 146.

constant, n is the principal quantum number associated with the Rydberg orbital, and δ is the so called quantum defect. Thus, if more than two members of a series are known I_0 and δ can be calculated. Values obtained by Ghosh and Verma[63] as well as Prudhomme and Coquart[79] are given in Table V. The details of the information available about the different states of this molecule are given in Table VI and VII.

5. Other Known States in AsO

All the states known in AsO except one namely $B^2\Sigma^+$ are of the non-Rydberg type. Recently Anderson and Callomon[18] have made an extensive study of the spectrum of this molecule and have reported a large number of states. Relevant information about these states are given in Table VIII. Some of these states have already been discussed above and we would like to consider the remaining ones. Many of the states identified by Anderson and Callomon[18] from observations of new bands involving direct transitions from or to these new states were surmised to exist by the observation of the perturbations produced by these states in other well-known transitions.

A low-lying excited state $Z^4\Sigma^+$ has been reported in AsO. This state has been taken as a repulsive state responsible for the predissociation of all the vibrational levels of the $B^2\Sigma^+$ state above $v = 0$. Though a $^4\Sigma^+$ stable state is known in NO (Ogawa[69]) no such state is known in PO, SbO, and BiO molecules. On the other hand the vibrational levels of the lowest Rydberg state in both NO and PO are known to be perturbed by a $^4\Sigma^-$ state and a stable $^4\Sigma^-$ state is well characterized in BiO. These observations raise doubt about the identification of this state. The $^4\Sigma^-$ state known in PO and in BiO is the lowest $^4\Sigma$ state arising from the configuration $(w\pi)^4(x\sigma)(v\pi)^2$ and is (expected to be) a bound state. It is therefore somewhat surprising that the corresponding $^4\Sigma^-$ state in AsO, could not be marked even after such an extensive study. The approximate constants for the $^4\Sigma^-$ state in AsO are $T_e \sim 31000$ cm^{-1} and $\omega_e \sim 680$ cm^{-1}.

The existence of another new state $M^2\Sigma^-$ (Huber and Herzberg[17] have renamed it a $D'^2\Sigma^-$ state) has been reported from observations of perturbations in the $D^2\Sigma^-$ state of AsO. The $v = 0$ and 1 levels of the $D^2\Sigma^-$ state

TABLE VI. Known Non-Rydberg States in PO and their Molecular Constants

states	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
$X^2\Pi_r$	0 224.03	1233.34	0.7337	Twelve vibrational levels ($v = 0$–11) are known. The spin-orbit splitting is known to change appreciably with v.[72] The λ doubling is small ($p = -0.007$ cm^{-1}). $D_e \sim 6.06$ eV. IP ~ 8.30 eV.
$B^2\Sigma^+$	30 730.88	1164.51	0.7463	Eleven vibrational levels ($v = 0$–10) are known. The levels with $v > 6$ show extensive perturbations. The perturbing states are $A^2\Sigma^+$, $b^4\Sigma^-$, $B'^2\Pi_i$, and $a^4\Pi_i$. The spin splitting constant γ in this state is -0.0068 cm^{-1}. The lifetime in $v = 0$ of this state is found to be 250 ± 10 ns.
$B'^2\Pi_i$	33 120.7	759.2	0.5420	Only two vibrational levels ($v = 0$ and 1) were known earlier. However many new vibrational levels have been marked recently as belonging to it and perturbing $D^2\Pi_i$, $A^2\Sigma^+$, $B^2\Sigma^+$ states. It is confirmed that the $A^2\Pi_i$ and $D'^2\Pi_r$ are in fact the same state.
$C'^2\Delta$	43 742.7	825.7	0.640	Only five vibrational levels ($v = 0$–4) are known. (Levels $v = 14$–18 have been reported as perturbing the $E^2\Delta$ state). All levels show the effect of homogeneous or heterogeneous perturbation. The spin orbit coupling constant A is negligibly small and the spin splitting constant γ is 0.0085 cm^{-1}.
$C^2\Sigma^-$	44 831.7	779.2	0.590	This state has the smallest w_e and B_e values (except $P^2\Pi$) among all the states known in PO. No extensive perturbations are observed in any of the six known ($v = 0$–5) vibrational levels. It has been suggested that the negative λ doubling in the ground state is due to the interaction with this state.
$F^2\Sigma^+$	49 880.0	850	0.608	The eight known vibrational levels are so strongly perturbed that no regular vibrational separation is apparent. The bands involving levels $v = 0$, 1, 6, and 7 are anomalously weak. The perturbations have been attributed to $A^2\Sigma^+$, $G^2\Sigma^+$, $I^2\Sigma^+$, $H^2\Sigma^+$ states. Because of the perturbations the B_v and γ values in the different vibrational levels show no regular behavior.
$P^2\Pi$	51 988.7	475.48	0.5538	Bands recently observed in the vacuum ultraviolet region of the spectrum have been tentatively assigned to a transition from this regular $^2\Pi$ state to the ground state. Though a large number of vibrational levels are known to exist with $A \sim 200$ cm^{-1} their vibrational numbering is still uncertain. Bands involving the $^2\Pi_{1/2}$ component are overwhelmingly predominant and a large number of perturbations as well as localized predissociations have been observed.

show two sets of perturbations namely (1) a weak localized perturbation which is of heterogeneous type probably due to $H^2\Pi_{3/2}$ state (to be discussed later) and (2) strong homogeneous perturbations in both the components at the same J value. This latter observation clearly indicates that the perturbing state is a $^2\Sigma^-$ state. Anderson and Callomon[18] have given the approximate T_e and B_e values for this state. Since no similar homogeneous perturbations are known in any higher vibrational levels of the $D^2\Sigma^-$ state, it is expected that the vibrational frequencies in the $M^2\Sigma^-(D'^2\Sigma^-)$ and $D^2\Sigma^-$ states differ considerably.

A $H^2\Pi$ state arising from the configuration $(w\pi)^3-(x\sigma)^2(v\pi)^2$ is involved in a transition to the ground state giving rise to bands in the ultraviolet region. A peculiar feature of this state is that even though three vibrational levels, viz., 0, 1, and 2 are known in the $^2\Pi_{3/2}$ component, no transition involving the other component, i.e., $^2\Pi_{1/2}$ is observed. If the localized heteroge-

neous perturbations in the $D^2\Sigma^-$ state referred to above are caused by this $H^2\Pi$ state, then this state should either be a regular $^2\Pi$ state with $A \sim 82$–87 cm^{-1} with the perturbing vibrational level as the $v = 1$ level of the $H^2\Pi$ state. Otherwise the $^2\Pi$ state may be an inverted state with A value ~ 515 cm^{-1}, the perturbing level in this case being the $v = 0$ level of the $H^2\Pi_i$ state. The nonappearance of any transition to or from the $^2\Pi_{1/2}$ component (though a weak band has been assigned[18] to the $^2\Pi_{1/2}$–$^2\Pi_{1/2}$ transition, the assignment seems uncertain) has been explained by Anderson and Callomon[18] as due to the large shift of this component caused by a strong interaction with the $A'^2\Pi_i$ state which also arises from the same configuration. Since only one $^2\Pi_i$ state can be attributed to the configuration $(w\pi)^3-(x\sigma)^2(v\pi)^2$, it seems very likely that the $H^2\Pi$ state is a regular doublet with $A = 82$–87 cm^{-1}.

Six vibrational levels ($v = 0$–5) are known in the $A^2\Sigma^+$ state which combined radiatively with the ground state

TABLE VII. Known Rydberg States in PO and their Molecular Constants

states	configu-ration	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
$A^2\Sigma^+$	$4s\sigma$	40 406.8	1390.94	0.7801	This state is involved in a very large number of observed transitions both to non-Rydberg ($X^2\Pi$, $B^2\Sigma^+$, $F^2\Sigma^+$) and Rydberg $I^2\Sigma^+$, $G^2\Sigma^+$ states. Vibrational levels up to $v = 12$ are known and show extensive rotational perturbations. The perturbations are of both homogeneous and heterogeneous type and the perturbing states have been identified as $b^4\Sigma^-$, $B'^2\Pi_i$, $F^2\Sigma^+$, $G^2\Sigma^+$, etc. The spin splitting constant γ in this state is 0.0013 cm^{-1}.
$E^2\Delta$	$3d\delta$	53 091	1456.28	0.7583	All the bands having $v = 2$ are not observed due to predissociation. Even bands with $v = 0$ and 1 also show the effect of perturbations.
$I^2\Sigma^+$	$5s\sigma$	55 458.1	1390.2	0.7798	This state combines with $A^2\Sigma^+$, $B^2\Sigma^+$, $X^2\Pi$, giving rise to bands in the visible and the ultraviolet region. All the three known vibrational levels $v = 0$, 1 and 2 are rotationally perturbed by a $^2\Pi$ state. Levels with $v > 2$ are predissociated by repulsive $A'^2\Sigma^+$ state.
$^2\Sigma^+$	$6s\sigma$	60 729	$\sim$1365	0.785 (B_0)	The $v = 0$ level of this state is involved in bands observed in the vacuum UV region by transition to the ground state. Rotational structure in the $^2\Sigma^+ - {}^2\Pi_{1/2}$ subband could only be analyzed as the $^2\Sigma^+(6s\sigma) - X^2\Pi_{3/2}$ component is strongly overlapped by the (2, 0) band of the E-X system.
$^2\Sigma^+$	$7s\sigma$	63 171		0.783 (B_0)	Only the two subbands of the (0, 0) band of $^2\Sigma^+(7s\sigma) - X^2\Pi$ have been observed. The intensity is very poor and only a few rotational lines could be measured.
$D^2\Pi_r$	$4p\pi$	48 520.0	1358.1	0.755	The $D^2\Pi_r$ state is known to combine with the $B^2\Sigma^+$ state as well as the ground state. All the known vibrational levels ($v = 0$–3) are heavily perturbed by the $B'^2\Pi_i$ state. The rotational structure in all the observed bands is predissociated by the $^4\Pi_i$ state. The coupling in the $D^2\Pi_r$ state is intermediate between case a and case b.
$G^2\Sigma^+$	$4p\pi$	52 412.0	1382.0	0.780	Many transitions from this state to the A, B, and the X states are known. Four vibrational levels ($v = 0$–3) are known. The $v = 1$ level is strongly perturbed homogeneously by the $A^2\Sigma^+$ and the $F^2\Sigma^+$ states and yields an anomalous B_v value. Other levels also show weak perturbations.
$^2\Pi$	$5p\pi$	58 171			Only the (0, 0) band involving $^2\Pi(5p\pi) - X^2\Pi$ has been observed. The rotational structure of the band appears to be homogeneously perturbed. No other component of the 5p complex is known. No accurate vibrational or rotational analyses are as yet available.
$^2\Pi$	$6p\pi$	61 911			The band observed at 1613 Å has been assigned to $^2\Pi(6p\pi) - X^2\Pi$ system. The A value in this state is ~ 0 cm^{-1} indicating that the state belongs to pure case b. The rotational lines are not resolved and only a broad feature near the head is observed.
$^2\Delta$	$4d\delta$	59 922		0.720	Only the (0, 0) band of this transition ($^2\Delta - X^2\Pi$) could be observed for $P^{18}O$. The rotational analysis indicates that F_1 level of this state is perturbed below $J = 14.5$ and F_2 below $J = 10.5$.

and arises from the configuration $(w\pi)^4(x\sigma)(v\pi)^2$. Rotational structure of bands involving the vibrational levels $v = 0$, 1, and 2 have been analyzed and 11 different perturbations have been detected. Callomon and Morgan[35] concluded that seven out of these eleven perturbation are of the heterogeneous type, six of which are due to the crossing of four successive vibrational levels of the $A'^2\Pi$ state and the seventh is due to an unknown $^2\Pi$ state. The four homogeneous perturbations have been explained by Anderson and Callomon[18] as being due to a new $L^2\Sigma^+$ state again arising from the same configuration.

Two more states $E^2\Pi_r$ and F have been reported by Venkataramaiah and Lakshman[70] and attributed to the configuration $(w\pi)^3(x\sigma)^2(v\pi)^2$. The $E^2\Pi_r$ state belongs to Hunds case a with $A = 732$ cm^{-1} whereas the nature of the F state is not yet known. These states have been reported to combine with the ground state but no vibrational or rotational analysis of the bands involving these stats are as yet available. In fact several of the bands assigned to these two systems have been shown to belong to the $A'^2\Pi$–$X^2\Pi$ or the $D^2\Sigma^-$–$X^2\Pi$ systems.

The $L^2\Sigma^+$ state and the F state are quite close in energy to each other and have similar ω_e values. Now

if we agree to the existence of a $^4\Sigma^-$ state parallel to PO in the AsO also, the T_e value for the $^4\Sigma^-$ state, is expected to be $\sim$31 000 cm^{-1}. The estimated ω_e value for this state is also $\sim$680 cm^{-1}. This suggests the possibility that the L and the F states are just two components of the same $^4\Sigma^-$ state. Further study of the perturbations caused by these states is needed before a definite conclusion can be arrived at.

The only Rydberg state known in this molecule, i.e., $B^2\Sigma^+$ gets predissociated at $v = 0$, $N = 20$. It is observed that even though the intensity of some of the rotational lines becomes very small (almost zero) they remain completely unshifted from their expected positions. Beyond $N = 20$ the rotational lines slowly regain their intensity but become very weak again at $N = 35$ (F_1) and at $N = 38$(F_2) before finally regaining their original intensity. No bands with $v > 0$ are observed showing a complete predissociation however Connelly[47] could mark bands up to $v' = 5$ in this state. From this predissociation the dissociation energy of AsO is estimated as 4.98 eV. This value is in good agreement with the value reported by Lau et al.[82] by mass spectroscopic measurements. A summary of the details known about the $B^2\Sigma^+$ state of AsO are given in Table IX.

TABLE VIII. Non-Rydberg States of AsO and Their Molecular Constants

states	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
	0			
$X^2\Pi_r$	1025.97	965.90	0.4855	Bands involving vibrational levels up to $v = 16$ are known. The λ-doubling constant in this state is $p = 0.0179$ cm^{-1} and $A_e = 1026.9$ cm^{-1}. $D_e \sim 4.98$ eV (4.92 ± 0.08 eV).[82] LMR spectrum has been observed in $^2\Pi_{3/2}$ component of this state.
$A''^2\Sigma^+$	16 413	855		A large number of weakly observed bands have been attributed to transitions from this state. Doubts about its reality have been expressed by Anderson and Callomon[18] as well as by Huber and Herzberg.[17]
$A'^2\Pi_i$	26 326	631.87	0.3715	Though bands involving only levels $v = 0$-7 are observed, the higher levels $v = 9$-12 are known to perturb various vibrational levels of the $A^2\Sigma^+$ state. The λ-doubling constant $p \sim -0.002$ cm^{-1}. $A \sim -309$ cm^{-1}.
$E^2\Pi$	27 461	705.5		Most of the bands earlier attributed to the E-X transition have recently been shown to belong to the D-X and H-X systems. The existence of this state is thus doubtful.
F	29 829	689		Again nearly all the bands attributed to the F-X transition have been reassigned to the H-X and the D-X transitions. The reported w_e values for the E and the F states are almost equal. It is possible that these are the two components of a $^4\Sigma$ state.
$L^2\Sigma^+$	31 652	686	0.441	The existence of this state has been predicted on the basis of homogeneous perturbations observed in the $A^2\Sigma^+$ state. No direct transition from or to this state has been observed.
$A^2\Sigma^+$	31 652.45	686.7	0.4624	Bands involving $v = 0$-5 of this state have been observed. All these are affected by perturbations attributed to $A'^2\Pi_i$ and $L^2\Sigma^+$ states. The spin splitting constant $\gamma = -0.035$ cm^{-1}.
$H^2\Pi$	37 053 ($^2\Pi_{3/2}$)	606.9	0.3654	Only one component $^2\Pi_{3/2}$ of this state is known from transition to the ground state giving bands in the ultraviolet region. Three vibrational levels $v = 0$, 1, and 2 are known. The upper two levels $v = 1$ and 2 are known to perturb the $D^2\Sigma^-$ (0 and 1 levels) state. It is not known if the state is a regular one though it seems likely that it is so.
$D^2\Sigma^-$	37 555.4	629.9	0.3973	This state is a well-established $^3\Sigma^-$ state and eight vibrational levels ($v = 0$-7) are known. The $v = 0$ and 1 levels of this state are perturbed weakly by the levels of the $H^2\Pi_{3/2}$ state and more strongly by an unknown $^2\Sigma^-$ state. The spin splitting constant γ in this state changes rapidly with v. The λ doubling in the $^2\Pi$ ground state arises mainly due to the interaction with this state
$D'^2\Sigma^-$	37 857		0.360	This is the state which is homogeneously perturbing the $D^2\Sigma^-$ state. No direct evidence of its existence is available.
$C^2\Delta$	38 662	655.7	0.4164	Bands involving $v = 0$-4 of $^2\Delta_{5/2}$ component and $v = 0$ of the $^2\Delta_{3/2}$ component have been observed. All the levels are perturbed by either $k^2\phi_i$ or $^2\Delta_r$. All the levels of the $^2\Delta_{3/2}$ component above $v = 0$ appear to be predissociated. The spin orbit coupling constant A in this state is ~ 48 cm^{-1}.
$k^2\phi_i$ or $^2\Delta_r$	38 800	600	0.3798	This state is known only from the perturbation it causes in the $C^2\Delta$ state.
$Z^4\Sigma^+$	48 631			This is a repulsive state and is known to predissociate the $B^2\Sigma^+$ ($v = 0$) state.

TABLE IX. Known Rydberg States in AsO and their Molecular Constants

states	configuration	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
$B^2\Sigma^+$	$5s\sigma$	39 866	1098.3	0.5127 (B_0)	$B^2\Sigma^+$ state is the only known Rydberg state in AsO. Only one vibrational level $v = 0$ of this state is known. The higher vibrational levels of this state are predissociated by a repulsive $^4\Sigma^+$ state dissociating into the ground-state atoms. The spin splitting constant in this state is 0.0043 cm^{-1}.

6. Other Known States in SbO

Among the known excited states of the SbO molecule, the states A, B, and C of the non-Rydberg type and the E of the Rydberg type have already been discussed. Three more excited states D($^2\Pi_{1/2}$), F, and G are known for this molecule but since not much is known about the F and the G states further classification of these states into Rydberg or non-Rydberg type is not possible.

The D$^2\Pi$ state in this molecule is peculiar in the sense that associated vibrational frequency is very small in comparison to the corresponding values in other states.

TABLE X. Non-Rydberg States Known in SbO Molecule and Their Molecular Constants

states	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
$X^2\Pi_r$	0 2272	816	0.3569 0.3580	Eight vibrational levels v = 0-7 are known. The spin orbit splitting is 2272 cm^{-1}, indicating that the state belongs to pure case a. The λ doubling in the state is quite large p = 0.107 cm^{-1}, $D_e \sim$ 4.06 eV.
$A^2\Pi$	20 801 20 668	569		This state gives rise to an extensive band system in combination with the ground state. The vibrational frequency in this state is very much smaller than in the ground state and the (0, 0) band is not observed. A is estimated to be 138 cm^{-1} but since rotational analysis has not been made it is not known whether it is a regular or an inverted state.
$B^2\Sigma^+$	26 594	582	0.333 79	The B-X transition is the most intense system in the spectrum of SbO. Except the $(0,0)_{3/2}$ and $(1,0)_{3/2}$ subbands, all the other bands are heavily overlapped by bands of other sequences.
$C^2\Delta_r$	30 315 29 747	568 570	0.3006	A large number of vibrational levels (with v = 0-9 in $^2\Delta_{5/2}$ and v = 0-11 in $^2\Delta_{3/2}$) are known in bands involving transitions to the ground state. It is a regular state with A ~ 562 cm^{-1}. Rotational structure of only one component $^2\Delta_{3/2}$ – $^2\Pi_{1/2}$ has been analyzed.
$D^2\Pi$	35 049	500	0.2777 (B$_1$)	This is a regular $^2\Pi$ state with a small spin orbit coupling (A = 13 cm^{-1}). Rotational structure of bands involving the $^2\Pi_{1/2}$ component only has been analyzed. The band lying at 2959.2 Å assigned earlier as the (2,2) band of the D-X system is now suspected to involve an entirely unknown $^2\Pi$ state as the upper state.
$F^2\Delta$ or $^2\Sigma^+$	38 960	590		Bands involving two vibrational levels v = 0 and 1 have been observed both in emission and absorption. No bands with $v > 2$ appear suggesting a predissociation. No rotational analysis is as yet available, so that its characterization is not yet definite.

TABLE XI. Rydberg State Known in SbO and Its Molecular Constants

state	configuration	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
$E^2\Sigma^+$	$6s\sigma$	39 785	849		$E^2\Sigma^+$ is the only known Rydberg state in SbO and has been observed in emission as well as absorption. Bands involving the levels v = 0 and 1 of this state have a quite simple structure and show double-headed character. The v = 2 level appears to be vibrationally perturbed. Bands with higher vibrational levels are severely overlapped.

This suggests that this state involves the excitation of an electron from a bonding to a strongly antibonding orbital. One possible configuration for this state may be $(w\pi)^4(x\sigma)(v\pi)(u\sigma)$ where $(u\sigma)$ is a strongly antibonding orbital. Only one component of this state has so far been observed and even in that only three vibrational levels v = 0, 1, and 2 are known. The nonobservation of the vibrational levels with $v > 2$ and the observation of the onset of rotational predissociation in a band assigned as (2,0) of the D-X system had been interpreted as evidence that the D state is predissociated beyond v = 2. A recent study[71] of the rotational structure in this (2,0) band has however yielded molecular constants which are very different than those expected on the basis of the known constants for the v = 1 level of the D state. This raises the interesting possibility that perhaps this level earlier assumed as the v = 2 level of the D state belongs to another electronic state.[71] In view of this, nothing definite can be said about the predissociating state but on the assumption that this state arises from ground-state atoms one gets a value ~ 4.48 eV for the dissociation energy of SbO.

The D state was identified earlier as a $^2\Sigma^+$ state by Lakshman[20] but this was modified by Shimauchi[40] who listed it as a $^2\Pi$ state. The study of the rotational structure[22] has confirmed the latter assignment. The observed doublet splitting is only 13 cm^{-1}, indicating that this state is analogous to the $D^2\Pi$ state of BiO and the $H^2\Pi$ state in AsO. In all these cases only one component of the $^2\Pi$ state is observed and the vibrational

frequency in these states is very small in comparison to the value in the respective ground states. It seems very likely that the $H^2\Pi$ state of AsO is also a $^2\Pi_r$ state with a (more probable) configuration $(w\pi)^4(x\sigma)(v\pi)(u\sigma)$ rather than $(w\pi)^3(x\sigma)(v\pi)^2$.

The bands arising from the F-X transition lie in the same region of the spectrum as those ascribed to the E-X system but have opposite degradation. The bands of the F-X system show double heads and the two observed subbands are separated by 2272 cm^{-1}, suggesting that the excited F state is either a $^2\Sigma$ state or a case b $^2\Delta$ state with negligible spin orbit splitting. Only two vibrational levels v = 0 and v = 1 have so far been observed. All the bands with $v > 1$ appear to be predissociated and even the band with v = 1 appears with very poor intensity. Another band system G–X$^2\Pi$ has also been observed by Shimauchi[40] in the same region. The bands of this system have violet degradation but are diffuse and of small intensity. The two components of each band in this transition are again separated by 2272 cm^{-1} showing that the excited state has again negligible doublet splitting and probably belongs to Hunds case b. No rotational analysis of any of these two systems is available so far. The T_e and ω_e and other information available for the different states of SbO are summarized in Tables X and XI.

In addition to these systems a very large number of bands have been observed in the spectrum of this molecule but they are as yet unassigned. Recently some of the unassigned bands observed earlier have been

TABLE XII. Non-Rydberg States Known in BiO and Their Molecular Constants

states	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
$X^2\Pi_r$	0 8000	692	0.3034	Transitions from only one component namely $^2\Pi_{1/2}$ are observed. Seven vibrational levels $v = 0$-6 are known. The λ-doubling in this state is quite large with $p \sim -0.187$ cm^{-1}. A is ~ 8000 cm^{-1} indicating that this state belongs to Hund's case a with a tendency towards case c. $D_e \sim 3.47$ eV.
$A^2\Pi_{1/2}$	14 187	508.8	0.247 10	Only one component $\Omega = {}^1/_2$ of this state could be observed. Vibrational levels with $v = 2$-9 are known of which $v = 6$ and $v = 7$ show effect of perturbations by the ground state levels. λ doubling is quite small with $p \sim 0.025$ cm^{-1}.
$B^4\Sigma^-_{1/2}$	28 738.2	438	0.260	$B^4\Sigma^-$ state of BiO is the only well-characterized $^4\Sigma^-$ state in this group of molecules. Vibrational levels up to $v = 0$-5 of this state are known from bands involving transition from the $\Omega = {}^1/_2$ component to the $^2\Pi_{1/2}$ component of the ground state. Levels with $v > 6$ are predissociated by a state dissociating into ground-state atoms.
$C^2\Delta_{3/2}$	30 700	465 ± 10	0.2548 (B_0)	Only one component of the doublet $\Omega = {}^3/_2$ and in that only the $v = 0$ level is known. The higher levels of this state are predissociated. The λ doubling is very small leading to simple structure of the bands involving this state.
$D^2\Pi_{1/2}$	32 805	343 ± 60	0.2284	$D^2\Pi$ state of BiO is very similar to the $D^2\Pi$ state of SbO. In both the cases the w_e value is very small in comparison to that in the respective ground state. Here again only one component namely $^2\Pi_{1/2}$ is observed. Not only levels with $v > 1$ are predissociated, even in the 0th level higher rotational levels are predissociated as evidenced by a cut off of the structure.

TABLE XIII. Rydberg States Known in BiO and Their Molecular Constants

state	configu-ration	T_e, cm^{-1}	w_e, cm^{-1}	B_e, cm^{-1}	details
E	$7s\sigma$	38 550	769.3		The upper state involved in bands assigned to the E-X transition is expected to be a Rydberg state arising from the $7s\sigma$ configuration. These bands are very intense but are quite diffuse indicating the existence of predissociation.
F		40 941	748		A group of weak bands in the region 2400-2700 Å have been assigned to this transition involving a Rydberg state. The T_e and w_e values of the E and the F states are very similar and it is possible that the two states are just two components of a multiplet state.

shown to belong to SbO$^+$.[73]

7. Other Known States In BiO

Four more states, in addition to the states already described are known in BiO. The D$^2\Pi$ state of BiO molecule is similar to the D$^2\Pi$ state of SbO in having a very small vibrational frequency. Only one component namely $^2\Pi_{1/2}$ is observed and here too only the $v = 0$ level has been observed indicating the presence of a predissociation. Barrow et al.[26] have pointed out that the rotational lines of the bands involving the $v = 0$ level also show predissociation at low as well as at high J values. At intermediate values of J the structure is very intense and sharp. The predissociations in the two λ components of any level appear at different J values indicating that the rotational constant of the predissociating state is very different from the constants for the D state. Hyperfine splitting in the rotational lines have been observed and it is found that the sign of the splitting constant for the D state is opposite to that for the ground state.

The B$^4\Sigma^-$ state in BiO is the only well-characterized $^4\Sigma^-$ state in this group of molecules. Only one component $\Omega = {}^1/_2$ of this state is known. Local perturbations observed in the sixth and seventh vibrational levels of this state have been explained by Barrow et al.[26] as due to higher vibrational levels of the ground state. The $v = 6$ level of this state also shows a predissociation by a state dissociating into ground-state atoms leading to a dissociation energy of $\sim 31\,000$ cm^{-1} for the BiO molecule.

Bridge and Howell[24] had observed two Rydberg type states E and F leading to absorption bands in the region 2400-2700 Å. Later on Barrow et al.[26] rephotographed these bands under higher resolution and dispersion and found that the rotational structure of the bands in both the systems is diffuse and appears to be predissociated. It is not yet clear whether the two groups of bands involve two different excited states or just two components of a common state. The difference in w_e values for the two states is only 0.7 cm^{-1}. The classification made by Bridge and Howell[24] was based on the intensity of the bands. The intense bands were assigned to the E-X transition and the weak bands to the F-X transition. The E state has been assigned to the ....$7s\sigma$ complex. The molecular constants for all the known states of BiO are given in Tables XII and XIII.

8. References

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