ISOTOPE SHIFT STUDIES OF THE ULTRA-VIOLET AND VISIBLE BANDS OF $P^{16}O$ AND $P^{18}O$*

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ABSTRACT

The spectra of $P^{16}O$ and $P^{18}O$ were excited in sealed discharge tubes containing neon (2–3 mm. pressure), oxygen gas enriched to 65 per cent. of ^{18}O and trace amounts of phosphorus vapour and photographed on a 3 m. grating spectrograph at a dispersion of 2·5 Å/mm. Isotope shift studies in the β-bands confirmed the earlier vibrational scheme of Curry *et al.* and showed conclusively that the red as well as the violet degraded bands belonged to the same β-system. The present studies of isotope shifts also confirmed the vibrational assignments of the extensive ultra-violet bands involving the $^2\Sigma^- - X^2\Pi$ transition and the γ-bands ($A^2\Sigma^+ - X^2\Pi$). In the case of the visible bands, they provided evidence for the first time that the bands at 5585 Å, 5962 Å and 6385 Å belonged to one system and involved 0-0, 0-1 and 0-2 transitions respectively.

INTRODUCTION

ISOTOPE effect is of great value in the study of molecular spectra. In the case of extensive bands, such as the $^2\Sigma^- - X^2\Pi$ bands of PO, vibrational analysis is not unique unless confirmed by isotope shift studies. Another important application of isotope effect is the identification of a band system. Often, several bands are assigned on the basis of their appearance and expected differences in the vibrational frequencies of successive bands of a progression or a sequence. In the case of the β-system of PO, the bands are found to change their shading and hence some authors have attempted to assign the bands to two different systems, one red and the other violet degraded. It is realised, however, that degradation of bands is not a sensitive criterion for the assignment of bands. A study of the β-bands of $P^{16}O$ and $P^{18}O$ in the present investigations has shown conclusively that both

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the red and violet degraded bands belong to the same $B^2\Sigma^+ - X^2\Pi$ band system. Isotope shifts of the visible bands have given evidence for the first time that the bands at 5585 Å, 5962 Å and 6385 Å belong to one system and involve 0–0, 0–1 and 0–2 transitions. These and other studies relating to the γ-bands of PO are described in the present paper.

EXPERIMENTAL

The spectra of PO were excited in sealed discharge tubes containing neon (at 2–3 mm. pressure), oxygen gas enriched to 65 per cent. of ^{18}O and trace amounts of phosphorus vapour. The discharge tubes were prepared in the manner described by Tomkins and Fred and were excited by a micro-wave oscillator of frequency 2450 mc./sec. The resulting spectra were photographed on a Jarrell-Ash grating spectrograph at a dispersion of 2·5 Å/mm.

VIBRATIONAL STRUCTURE ANALYSIS AND ISOTOPE SHIFT STUDIES

(i) *The β-bands: $B^2\Sigma^+ - X^2\Pi$ system.*—The β-bands, which are readily excited in discharges through oxygen and traces of phosphorus, lie in the region of 3000–3700 Å. They are shown in Fig. 1. Some of the bands are degraded to red while others are degraded to violet. There are also a few headless bands. Curry, Herzberg and Herzberg (1933) proposed all of these bands to belong to a single system. Ramanadham, Rao and Ramasastry (1946) assigned the bands to two systems, one containing the red degraded bands and the second containing violet degraded bands. Dressler (1955) made a detailed investigation of the β-bands and proposed only a single vibrational scheme, wherein he included the red as well as the violet degraded bands.

A rotational structure analysis of the red as well as violet degraded bands would enable which of them have a common upper or lower state, and thus confirm their vibrational scheme. The only satisfactory rotational analysis thus far made was by Singh (1959) who showed the three violet degraded bands at 3246, 3255 and 3380 Å to be the 0–0, 1–1 and 0–1 bands respectively of the β-system. The uncertainty of assignment of the rest of the bands, especially the red degraded ones, still remains unsolved as their rotational structures are yet to be analysed. The present investigations of the β-bands of $P^{16}O$ and $P^{18}O$ are undertaken with a view to provide their correct vibrational assignment.

In these investigations, the band heads of $P^{16}O$ and $P^{18}O$ bands are measured (Table I) and the isotope shifts observed in them are compared

TABLE I

Isotope shifts of PO β-bands

Band $v'-v''$	$P^{16}O$		$P^{18}O$		$v^i - v$	
	λ	ν	ν^i	λ^i	Obs.	Cal.
6–5	3198·78 R	31252·9	..	..	..	−0·86
	3218·06 R	31065·6	31076·2	3216·97	10·6	10·3
0–0	3245·01 V	30807·7	30808·5	3244·92	0·8	1·4
	3246·31 V	795·4	795·6	3246·28	0·2	..
	3268·60 V	585·3	30586·1	3268·52	0·8	..
	3270·55 V	30567·1	569·8	3270·26	2·7	..
1–1	3253·78 V	30724·6	30729·6	3253·6	5·0	5·0
	3255·39 V	709·5	715·4	54·76	5·9	..
3–3	3296·38 R	30327·6	39344·2	3294·58	16·6	15·5
4–4	3311·84 R	30186·0	30208·5	3309·37	22·5	22·4
5–5	3302·91 R	30267·6	30297·9	3299·61	30·3	30·4
	3328·31 R	30036·6	30067·0	3324·95	30·4	..
6–6	3321·05 R	30102·3	30142·0	3316·68	39·7	39·5
	3346·27 R	29875·4	29915·0	3341·85	39·6	..
7–7	3340·69 R	29925·4	29975·5	3335·10	60·1	49·7
	3365·99 R	29700·4	29750·3	3360·34	49·9	..
8–8	3362·10 R	29734·8	29795·7	3355·23	60·9	61·0
	3387·80 R	29509·3	29571·2	3380·70	61·0	..
0–1	3379·77 V	29579·3	29626·0	3374·45	46·7	46·5
	3405·71 V	29354·0	29401·1	3400·26	47·1	..
9–9	3385·58 R	29528·6	29603·0	3377·07	74·4	73·4
1–2	3387·80 V	29509·3	29557·7	3382·25	48·4	49·1
	3414·13 V	29281·7	29331·5	3408·32	49·8	..

TABLE I (*Contd.*)

Band $v' - v''$	P ^{16}O		P ^{18}O		$\nu^i - \nu$	
	λ	ν	ν^i	λ^i	Obs.	Cal.
2–3	3397·79 V	29422·4	29475·8	3391·64	53·4	52·9
	3324·57 V	29192·4	29246·4	3418·25	54·0	..
3–4	3409·81 V	29318·7	29378·6	3402·86	59·9	57·7
5–6	3460·33 R	28890·7	28964·4	3451·52	73·7	70·7
6–7	3478·54 R	28739·5	28818·7	3468·98	79·2	78·8
0–2	3523·31 V	28374·3	28464·9	3512·09	90·6	90·7
	3551·38 V	28150·0	28241·2	3539·92	91·2	..
1–3	3530·38 V	28317·5	28409·4	3518·96	91·9	92·4
	3558·70 V	28092·1	28184·9	3546·98	92·8	..
2–4	3539·37 V	28245·5	28340·6	3527·50	95·1	95·1
3–5	3550·32 V	28158·4	28257·8	3537·83	99·4	99·0

with those calculated on the basis of vibrational assignments made by Dressler and given in Columns 6 and 7 of Table I. Since the agreement between the isotope shifts is well within the experimental errors, the vibrational assignment of the bands proposed by Curry *et al.* (1933) and later by Herzberg (1950) and by Dressler (1955) is confirmed.

It is interesting to note that the broad structure at 3387·8 Å in the β-system of P ^{16}O is indeed the superposition of two bands, one of which is the red degraded, 8–8 band and the other, the violet degraded 1–2 band. The corresponding band heads in the spectrum of P ^{18}O occur at 3380·7 Å (8–8 band degraded to the red) and 3382·2 Å (1–2 band degraded to the violet). The isotope shift of 8–8 band is 61·0 cm.$^{-1}$ while that of 1–2 band is 49·0 cm.$^{-1}$, and these shifts agree with calculated values.

(ii) *The γ-bands: $A^2\Sigma^+ - X^2\Pi$ system.*—During the course of the present studies, the γ-system of P ^{18}O is also recorded. The band heads of P ^{16}O and P ^{18}O shown in Fig. 2 are measured and their shifts in vacuum wave numbers are given in Table II. A few band heads not listed earlier have now been included in Table II and marked with an asterisk. There

TABLE II

Isotope shifts of PO γ-bands

Band $v' - v''$		P ^{16}O		P ^{18}O		$\nu^{18} - \nu$ (cm.$^{-1}$)	
		λ(A)	ν (cm.$^{-1}$)	ν^{18} (cm.$^{-1}$)	λ(A)	Obs.	Cal.
5–3	Q_1	2286·50	43721·6	43605·7	2292·57	−115·9	−115·3
	P_1	2287·95	693·8	43580·8	93·88	−113·0	
	P_2	2298·28	43497·3	43382·3	2304·38	−115·0	
	$^0P_{12}$	2299·98	465·4	357·0	05·73	−108·4	
4–2	Q_1	2293·19	43594·0	43482·7	2299·06	−111·3	−111·6
	P_1	2294·65	566·3	457·3	2300·40	−109·0	
	P_2	2305·00	43370·6	43258·5	2310·98	−112·1	
	$^0P_{12}$	2306·79	337·0	230·5	12·47	−106·5	
3–1	Q_1	..	..	43357·0	2305·73		−107·8
	P_1	2301·42	43438·0	331·7	2306·79	−106·3	
	P_2	2311·91	241·1	43133·9	2317·65	−107·2	
	$^0P_{12}$	2313·57	209·9	104·0	2319·26	−105·9	
2–0	Q_1						−104·0
	P_1						
	P_2	2318·78	43112·9	43007·9	2324·44	−105·0	
	$^0P_{12}$	2320·77	075·9	42978·4	2326·04	− 97·5	
2–1	Q_1	2373·71	42108·2	42056·5	2377·03	− 51·7	− 58·8
	P_1	2375·13	42090·2	033·8	2378·32	− 56·4	
	P_2	2386·35	41892·2	41833·1	2389·72	− 59·1	
	$^0P_{12}$	2387·97	863·9	807·8	2391·17	− 56·1	
1–0	Q_1	2381·84	41971·6	41918·3	2384·86	− 53·3	− 54·0
	P_1	2383·22	947·3	892·2	86·35	− 55·1	
	P_2	2394·52	41749·4	41695·0	2397·64	− 54·4	
	$^0P_{12}$	96·16	720·8	668·8	99·15	− 52·0	

TABLE II (*Contd.*)

Band $v'-v''$		$P^{16}O$ λ (A)	$P^{16}O$ ν (cm.$^{-1}$)	$P^{16}O$ ν^1 (cm.$^{-1}$)	$P^{18}O$ λ (A)	$\nu^1-\nu$ (cm.$^{-1}$) Obs.	Cal.
	Q_1	2453·12	40752·1	40743·5	2453·64	− 8·6	
	P_1	54·45	729·9	722·3	54·01	− 7·6	
1–1							− 8·8
	P_2	2466·61	40529·2	520·5	2467·14	− 8·7	
	$^0P_{12}$	68·15	503·9	497·5	68·54	− 6·4	
	Q_1	2462·66	40594·3	40592·1	2462·79	− 2·2	
	P_1	63·99	572·2	571·2	2464·06	− 1·0	
0–0							3·0
	P_2	2476·20	40372·31	40369·2	2476·39	− 3·1	
	$^0P_{12}$	77·75	346·98	345·6	77·84	− 1·4	
	Q_1	2496·04	40051·5	40067·0	2495·07	+ 15·5	
	P_1	97·36	30·24	49·3	96·17	+ 19·1	
4–5							+ 15·2
	P_2	..	..	..	..	..	
	$^0P_{12}$	..	..	..	..	..	
	Q_1	2517·18	39715·0	39744·0	2515·34	+ 29·0	
	P_1	18·43	695·3	724·9	16·56	+ 29·6	
2–3							+ 28·6
	P_2*	2531·38	39492·3	39521·0	2529·64	+ 28·7	
	$^0P_{12}$*	32·76	470·8	..	..	..	
	Q_1	2527·95	39545·9	39582·5	2525·61	+ 36·6	
	P_1	29·19	526·4	563·5	26·82	+ 37·1	
1–2							+ 35·3
	P_2	2542·25	39323·4	39358·9	2539·96	+ 35·5	
	$^0P_{12}$	43·65	301·8	338·2	2541·30	+ 36·4	
	Q_1	2538·89	39375·5	39418·2	2536·14	+ 42·7	
	P_1	40·13	356·3	399·3	37·36	+ 43·0	
0–1							+ 42·2
	P_2	2553·24	39154·3	39195·5	2550·55	+ 41·2	
	$^0P_{12}$	54·85	129·5	174·5	51·91	+ 45·0	
	$^0P_{12}$	2573·00	38853·5	38903·0	2569·73	+ 49·5	
	P_2	74·17	835·9	885·8	70·86	+ 49·9	
5–7							+ 48·0
	Q_1*	2558·22	39078·0	39129·4	2554·85	+ 51·4	
	P_1*	559·35	060·8	110·2	56·11	+ 49·4	

TABLE II (*Contd.*)

Band $v' - v''$		P ^{16}O		P ^{18}O		$\nu^1 - \nu$ (cm.$^{-1}$)	
		λ (A)	ν (cm.$^{-1}$)	ν^1 (cm.$^{-1}$)	λ (A)	Obs.	Cal.
4–6	P_2	2584·88	38674·9	38730·7	2581·16	+ 55·8	+ 55·5
	$^0P_{12}$	86·14	656·1	712·4	82·38	+ 56·3	
	Q_1*	2570·02	38898·6	38953·7	2566·38	+ 55·1	
	P_1*	71·19	881·0	938·0	67·46	+ 57·0	
1–3	Q_1	2606·65	38352·0	38431·8	2601·24	+ 79·8	+ 78·6
	P_1	07·19	344·0	414·7	02·39	+ 70·7	
	P_2	2621·89	38129·3	38207·7	2616·49	+ 78·4	
	$^0P_{12}$	23·21	109·9	189·5	17·74	+ 79·6	
0–2	Q_1	2619·12	38169·3	38256·3	2613·16	+ 87·0	+ 86·4
	P_1	20·36	151·3	238·8	14·36	+ 87·5	
	P_2	2634·55	37945·8	38032·2	2628·57	+ 86·4	
	$^0P_{12}$	35·94	925·9	013·9	29·83	+ 88·0	
4–7	Q_1	2647·76	37756·6	37850·8	2641·16	+ 94·2	+ 94·9
	P_1	48·91	740·2	836·5	42·16	+ 96·3	
	P_2	2663·57	37532·5	..	..	..	
	$^0P_{12}$	64·65	517·2	..	..	..	
5–8	Q_1	2649·93	37725·6	37811·8	2643·89	+ 86·2	+ 86·3
	P_1	51·08	709·2	796·2	44·98	+ 87·0	
	P_2	..	..	..	..	..	
	$^0P_{12}$	..	..	..	..	..	
3–6	Q_1	2661·10	37567·3	..	..	..	+ 103·5
	P_1	62·53	547·1	37650·8	2655·20	+ 103·7	
	P_2	..	..	37442·3	2669·98	..	
	$^0P_{12}$	..	..	426·2	71·14	..	
2–5	Q_1	2675·31	37367·8	37480·1	2667·29	+ 112·3	+ 112·1
	P_1	76·47	351·6	464·9	68·37	+ 113·3	
	P_2	2691·44	37143·9	37255·8	2683·35	+ 111·9	
	$^0P_{12}$	92·67	126·9	239·4	84·53	+ 112·5	

TABLE II (*Contd.*)

Band $v' - v''$		$P^{16}O$ λ(A)	$P^{16}O$ ν(cm.$^{-1}$)	$P^{18}O$ ν^1 (cm.$^{-1}$)	$P^{18}O$ λ(A)	$\nu^1 - \nu$ (cm.$^{-1}$) Obs.	Cal.
1–4	Q_1	2689·41	37171·9	..	..	..	
	P_1	90·63	155·0	37277·5	2681·79	122·5	120·8
	P_2	2705·67	36948·4	37069·8	2696·82	121·4	
	$^0P_{12}$	06·98	930·5	053·5	98·00	123·0	

* These bands were observed for the first time.

is a fairly good agreement between the observed and calculated isotope shifts indicating that the assignment of vibrational quantum numbers of the PO-γ bands including the new bands observed in the present investigation, is correct.

(iii) *The new* $^2\Sigma^- - X^2\Pi$ *system.*—This is an extensive band system (Santaram and P. T. Rao, 1962; Narasimham *et al.*, 1965) and lies in the spectral region overlapping the strong γ-bands (Fig. 3). In view of the large change in the equilibrium internuclear distances of the $^2\Sigma^-$ initial state, and the $^2\Pi$ final state, only those bands that lie on the open limb of the Condon parabola are intense while the bands along the 0-0 sequence are very weak. Hence from an arrangement of the observed bands in a Deslandres Table, it is not possible to uniquely assign the vibrational quantum numbers for the bands. The lower state is found to be the $X^2\Pi$ ground state, since successive vibrational quanta of this state agree with those of $\Delta G(v + \frac{1}{2})$ of the ground state. The v'' numbering is thus established but the v' numbering is still tentative. The present studies of the isotope shifts of the $^2\Sigma^- - X^2\Pi$ bands allow a correct assignment of the vibrational scheme. Observed isotope shifts, given in Table III, show good agreement with calculated values.

(iv) *Red degraded band system in the visible region.*—Kanaka Durga and P. T. Rao (1958) reported two band systems in the region 5400–6000 Å, both of which have the $B^2\Sigma^+$ state (the initial state of the β-bands) as the common final state. Both the systems are fragmentary. The bands are now obtained using ^{18}O enriched oxygen. Figure 4 shows the band heads due to $P^{16}O$ and $P^{18}O$. The isotope shift is 9 cm.$^{-1}$ for the band at 5585 Å

TABLE III

Vacuum wave numbers of R_1 and Q_2 heads of the bands of $^2\Sigma^- - X^2\Pi_{reg.}$ system of PO

The same have been calculated from the expression:

$$\nu_h = \begin{matrix}43852{\cdot}43\\43628{\cdot}60\end{matrix} + 826{\cdot}37\ (v' + \tfrac{1}{2}) - 6{\cdot}96\ (v' + \tfrac{1}{2})^2 - 1233{\cdot}38\ (v'' + \tfrac{1}{2}) + 6{\cdot}56\ (v'' + \tfrac{1}{2})^2$$

and their differences from the observed values are given in column 5.

$v'-v''$	Sub-heads	Wave-length in air Å	Wave numbers in vacuum cm.$^{-1}$	Obs.–Cal.	Isotope shift	
					Obs.	Cal.
0–0	R_1	2290·292	43649·10	+0·27	..	..
	Q_2	2302·102	43425·20	+0·20	..	..
1–1	R_1	2311·957	43240·10	−0·92	..	..
	Q_2	2323·970	43016·60	−0·59	..	..
2–2	R_1	2334·033	42831·16	−1·25	37·7	38·2
	Q_2	2346·277	42607·63	−0·95	38·4	..
0–1	R_1	2356·208	42428·10	−0·47	52·1	52·8
	Q_2	2368·709	42204·20	−0·54	53·0	..
2–3	R_1	2400·952	41637·46	−0·93	..	..
	Q_2	2413·910	41413·97	−0·59	..	..
3–4	R_1	2424·019	41241·28	−0·82	96·3	95·8
	Q_2	2437·257	41017·29	−0·98	..	..
0–2	R_1	2425·199	41221·22	−0·21	97·3	96·9
	Q_2	2438·440	40997·40	−0·20	97·2	..
1–3	R_1	2447·851	40839·79	−0·07	109·7	110·3
	Q_2	..	..	..	..	..
0–3	R_1	2497·525	40027·57	+0·16	140·3	140·2
	Q_2	2511·570	39803·75	+0·17	140·2	..
1–4	R_1	2520·729	39659·13	+0·17	151·9	152·5
	Q_2	..	..	..	..	..

TABLE III (*Contd.*)

$v' - v''$	Sub-heads	Wave-length in air Å	Wave numbers in vacuum cm.$^{-1}$	Obs.-Cal.	Isotope shift	
					Obs.	Cal.
2–5	R_1	..	..	..	..	..
	Q_2	2559·027	39065·64	−0·24	..	..
0–4	R_1	2573·463	38846·51	0·00	..	..
	Q_2	2588·380	38622·64	−0·04	..	..
1–5	R_1	2597·205	38491·42	+0·24	193·9	193·8
	Q_2	2612·410	38267·39	+0·04	193·5	..
2–6	R_1	2621·493	38134·82	−0·23	205·7	205·3
	Q_2	2636·951	37911·29	+0·07	205·7	..
3–7	R_1	2646·243	37778·17	+0·05	216·7	316·8
	Q_2	2662·017	37554·33	+0·04	216·5	..
1–6	R_1	2677·507	37337·08	+0·56	234·1	234·1
	Q_2	2693·657	37113·24	+0·55	..	..
2–7	R_1	2702·333	36994·09	+0·58	244·6	244·6
	Q_2	2718·780	36770·31	+0·63	244·0	..
3–8	R_1	2727·750	36649·40	−0·30	255·6	255·2
	Q_2	2744·505	36425·67	−0·20	255·3	..
4–9	R_1	2753·663	36304·53	−0·56	..	..
	Q_2	2770·740	36080–79	−0·47	..	..
5–10	R_1	..	..	..	..	..
	Q_2	2797·458	35736·20	+0·35	..	..
2–8	R_1	2787·379	35865·42	+0·33	283·1	283·0
	Q_2	2804·880	35641·64	+0·38	283·0	..
3–9	R_1	2813·210	35534·11	−0·29	292·0	292·6
	Q_2	2831·199	35310·34	−0·23	292·9	..
4–10	R_1	2839·868	35202·55	−0·36	302·4	302·2
	Q_2	2858·010	34979·10	+0·02	301·8	..

TABLE III (*Contd.*)

$v' - v''$	Sub-heads	Wave-length in air A	Wave numbers in vacuum cm.$^{-1}$	Obs.-Cal.	Isotope shift	
					Obs.	Cal.
5–11	R_1	2866·920	34870·40	−0·22	311·0	311·9
	Q_2	..	..	..	..	..
3–10	R_1	2903·374	34432·60	+0·38	328·6	329·0
	Q_2	2922·370	34208·80	+0·41	329·1	..
4–11	R_1	2930·500	34113·90	+0·05	337·5	337·7
	Q_2	2949·817	33890·50	+0·48	337·0	..
5–12	R_1	2958·180	33794·70	+0·02	..	..
	Q_2	2977·857	33571·40	+0·05	..	..
4–12	R_1	3025·979	33037·60	−0·31	..	..
	Q_2	..	..	..	..	..

TABLE IV

Isotope shifts of PO visible bands

Band $v'-v''$		P ^{16}O		P ^{18}O		$v^4 - v$ (cm.$^{-1}$) Obs.
		λ (A)	v (cm.$^{-1}$)	v^4 (cm.$^{-1}$)	λ (A)	
0–0	R_2	5584·69	17901·1	17911·0	5581·62	+ 9·9
	R_1	5588·42	17889·2	17899·6	5585·18	+10·4
	Q_1	5592·97	17874·6	17882·8	5590·42	+ 8·2
0–1	R_2	5962·50	16766·8	16816·7	5944·81	+49·9
	R_1	5967·36	16753·2	16805·7	5948·70	+52·5
	Q_1	5792·99	16737·4	16787·5	5955·16	+50·1
0–2	R_2	6384·7	15658·1	15748·8	6347·93	+90·7
	R_1	6390·0	15645·1	15738·0	6352·28	+92·9
	Q_1	6398·6	15624·1	15717·5	6360·59	+93·4

and increases progressively to 50 cm.$^{-1}$ for 5962 Å band and 90 cm.$^{-1}$ for 6385 Å band (Table IV). These shifts indicate that the bands are the 0–0, 0–1 and 0–2 bands as assigned in Table IV.

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FIG. 1. Isotope shift in the B²Σ - X²Π system of PO

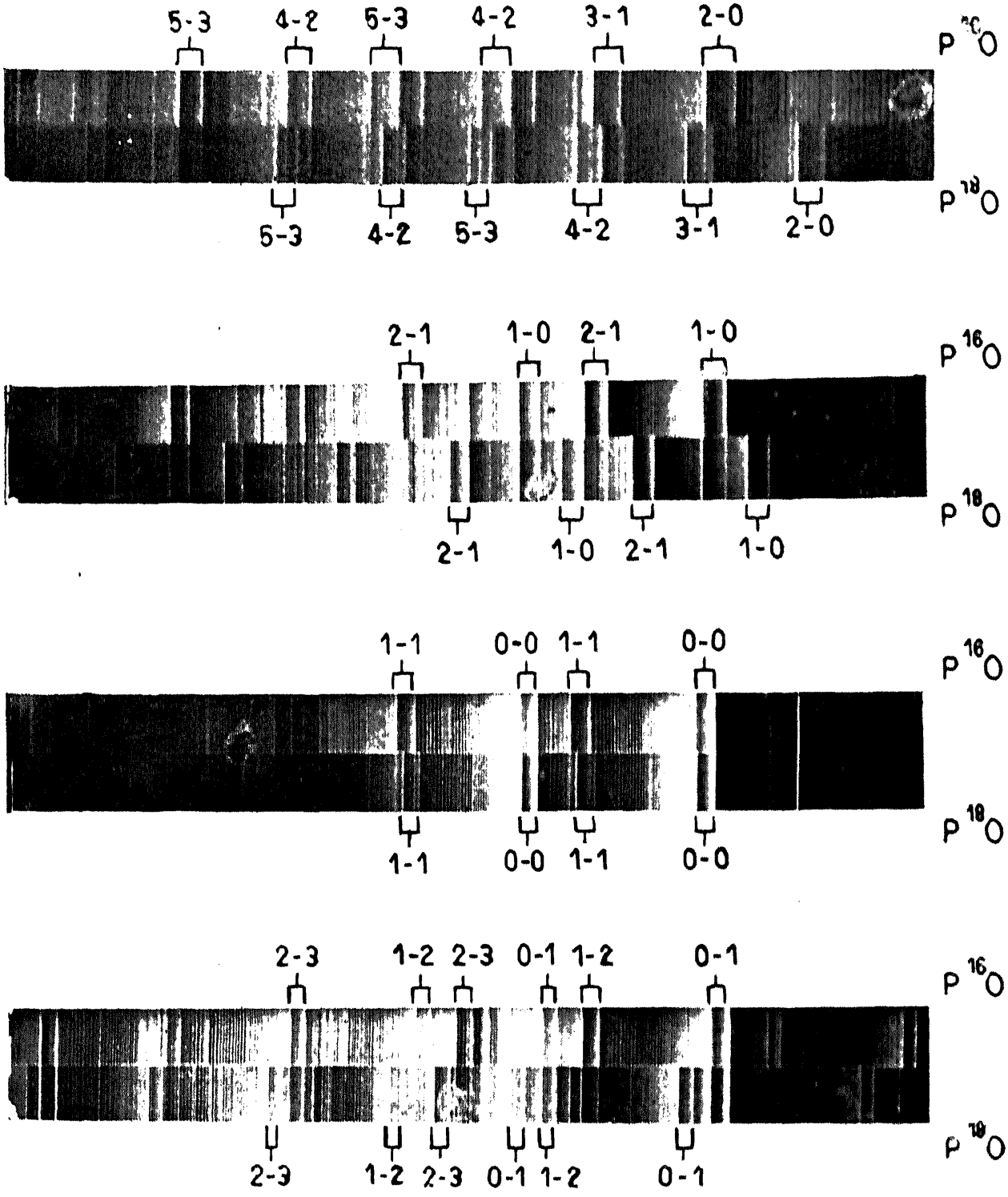

Fig. 2. Isotope shifts in (γ) $A^2\Sigma^+ - X^2\Pi$ system.

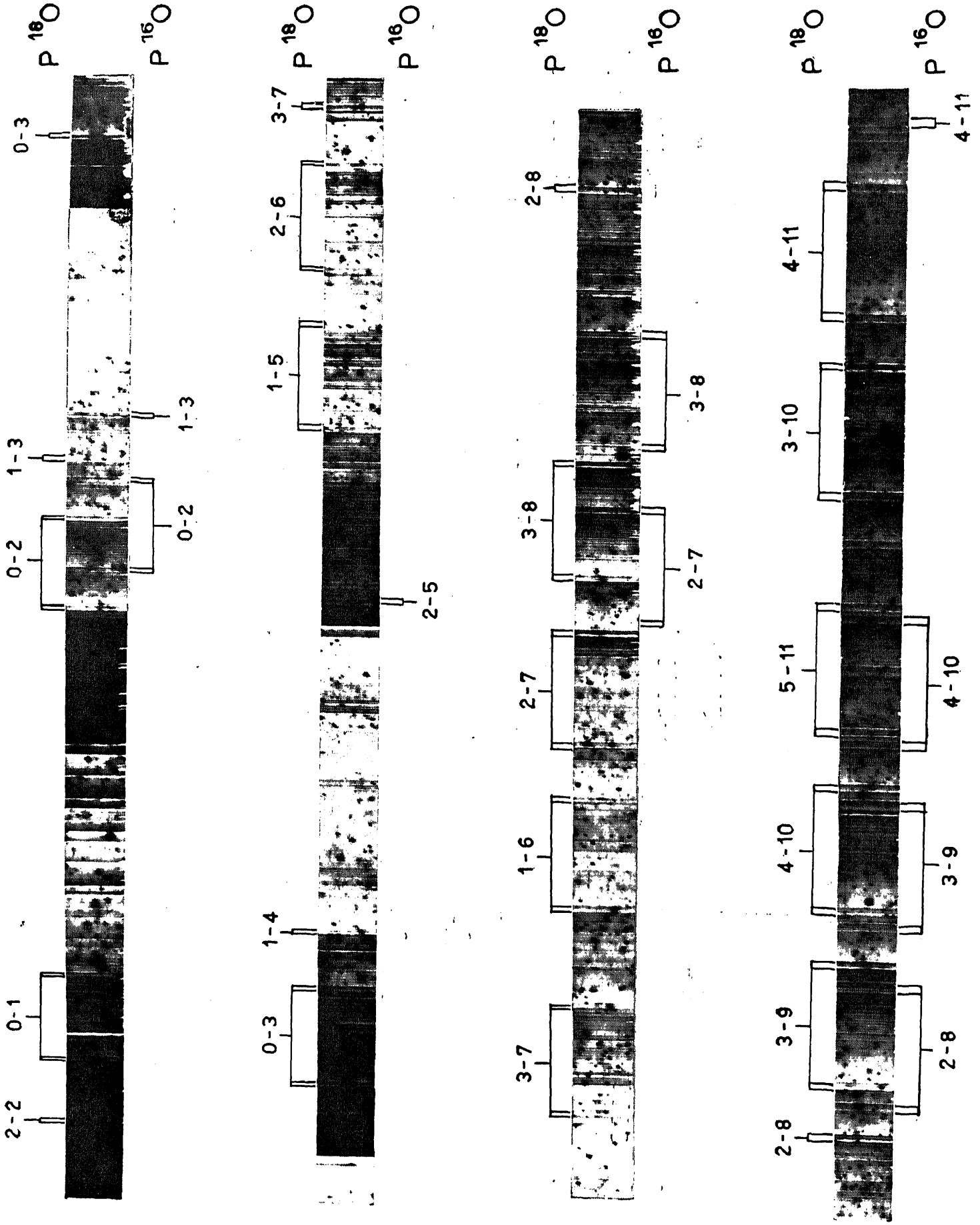

FIG. 3. $^2\Sigma^- - X^2\Pi$ system of P ^{18}O.

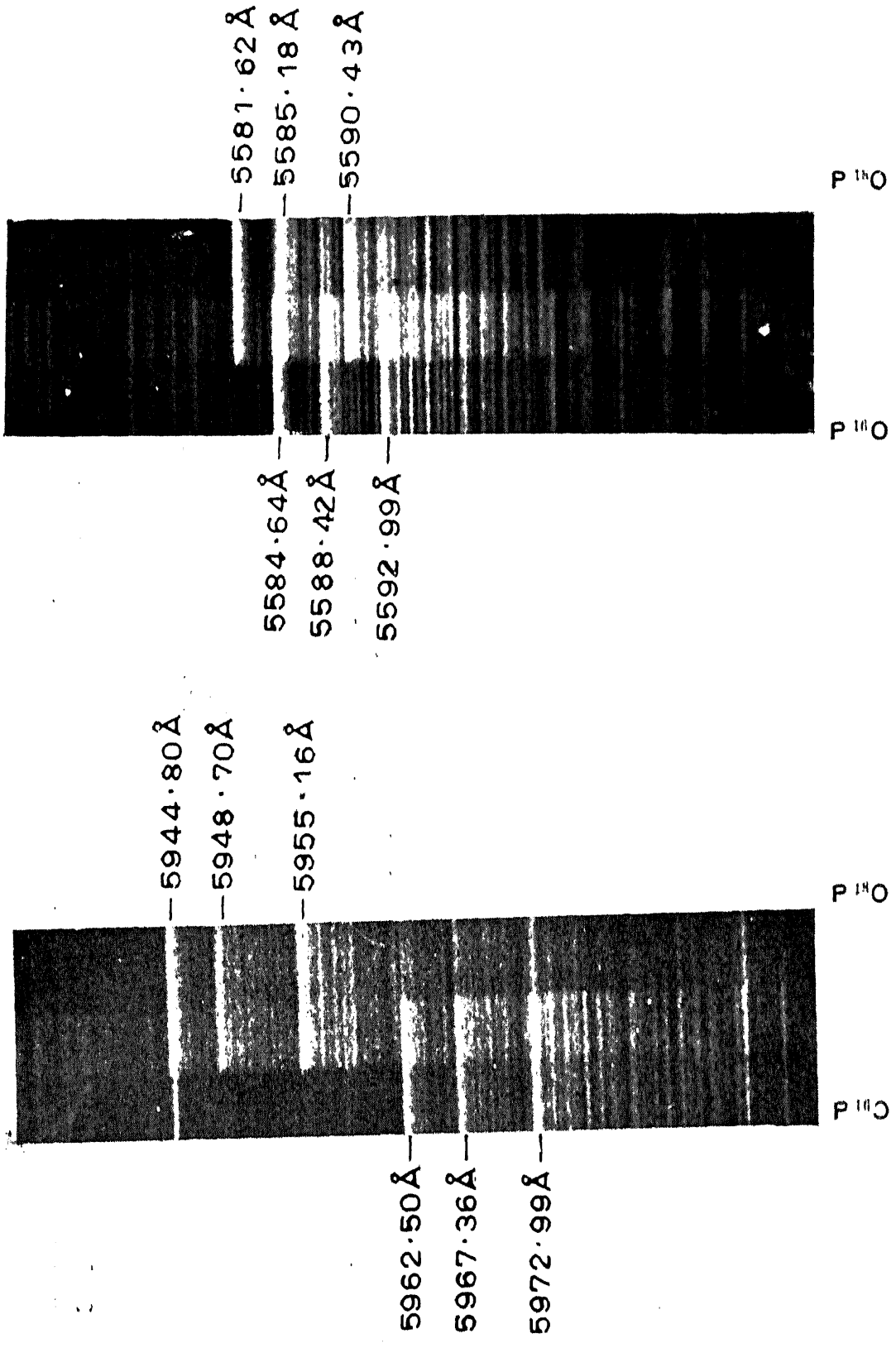

FIG. 4. Isotope shifts in the visible system of PO