JANUARY 15, 1935 PHYSICAL REVIEW VOLUME 47

The Spectrum of AsO

F. A. Jenkins and L. A. Strait, *University of California*

(Received December 3, 1934)

The band-heads of two systems due to AsO have been measured, and the following equations deduced as the best representation of the vibrational structure

$$A:\quad \nu=\begin{Bmatrix}31{,}655.8\\30{,}631.1\end{Bmatrix}+683.8(v'+\tfrac{1}{2})-9.42(v'+\tfrac{1}{2})^2-966.6(v''+\tfrac{1}{2})+4.92(v''+\tfrac{1}{2})^2$$

$$B:\quad \nu=\begin{Bmatrix}39{,}862.0\\38{,}838.3\end{Bmatrix}+1098(v'+\tfrac{1}{2})-6(v'+\tfrac{1}{2})^2-966.6(v''+\tfrac{1}{2})+4.92(v''+\tfrac{1}{2})^2.$$

The intensity distribution in system *A* is normal, but in system *B* the $v'=0$ progression is predominant. This is explained by predissociation, and a value of 4.93 volts is found for the heat of dissociation of AsO.

THE only previous measurements of the bands here ascribed to diatomic arsenic oxide are those of de Watteville,[1] who photographed the ultraviolet spectrum of a flame fed with different arsenic solutions. Because of the small dispersion used, his measurements were accurate to only 0.5A. In the present work, the spectrum was excited by a discharge through the vapors of arsenic and arsenic oxide in a sealed tube, and, considered in connection with de Watteville's work, the experimental conditions indicate that the bands belong to the oxide. This origin is verified, as shown below, by a comparison of the bands with those of the homologous molecules PO and NO. Arsenic consists of a single isotope of mass-number 75, and the chief interest of this spectrum lies in the fact that it extends our knowledge of the spectra of the oxides of the nitrogen group a step further.

Experimental Data

The discharge tube was made entirely of quartz, with a constricted portion 5 cm long and 3 mm in diameter. A plane window was fused on one end, and the other end was sealed off after the introduction of the arsenic oxide and 2 cm of helium. Arsenic was prepared by the thermal decomposition of arsine, and subsequently oxidized by contact with the air. The discharge was obtained by using external electrodes connected to a power oscillator[2] of 5 kw capacity oscillating at a wavelength of 80 m. At room temperature the spectrum of pure helium was obtained, but upon heating to about 400°C the discharge turned a greenish blue. In this stage the spectrum of AsO was strong enough to be photographed in the second order of the 21-foot grating with an exposure of $\frac{1}{2}$ to 4 hours. Iron comparison spectra taken before and after the bands showed no relative shift. In the region λ2327 to λ3091 standards were taken from Jackson's measurements[3] of the iron arc wavelengths.

Two band systems were found, of which that of shorter wavelength corresponded to de Watteville's description. Fig. 1 shows the two regions of the spectrum containing the most intense portions of these systems. The rotational structure is only partially resolved. Each head is a close doublet, and, as will be seen from the measurements of Table I, the double heads are associated in pairs of a constant frequency separation which is the same (1024 cm^{-1}) in both systems. Hence we evidently have a wide electronic doublet, which represents a splitting of the lower state because this state is common to the two systems (cf. Eqs. (1) and (2), below). The two components of the close doublets are probably *R* and *Q* heads in system *A*, which is shaded to the red, and *P* and *Q* heads in system *B*, which is shaded to the violet. In deriving equations to represent the vibrational structure, the *Q* heads

---

[1] M. C. de Watteville, Zeits. f. wiss. Phot. **7**, 279 (1909).

[2] The electrical circuit used here, and a description of the demountable oscillator tube, will be found in a paper by D. H. Sloan, R. L. Thornton and F. A. Jenkins to appear soon in the Rev. Sci. Inst.

[3] C. V. Jackson, Proc. Roy. Soc. **A130**, 395 (1931).

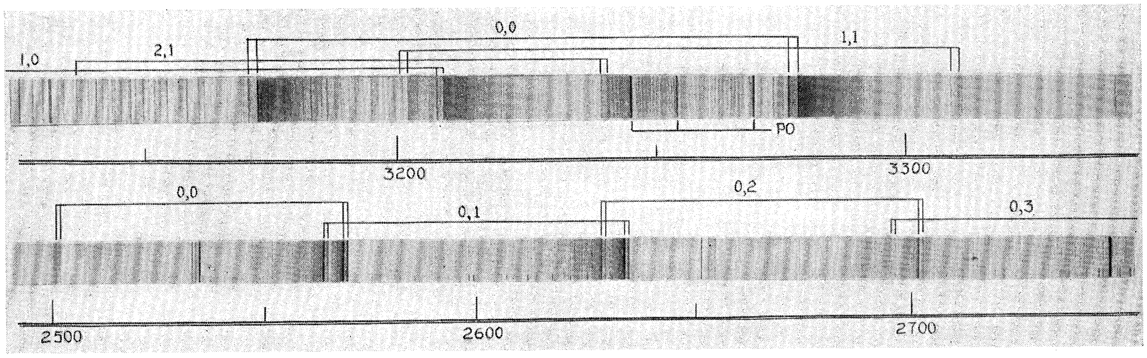

FIG. 1. Enlargements of the AsO bands from first order plates. In the upper system (system A), the 0,0 band of the corresponding system in PO appears as an impurity.

TABLE I. *Band-head frequencies in the spectrum of AsO.*

System A

v' \ v''	0	1	2
0	31,531.8 (3) 31,513.9 (8) 30,505.5 (8) 30,487.9 (10)	30,564.2 (0) 30,556.6 (3) 29,552.3 (3) 29,531.9 (3)	
1	32,192.8 (4) 32,179.1 (5) 31,167.0 (4) 31,153.3 (6)	31,236.9 (1) 31,221.8 (4) 30,212.2 (2) 30,197.2 (4)	
2	32,835.6 (1) 32,824.7 (2) — —	31,878.7 (0) 31,866.9 (3) 30,855.0 (3) 30,842.4 (6)	— 30,919.6 (2) 29,910.0 (1) 29,896.6 (3)
3		— 32,494.5 (1) — —	

System B

v' \ v''	0	1	2	3
0	39,929.7 (4) 39,913.9 (2) 38,903.7 (9) 38,887.1 (5)	38,971.9 (7) 38,957.5 (3) 37,947.4 (10) 37,930.7 (6)	38,024.6 (4) 38,010.6 (2) 37,001.7 (8) 36,988.1 (4)	37,086.6 (1) 37,073.3 (1) 36,065.3 (2) 36,053.1 (1)

were used exclusively. Thus in system A the second and fourth heads listed in Table I under each vibrational transition were used, while in system B, the first and third were used. The results were as follows:

System A

$$\nu=\begin{cases}31,655.8\\30,631.1\end{cases}+683.8(v'+\tfrac{1}{2})-9.42(v'+\tfrac{1}{2})^2-966.6(v''+\tfrac{1}{2})+4.92(v''+\tfrac{1}{2})^2, \quad (1)$$

System B

$$\nu=\begin{cases}40,410.5\\39,386.8\end{cases}-966.6(v''+\tfrac{1}{2})+4.92(v''+\tfrac{1}{2})^2. \quad (2)$$

The mean deviation from the values given by Eqs. (1) and (2) is 0.5 cm^{-1}. However, this does not represent the error of measurement, as is shown by the fact that the combination differences show systematic discrepancies due to the finite distance of the Q heads from the origins. Further data on the rotational structure would be necessary if the vibrational constants in these equations were to be much improved.

Another band of system B was observed by de Watteville at 40,996.4 and 41,016.6. No trace of this occurs on our plates. If it actually belongs to this system, it probably represents the high-frequency component of the 1,0 band. With this assignment, the value of $\Delta G_{\frac{1}{2}}'$ becomes 1086.9, and the system origins are approximately 39,867 and 38,843 cm^{-1}. The levels of Fig. 2a are drawn using these values.

DISCUSSION

Fig. 2 represents the known electronic states of NO, PO and AsO, with the vibration frequencies, ω_e, associated with each and the observed

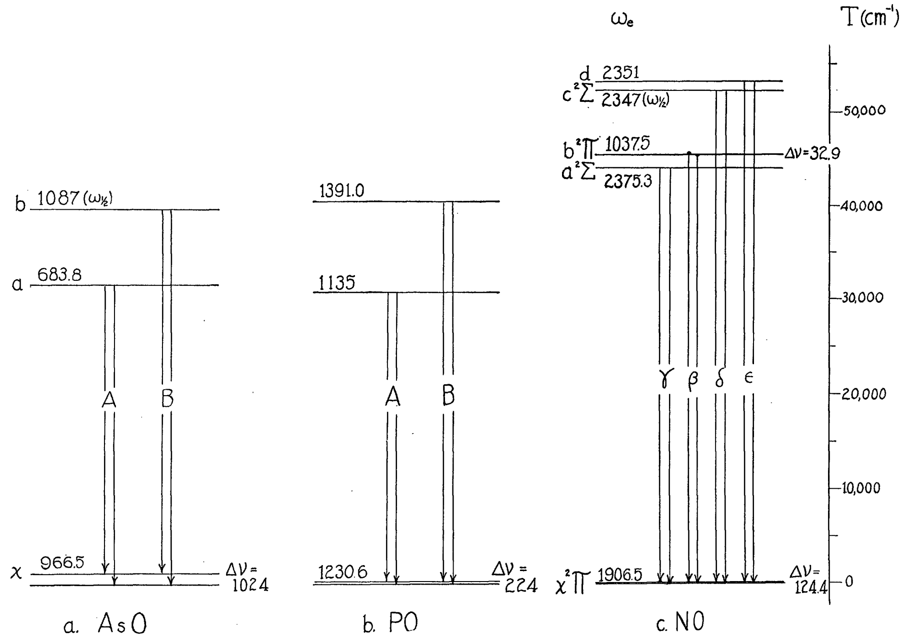

FIG. 2. Known electronic states of the oxides of the nitrogen group.

transitions. In PO, the higher-frequency system (Geuter's B system) has been measured very completely by Ghosh and Ball,[4] while the data on the A system are taken from unpublished work by R. Grinfeld and one of us. The analogy between the spectra of AsO and PO is very close. In each case we have one loosely-bound and one tightly-bound excited state. The latter was assumed by Ghosh and Ball to correspond to the $a^2\Sigma$ state in NO, and the same analogy can be carried over to the b state of AsO. That the a state of AsO is of the same character is shown by the similarity of the A and B systems with regard to number of heads and variations in the separation of the close double heads, the chief difference being that the binding is much weaker in the a state. The A system shows none of the characteristics of a $^2\Pi$, $^2\Pi$ system, and hence is not the analogue of the β system of NO. More probably it is to be correlated with the δ system, whose upper state is $c\ ^2\Sigma$.

It will be seen from Table I that only the $v'=0$ progression is observed in system B. This is the more remarkable because the vibration frequencies in the upper and lower states are not very different, so that we should expect by the Franck-Condon principle the occurrence of fairly long sequences. It indicates strongly the existence of predissociation for the states above $v'=0$. A similar effect is found in the β system of NO, where the breaking-off occurs at $v'=4$, and has been ascribed to predissociation by Kaplan.[5] The possible observation of a 1,0 band in the flame spectrum by de Watteville does not rule out the possibility of predissociation, since it is well known that bands from predissociated states may appear in emission at higher pressures.[6]

The marked difference in intensity between the electronic doublet components of system B, which can be seen from the visual estimates given in parentheses in Table I and also from inspection of Fig. 1, is another peculiarity of this system, undoubtedly related to the predissociation. The low-frequency component is about twice as strong. Some preferential effect of the predissociation for one of the components of the upper state (F_1 or F_2 if it is $^2\Sigma$) is here indicated.

A fairly exact value of the heat of dissociation of AsO can be obtained from the predissociation limit. The height of the $v=0$ level of the b state is 39,929 cm^{-1}, or 4.93 volts. The products of dissociation are almost certainly two normal

---

[4] P. N. Ghosh and G. N. Ball, Zeits. f. Physik **71**, 362 (1931).

[5] J. Kaplan, Phys. Rev. **37**, 1406 (1931).

[6] G. Herzberg, Erg. Exakt. Naturw. **10**, 207 (1931).

atoms, ^4S and ^3P of As and O, respectively, since there are a number of repulsive states derived from this combination. Furthermore, a linear extrapolation to convergence of the vibrational levels of the normal state gives 46,943 cm^{-1}, and such a procedure usually leads to values which are 20 to 30 percent too high. Therefore we conclude that 4.93 volts is a reliable value for the heat of dissociation.

During the present investigation, there appeared a report of work on the AsO bands by Shawhan and Morgan.[7] Their analysis of system *A* is different from ours, in that the electronic doubling is given as 644 cm^{-1}, and the vibration frequency in the upper state 372 cm^{-1}. In view of the good agreement we find for the doubling in the two systems, and of the fact that 372 cm^{-1} is almost impossibly low in comparison to 966 for the normal state, there seems no doubt as to the correctness of our values for this system. These authors have apparently mistaken the vibration frequency in the upper state for the electronic difference. Their analysis of system *B* is in essential agreement with ours, and extends it to higher vibrational states in the upper state by the equation $G'=1098(v'+\frac{1}{2})-6(v'+\frac{1}{2})^2$. Assuming the correctness of these constants, we calculate the origins of system *B* to be 39,862.0 and 38,838.3 cm^{-1}. In their preliminary report, Shawhan and Morgan give no statement about the specific bands with $v'>0$ which are observed, nor about their intensities. It is stated, however, that the bands were excited in the arc and the flame in emission, and also observed in absorption in the flame. If our conclusions are correct as to the predissociation, it seems probable that these additional bands were observed in absorption.

---

[7] E. N. Shawhan and F. Morgan, Phys. Rev. **47**, 199A (1935) (St. Louis Meeting, 1934).

JANUARY 15, 1935 PHYSICAL REVIEW VOLUME 47

A New Type of Expansion in Radiation Problems

W. W. HANSEN,* *Stanford University*

(Received August 9, 1934)

A new type of expansion of $\mathbf{i}(1)e^{ikr_{12}}/r_{12}$ is developed. Here $\mathbf{i}$ is a vector function of the spherical coordinates denoted by 1 and r_{12} is the distance between two points denoted by 1 and 2. This expansion is used in the solution of Maxwell's equations and a simple general expression is found for the energy radiated from a known current distribution. A brief application to Dirac's theory of radiation is given. An expansion for $\mathbf{i}(1)/r_{12}$ is developed which can be used to find the vector potential due to a steady current distribution.

THE well-known expansion of $e^{ikr_{12}}/r_{12}$ in terms of spherical harmonics and half-order Bessel functions provides a method of evaluating $\int(e^{ikr_{12}}/r_{12})\rho(1)d\tau_1$, which is a solution of the inhomogenous wave equation. But the same method is not very satisfactory for the solution of the corresponding vector wave equation because in any coordinates except Cartesian it is rather difficult to keep the various components separate. In the present paper a new type of expansion is found which avoids this difficulty.

Guided somewhat by the expansion for the scalar case we anticipate an expansion of the form

$$\mathbf{i}(1)e^{ikr_{12}}/r_{12}=\sum a_{kl}\mathbf{A}_k'(2)\mathbf{A}_l(1)\cdot\mathbf{i}(1). \quad r_2>r_1 \quad (1)$$

Here vectors are in bold faced type, and the **A**'s are solutions of the vector wave equation; **A**$'$ is to bear the same relation to **A** as the Hankel function does to the Bessel function in the scalar case.

Now from each solution of the scalar wave equation we can construct three and only three independent solutions of the vector wave equation; for example in Cartesian coordinates we have only to multiply the scalar function by each of the three unit vectors. There are, of course, an infinite number of possible sets of functions but the ones most suited for present purposes are constructed as follows. Let ξ be a solution of the scalar wave equation, say

---

* National Research Fellow at Massachusetts Institute of Technology.

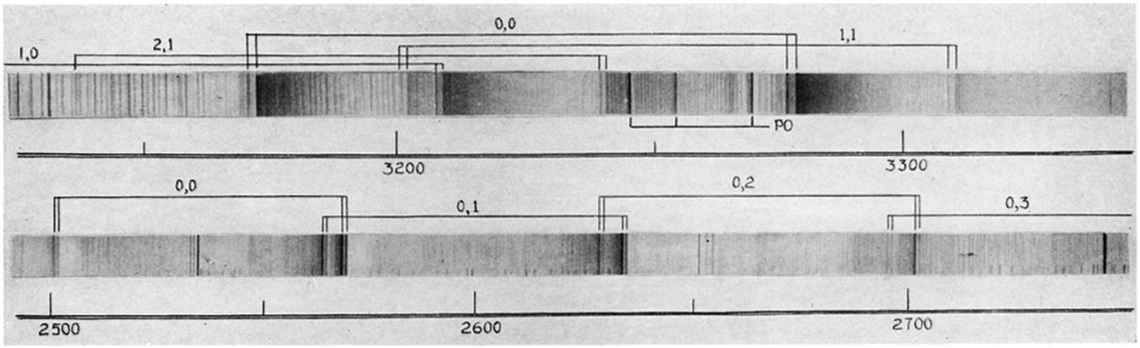

FIG. 1. Enlargements of the AsO bands from first order plates. In the upper system (system *A*), the 0,0 band of the corresponding system in PO appears as an impurity.