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ABSTRACT

The emission spectrum of $As^{16}O$ and $As^{18}O$ was excited in low pressure vapors and photographed with dispersions between 2.5 and 0.1 Å/mm. Vibrational isotope analysis confirmed the earlier assignment of bands in the systems A and B, but lead to a new assignment of bands belonging to the C-X and D-X system. A rotational analysis of the B-X system indicated that the transition is $^2\Sigma^+ - {}^2\Pi(a)$ with $B' = 0.525\ cm^{-1}$ and $B'' = 0.492\ cm^{-1}$. A strong predissociation in state B at v=0 and N = 20 ($As^{18}O$: N = 23) indicates that the dissociation energy of AsO is $\geq 40100\ cm^{-1}$ (4.98 eV). From partial analysis of fine structure it was concluded that the character of states A and D is $A^2\Sigma$ and $D^2\Delta$ with a $B_A \sim 0.46$ and $B_D \sim 0.43\ cm^{-1}$.

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I. INTRODUCTION

Bands of spectra assigned to arsenic monoxide have been correlated to transitions between six excited electronic energy levels and the ground state. Two of these transitions, A-X and B-X, consist of very strong pairs of double headed bands. Both have been vibrationally analyzed twice and independently[1,2] and it was assumed that both, A (T_e ~31700 cm^{-1}) and B (T_e ~39900 cm^{-1}) were $^2\Sigma^+$, while the ground state X (T_e ~0, and 1025), in agreement with NO, almost certainly must be $^2\Pi(a)$. The bands of transition B-X are blue degraded, and B is, therefore, a Rydberg state. In recent years some weaker bands were reported and vibrationally assigned to transitions from states C and D,[3] one probably $^2\Pi$, the other $^2\Delta$, and to two states E and F,[4] both probably $^2\Pi$.

The purpose of the present work was to confirm the assignment of the new bands to AsO, to confirm vibrational numbering and to study the rotational fine structure of selected bands. It was also hoped that rotational constants, at least for the ground state, could be computed, since AsO is the last V-row oxide for which the internuclear distance is not yet available.

II. EXPERIMENTAL

The emission spectrum of $As^{16}O$ and $As^{18}O$ was excited in an electrodeless discharge with a 2450-Mc/sec microwave generator. Sealed quartz tubes, 12 cm long and 8 or 12 mm in diameter, containing 100μg or less arsenic oxide and a pressure of 0.1 mm Hg of krypton, served as light source. The tubes were prepared by outgassing the quartz at 1000°C and a pressure below 10^{-6} mm Hg. The arsenic oxide was produced in the tubes by burning 100 μg arsenic metal (99.9999+%) in an oxygen (99.999+%$^{16}O_2$, or 98.+%$^{18}O_2$) atmosphere at a pressure of 10 mm Hg. After removal of the oxygen excess, and after addition of 0.1 mm Hg krypton as starter gas, the tubes were sealed. Tubes prepared in this way were free from impurities for 12 or more hours of operation. At room temperature the emission was mainly from arsenic atoms. Optimum emission from diatomics was obtained by heating the tubes to 300°C. Spectra were recorded on three spectrometers: (1) low dispersion spectra (2.5 Å/mm) for the measurement of band heads and vibrational isotope shifts were photographed on a Jarrell-Ash 3.4 Wadsworth instrument, using an iron arc as wavelength standard, (2) high dispersion spectra for analysis of high vibrational levels were recorded in the third order of a 21 ft. Paschen instrument with concave grating, giving a dispersion of 0.4 Å/mm; and (3) high dispersion spectra for the analysis of fine structure and band heads were studied in the 18th to 23rd order of a 20 ft. Czerny-Turner spectrometer equipped with a $5\frac{1}{4}$ in Harrison grating blazed for 64°, giving a dispersion of 0.15 to 0.10 Å/mm. The isolation of high orders was controlled by passing the light, before entrance into the spectrometer, through a predispersing set up consisting of an adjustable slit, a 60° quartz prism and three lenses. Thorium lines were used as wavelength standards on instrument (2) and (3). All spectra were recorded on 103a-O Kodak spectroscopic plates with exposure times varying between 10 sec and 30 min.

III. RESULTS AND INTERPRETATION

A. System $B^2\Sigma^+ - X^2\Pi(a)$

While Connelly[2] observed this system up to high v', Jenkins and Strait, using low pressure sources, found no indication of levels with $v' \geq 0$. They also concluded that a strong predissociation was responsible for an anomalous intensity distribution between $\Pi_{1/2}$ and $\Pi_{3/2}$. In Table I, band heads for $As^{16}O$ and $As^{18}O$, and measured as well as computed isotope shifts are listed. We could not observe $v' = 1$ or higher, confirming Jenkins and Strait's[1] observation. High dispersion spectra of (0.0) $\Pi_{1/2}$ and (0.0)$\Pi_{3/2}$ showed that each double headed band consists of four branches. The rotational analysis indicated that the long wavelength band head $\Pi_{1/2}$ is formed by P_1 lines, while the head towards shorter wavelength contains Q_1 and R_1 lines (Fig. 1). The ^{S}R lines are very weak, and the ^{Q}P and ^{R}Q lines are either too weak for observation or coincide with the corresponding Q_1 and R_1 lines. The $\Pi_{3/2}$ heads are much stronger and consist, at longer wavelengths, of a ^{O}P head, and, at shorter wavelengths, of P_2 head. The Q_2 and R_2 lines are also very strong, while the satellites ^{P}Q and ^{Q}R are missing. This analysis indicates that the upper state of the transition is $^2\Sigma^+$. Table II lists the stronger lines of the $(0.0)_{1/2}$ head at 2504 Å. It can be seen that lines to levels with $N' \geq 20$ are missing. In $As^{18}O$ the predissociation starts at levels with $v' = 0$ and $N' > 23$. The lack of lines with $N' \geq 20$ and 23 respectively makes a rotational analysis at medium dispersion impossible, and even at d = 0.12 Å/mm only 10 Q lines are sufficiently resolved for measurement, but the predissociation helped in establishing the relative numbering of lines in the different branches. The B values deduced from Δ_1F and Δ_2F

differ less than 0.2%, indicating that the rotational levels are unperturbed below the predissociation limit. The effective B_0 value of the $\Pi_{1/2}$ and $\Pi_{3/2}$ components are, within experimental limits, the same with $B''_{eff} = 0.492\ cm^{-1}$ and $B' = 0.525\ cm^{-1}$.

B. The Dissociation Energy of AsO

From the predissociation v = 0 N = 20 of the B state conclusions about the dissociation energy of arsenic oxide can be drawn. Since lines with $N > 20$ are missing or too weak for observation, it can be concluded from Kronig's rules that the predissociation is caused by a state with $\Delta\Lambda = \pm 1$ and probably the same multiplicity as the perturbed B state which has $^2\Sigma^+$ character. The predissociation is, therefore, likely to be caused by a $^2\Pi$ or a $^2\Sigma^+$ state. The combined ground state atoms As(^4S) and O(^3P) form, besides several quartet and sextet states, only one $^2\Pi$ and one $^2\Sigma^+$ each, the $^2\Pi$ state being the ground state of the molecule. The perturber might, therefore, be $^2\Sigma^+$. This conclusion agrees well with the fact that the D state (see below), presumed to be $^2\Delta$, does not predissociate at energies as high as 45,000 cm^{-1}. The perturbing $^2\Sigma^+$ state arises from a molecular orbital configuration:

$$\ldots (\sigma\, 2p)^2 \ (\pi\, 2p)^4\ \overline{\sigma}\, 2p$$

and corresponds to the repulsive A' state in the electronically isovalent molecule NO.[5] The upper limit for the dissociation energy of AsO is, therefore, $D_0^\circ \leq 40,100\ cm^{-1}$ (4.98 eV).

C. System A-X

The vibrational analysis of the A-X system was reported earlier.[1,2] Table III lists some strong bands and includes the corresponding heads of $As^{18}O$, together with measured and calculated isotpoe shifts. The transition was assumed to be $^2\Sigma - {}^2\Pi$, the ground state being the X state since the bands appear in paris separated by 1025 cm^{-1}. The splitting also indicates that the upper state, A, has no or only a very small multiplet separation. High dispersion photographs show that the strong double heads are accompanied on the low wavelength side by at least one weak satellite not listed in Table III. The rotational lines show doubling in all branches. The doubling increases in the (0.0) band linearly with N with a γ value of ~ 0.013 cm^{-1}. This large splitting could be due to the large magnetic moment caused by the contribution of the close by $E^2\Pi$ state to the electronic orbital angular momentum. An approximate effective B value for the A state was deduced from averaged R_c and R_d lines, using the ground state $B_0 = 0.492$ cm^{-1} as obtained from the B-X system. Thus B was determined to be ~ 0.45 cm^{-1}. A detailed analysis of this band system is with the present excitation not possible, but since the line doubling increases linearly with N, it is probable that the state A is indeed $^2\Sigma$.

D. System D-X and C-X

Weak bands have been recently reported[3] which fit in a vibrational analysis for two new states of AsO. In the present work some of these bands were also observed, and isotope shifts were measured. Fig. 2 shows some of the bands of system C which overlaps system D.

Two sets of bands were observed: (1) Sharp double headed bands with strong Q heads forming and extended system, and (2) bands consisting of strongly blended overlapping heads. The latter resolved, in high dispersion, into a large number of weak branches. The true band heads of this system were very weak, and the low dispersion heads proved to be apparent heads only, formed by coinciding strong lines of different branches. The isotope and Deslandres correlation of bands belonging to the blended system was therefore, much less accurate than the plate measurements, and bands of the weak system are not included in Table IV. Isotope shifts indicated that the origin of both systems are very close. The origin of the band system of Table IV is at approximately 37600 cm^{-1}. The listed heads are probably transitions of an upper state with small doublet splitting, perhaps a $^2\Sigma$, to one component of the $X^2\Pi$ ground state of AsO. A different excitation of systems C and D is needed before a rotational analysis becomes feasable.

IV. CONCLUSION

In the present work isotopic substitution was used to confirm the vibrational analysis of bands belonging to the systems A-X and B-X. A rotational analysis of the B-X system was performed and B_o and r_o were deduced for the states $X^2\Pi(a)$ and the B Rydberg state which was shown to have $^2\Sigma^+$ character. Approximate B values were also deduced for the states A and D, using the B values of the ground state and averaged R branches, of the (0.0) and (0.1) heads. The bands belonging to the system D were newly assigned, taking into account the isotope shifts observed for $As^{18}O$. The character of the not yet fully analyzed states A, C, and D could not be conclusively deduced, but the states seem to be $^2\Sigma$ and $^2\Delta$.

From Fig. 3, and molecular orbital comparisons,[3,5,6] it seems likely that the Rydberg state B corresponds to state A of PO and, probably, A of NO. The AsO state E,[4] which was not reinvestigated during this work, correlates most probably, to the B state of NO and NS. The $\Delta\ ^2\Delta$ state also correlates nicely with the states A of NS and B' of NO. The correlation of the two $^2\Sigma$ states A and C is not clear at this time, and it is, in view of the uncertainty of the character assignment, premature to discuss their relative position.

Further analysis of the 11 electron oxides would be greatly helped, if light sources could be found which give selective excitation. Preliminary experiments indicate that active oxygen flames might prove helpful.

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Table I. Strong Band Heads of $B^2\Sigma^+ \rightarrow X^2\Pi(a)$ Transition

$X^2\Pi$ Multiplet	v', v"	branch forming head	energy in cm^{-1}(a)		isotope shift in cm-1 (b)	
			$As^{16}O$	$As^{18}O$	obs.	comp.
1/2	0.0	Q_1	39929.7	39923.5	6.2	(c)
		P_1	39913.9	39910.6	3.3	
3/2	0.0	P_2	38900.4	38899.1	9.1	(c)
		^{O}P	38885.0	38882.0	3.2	
1/2	0.1	Q_1	38970.0	39010.0	40	45
		P_1	38956.0	38997.0	41	
3/2	0.1	P_2	37945.0	37989.1	44	45
		^{O}P	37931.0	37973.7	42	
1/2	0.2	Q_1	38022.0	38107.5	85	88
		P_1		38096.3		
3/2	0.2	P_2	36999.0	37084	85	88
		^{O}P		37071		

(a) ±0.2 cm^{-1} for (0.0), for all others ±1 cm^{-1}

(b) ±0.5 for (0.0), for all others ±2 cm^{-1}

(c) the (0.0) isotope shift was used to compute the experimentally not observed $\omega_e' = 1095 \pm 2\ cm^{-1}$.

Table II. Strong Lines of (0.0) $B^2\Sigma^+ \rightarrow X^2\Pi_{1/2}$ Head

(energies ± 0.5cm^{-1})

N^1	$R_1, {}^RQ$	$Q_1, {}^QP$	P_1
20		39933.66	39912.18
19	39953.78	32.95	13.50
18	52.12	32.32	13.77
17	50.49	31.76	14.14
16	48.95	31.22	14.56
15	47.44	30.82	15.07
14	46.00	30.75	15.64
13	44.54	30.39	16.21
12	43.29	30.00	16.82
11	42.02	29.96	17.60
10	40.84	29.68	18.37
9	39.68	29.49	19.21
8	38.61	29.37	20.17
7	37.56		21.04
6	36.61		
5	35.70		
4	34.84		
3	34.04		
2			
1			
0			

Table III. Strongest Band Heads of $A[^2\Sigma] \rightarrow X^2\Pi(a)$

$X^2\Pi$ multiplet	v',v"	Energy in cm^{-1}(a) $As^{16}O$	$As^{18}O$	Isotope Shift, in cm^{-1} (b) obs.	computed
1/2	0.0	31531			7
		31515			
3/2	0.0	30505.4	30510.0	5	7
		30487.3	30493.9	7	
1/2	1.1	31236	31256	20	21
		31220.6	31241.1	21	
3/2	1.1	30211.6	30230.7	19	21
		30196.7	30216.8	20	
1/2	2.2	29906	29943	37	36
3/2	2.2	29893	29931	38	36
1/2	1.0	32193	32167	-26	-26
		32179	32154	-25	
3/2	1.0	31166	31144	-22	-26
		31152.6	31134	-19	
1/2	0.1	30491	30541	50	53
		30469	30531	52	
3/2	0.1	29549	29600	51	53
		29529	29582	53	

(a) ±1 cm^{-1}; ±0.2 cm^{-1} if additional digit is listed. The bands are weak, but distinctive satellite heads, approximately 10-15 cm^{-1} above the high energy head.

(b) ±2 cm^{-1}.

Table IV. Strong Heads of D → X System

(Energies in cm^{-1})

$\Delta\nu$	As^{16}O (a)	As^{18}O (a)	Δ i		v', v"
			measured	calculated	
596	40426	40308	118	120	5.0
600	39830	39731	99	100	4.0
603	39230	39158	72	75	3.0
	38627	38580	47	50	2.0

(a) ± 2 cm^{-1}

Table V. Molecular Constants of $^{75}\mathrm{As}^{16}\mathrm{O}$

$D_0^\circ \leq 40100\ \mathrm{cm}^{-1}$ (4.98 eV)

	T_e	ω_e	$\omega_e x_e$	B_o	r_o
$B^2\Sigma^+$	39865	1098		0.525	1.561
$D\ [^2\Delta]$	~ 37600	610	4	0.46	
$[C^2\Sigma]$	~ 37500	660			
$A\ [^2\Sigma]$	31655	685	~ 5	0.43	
$[E^2\Pi]$	~ 27000	714			
$X\ ^2\Pi$	1025 0	967	~ 5	0.492	1.612