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The electronic absorption spectra of the SO_2, SeO_2, and TeO_2 molecules have been studied under widely varied experimental conditions. The vibrational analysis of the ultraviolet absorption region of SO_2 with center of gravity near 2000A reveals that it is formed by at least two electronic systems with the following vibrational constants:

System $\alpha_1 \cdots \nu_0 = 42,170$ cm^{-1}, $\nu_1' = 963$ cm^{-1}, $\nu_2' = 379$ cm^{-1}, $x'\nu_2' = 2$ cm^{-1}.

System $\alpha_2 \cdots \nu_0 = 44,236$ cm^{-1}, $\nu_1' = 775$ cm^{-1}, $\nu_2' = 375$ cm^{-1}.

The presence in the same region of a third electronic system, with $\nu_2' = 360$ cm^{-1} and $\nu_1' = 845$ cm^{-1}, seems highly probable.

The character of the vibrational structure of the band systems and a preliminary analysis of the rotational structure of several bands have enabled us to obtain some information about the molecular structure of the excited states.

The vibrational analysis of the c-system of SeO_2 in the visible, and the TeO_2 bands in the visible and ultraviolet, have enabled us to correlate the electronic states of the three similar molecules.

INTRODUCTION

A CONSIDERABLE amount of work has been done in the last few years, chiefly by Mulliken and his collaborators, in the field of electronic spectra of triatomic molecules. During the war we were engaged on similar problems and started investigations on the electronic spectra of the SO_2, SeO_2, and TeO_2 molecules. The wartime conditions prevented us from publishing our results, with the exception of one paper on the b-system of SeO_2.[1] The present paper deals with the analysis of the a-system of SO_2, in the far ultraviolet (center of gravity near 2000A), the c-system of SeO_2 in the visible, and with TeO_2 bands in the visible and near ultraviolet.

HISTORICAL CONSIDERATIONS

The a-system of SO_2 was first studied in absorption by V. Henri and by Wieland.[2] They correlated the observed bands with three fundamental frequencies of the ground level and assigned the frequencies 960 and 379.5 cm^{-1} to the upper level. In 1933, Chow[3] performed a new analysis and suggested that the bands belong to three electronic systems, each of them being characterized by a frequency of about 750–770 cm^{-1} in the upper evel.

Chow's analysis was criticized in 1938 by Price and Simpson[4] who considered that all the most prominent bands in the region 2300–2000A form a single progression with $\nu_2' = 380$ cm^{-1}.

The a-system of SO_2 was observed by Chow[3] in emission as well as in absorption. Later, Lotmar[5] studied the monochromatically-excited resonance spectra in SO_2 vapor and Kornfeld[6] extended the emission spectra, using electrodeless excitation.

While Chow and Lotmar interpreted the system using an asymmetrical vibration, ν_3'', Kornfeld succeeded in arranging the observed bands using only symmetrical frequencies in both states. In view of the application of the selection rules and the discussion of molecular configurations, these divergencies must be cleared up. On the other hand, the values for the band heads given by different authors are in some cases widely divergent, so that new measures of this system seemed to be of interest. For the present study, we were able to use some spectra taken by V. Henri in 1922 and 1930. The dispersion

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[1] J. Duchesne and B. Rosen, Physica 8, 540 (1941).
[2] V. Henri, *The Structure of Molecules*, edited by P. Debye (Blackie and Son Limited, London, 1932), p. 121; K. Wieland, Nature 130, 847 (1932).
[3] Tung-Ching Chow, Phys. Rev. 44, 638 (1933).
[4] W. C. Price and D. M. Simpson, Proc. Roy. Soc. A165, 272 (1938).
[5] W. Lotmar, Zeits. f. Physik 83, 765 (1933).
[6] G. Kornfeld, Trans. Faraday Soc 32, 1487 (1936).

was either 2A/mm or 5A/mm at 2200A, the pressure varied from 0.5 to 100 mm, and the temperature from $-80°$ to $500°$. The absorption lengths varied from 5 cm to one meter.

VIBRATIONAL ANALYSIS

In the first column of Table I we give the mean value for the band heads obtained on a series of plates taken at $-80°C$ and corresponding to widely varied conditions of pressure and absorption paths. The dispersion was 2A/mm at 2200A, and the difference between individual measures did not exceed 3 cm^{-1}. Some additional band heads measured only on low dispersion plates, and marked with an asterisk, are also included. For these bands the precision is not so good. This is also the case for the last bands situated towards the ultraviolet, where accurate measures of our high dispersion plates are no longer possible.

TABLE I.

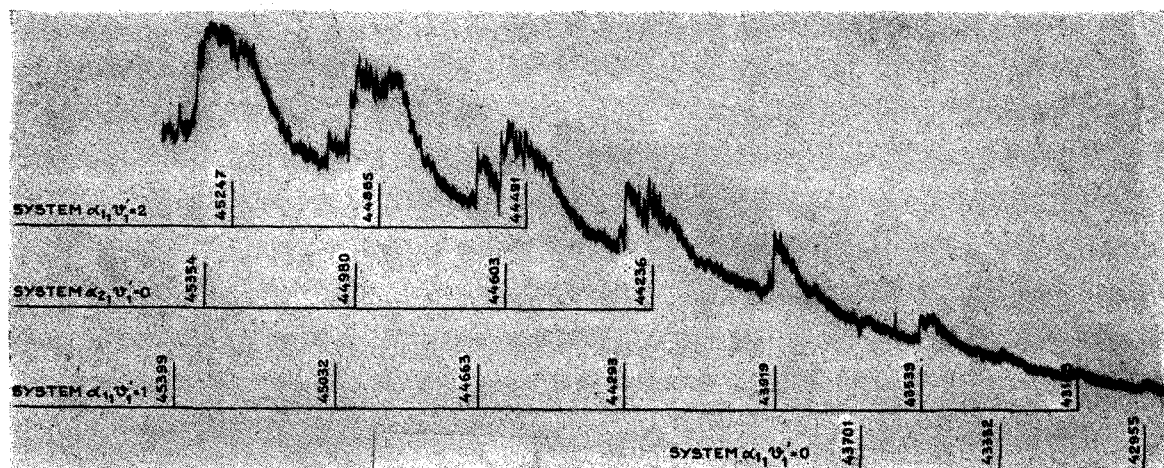| D. and R.	Chow	D. and R.	Chow	D. and R.	Chow	D. and R.	Chow
{42,170(?), 42,183(?)} α₁		{44,663, 44,677} α₁	44,663, 44,674	{46,218, 46,227} α₃	46,217		47,707
		44,885 α₁		46,353 α₃	46,348		47,742
{42,576, 42,589} α₁	42,575, 42,589						47,889
	42,759	{44,966*, 44,980} α₂	44,978, 44,987		46,444		47,922, 47,965
{42,955, 42,968} α₁	42,954, 42,966	{45,032, 45,046} α₁	45,030		46,464		48,000
	43,018	45,160(?)		{46,471*, 46,484} α₂	47,472, 46,482	48,015* α₂	48,005
{43,138, 43,148} α₁	43,137, 43,145	45,247* α₁		46,574 α₃	46,570		48,083
{43,332, 43,343} α₁	43,329, 43,340	{45,337, 45,354} α₂	45,333, 45,351		46,697		48,121
	43,407	{45,399, 45,413} α₁	45,393	46,704* α₃	46,704	48,390* α₂	48,355, 48,375
{43,539, 43,552} α₁	43,538, 43,550	45,499 α₃		46,820* α₂	46,818	α₂	48,724
{43,701, 43,713} α₁	43,714	45,601* α₁	45,572		46,829	α₂	48,781
			45,672, 45,686	{46,866, 46,878} α₂	46,865, 46,874	α₂	49,133
{43,919, 43,930} α₁	43,918, 43,929	{45,710, 45,726} α₂	45,706, 45,725	46,925* α₃		α₂	49,477
44,086 α₁	44,085, 44,100	45,759 {α₁, α₂}	45,757	47,057* α₃	47,052	α₂	49,550
		{45,858, 45,869} α₃	45,859		47,074	α₂	49,910
44,236 α₂	44,236		45,923		47,198	α₂	50,248
{44,293, 44,306} α₁	44,293, 44,305		46,077		47,223	α₂	50,302
44,491(?) α₁		46,085* α₂	46,084		47,232		
44,543(?)	44,570	{46,106, 46,122} α₂	46,104, 46,118	47,257* α₂	47,246		
44,603 α₂	44,603				47,391		
					47,548		
					47,576		
					47,623		
				47,627* α₂	47,636		

FIG. 1.

The third column of Table I contains the band heads observed by Chow[3] at room temperature. The two sets of values are in general in quite satisfactory agreement.

In 1931, V. Henri[2] pointed out that he had observed 120 band heads between 2445 and 2100A. A systematic study of our plates reveals, however, that many of these band heads are, in fact, sub-heads in the fine structure. This point will be discussed in detail below. In any case, the bands given in the first column of Table I are by far the most characteristic of the whole system. The analysis of the spectrum shows that the occurrence of the 380 cm⁻¹ v_2' frequency is beyond any doubt, but we cannot agree with the statement of Price and Simpson[4] that all the prominent bands are members of a single v_2' progression.

The microphotometer record of Fig. 1, corresponding to the long wave-length end of the spectrum, shows clearly that there are at least three superposed series with characteristic intensity distribution around a single maximum. Moreover, intensity-temperature variations indicate definitely that the observed series cannot arise from excited vibrational levels in the normal state. Thus, the distance between the corresponding members of two series must be correlated either to a frequency (fundamental or combination) of the upper level or to the distance between two neighboring electronic states.

The essential results of our new interpretation are summarized in Tables II to V. In Table II the columns represent v_2' series with $v_2' \sim 380$ cm⁻¹. Taking into account the constant difference of about 963 cm⁻¹ between bands of the first

TABLE II. System α_1.

v_2' \ v_1'	0			1			2
0	{42,170	(?)	968	{43,138	(3)		
	{42,183	(?)	965	{43,148	(2)		
	406			402			
1	{42,576	(2)	963	{43,539	(4)	952	44,491
	{42,589	(1)	963	{43,552	(3)		
	379			379			394
2	{42,955	(3)	964	{43,919	(5)	966	44,885
	{42,968	(2)	962	{43,930	(4)		
	376			375			362
3	{43,332	(3)	961	{44,293	(5)	954	45,247
	{43,343	(2)	963	{44,306	(4)		
	370			370			354
4	{43,701		962	{44,663	(5)	938	45,601
	{43,713		964	{44,677	(4)		
	373			369			
5	{—			{45,032	(3)		
	{44,086	(1)	960	{45,046	(2)		
	367						
6				{45,399	(2)		
				{45,413	(1)		
				360			
7				{45,759	(1)		
				{—			

TABLE III. System α_2.

$v_2' \backslash v_1'$	0	1	2	3	4	5	6
0	44,236 367						
1	44,603 377						
2	{44,966 — 44,980 (779) 45,759 373 363						
3	{45,337 (769) 45,354 (768) 372	{46,106 46,122 363					
4	{45,710 (761) 45,726 (758) 375	{46,471 46,484 395	(780) 47,257 (758) 370	48,015 (766) 375	48,781* (769) 352	49,550* (752) 360	50,302*
5	46,085 (781) — 359	{46,866 46,878 (755)	47,627 (763) 334	48,390 (743) 344	49,133* (777) 338	49,910*	
6	{(46,444)* (46,464)* 356			48,724* (753)	49,477* (771)	50,248*	
7	— 46,820						

* Measured by Chow only.

two columns of Table II, we obtain the second characteristic frequency mentioned by V. Henri and correlated with ν_1'. All the values 963 ± 380 cm^{-1} are of course alternative values for ν_1'. All the bands in the first two columns seem to have the same fine structure. For instance, they are all doublets with the same mean separation of about 13 cm^{-1}.

The first band in the second column of Table II shows irregular behavior inasmuch as its distance from the next one has an abnormally high value of 402 cm^{-1}. On the other hand, the doublet separation is definitely smaller than for the other bands (it is only 8 cm^{-1} according to Chow's measure). Both kinds of irregularities result probably from a perturbation affecting the first level of the second series (the first doublet of the first series is too faint and accurate measures are impossible; thus it is not possible to state definitely whether this level is also

perturbed). The other levels seem · regularly spaced, indicating an anharmonity $x'v_2'$ of about 2 cm^{-1}.

The distribution of intensity in the first two columns of Table II is very regular around a single maximum occurring for $v_2'=2$ or 3. The intensities indicated (between brackets) are rough visual estimations, valid only when comparing bands in the same column. It must be noted that bands of the first column appear only at pressures about 10 times larger than those necessary to observe the bands of the second one.

A third group of bands can be fitted into the scheme of Table II as a $v_1'=2$ series. They are blended by strong bands of other series (see Fig. 1) and it is rather difficult to estimate their intensity. Nevertheless, it seems that the maximum intensity for the bands of Table II is reached for the $(1'v_2'0)$ series, and this seems normal in view of the assumed ratio ν_1'/ν_1''

$=963/1151$. The following series could not be observed because their position coincides with strong bands belonging to another electronic transition.

The first column of Table III contains a very strong series, with nearly the same characteristic frequency difference of about 375 cm⁻¹. It also consists of doublets but, contrary to the first two series of Table II, the strongest head is situated towards the ultraviolet, and the doublet separation is larger (17 cm⁻¹ on the average).

The series given in the second column of Table III is not so regular, and at first sight it seems that it could form a continuation of the first one, the bands 46106–46122 following the bands 45710–45726. This arrangement, which would suppose some perturbations, cannot be definitely ruled out. But several arguments can be advanced against it. First of all, the characters of the bands in the first and second columns are somewhat different, the latter being less regular, for instance in regard to the relative intensity in the doublets. The fine structure seems also to be different, and the structures of the bands in the second column are on the whole more complex, probably as a consequence of superpositions of at least two series. A possible confirmation of this point of view is given by the observations made by Chow (at room temperature) of 4 bands at 46444, 46464, 46472, and 46482 cm⁻¹, instead of two bands 46471–46484 observed by us. These 4 bands can be interpreted as nearly superposed doublets belonging to two series. It is to be noted that the first doublet cannot be interpreted as arising from excited vibrational levels of the lower state. It is included (between brackets) in the first column of Table III.

Assuming the existence of two separate series, it is possible to interpret two additional bands which otherwise cannot be easily fitted in the scheme (bands 46085 and 46820 cm⁻¹).

The constant $\Delta\nu$ difference of about 770 ± 370 cm⁻¹ between the first two columns of Table III must correspond to the frequency ν_1'. We admit with Chow that the most probable value is $\nu_1' = 770$ cm⁻¹. The next columns of Table III contain further bands measured towards the ultraviolet, as well as the most characteristic bands measured by Chow. In this region the characteristic frequency difference of about 770

TABLE IV. System α_3.

	0		1		2
0	45,499	(854)	46,353	(845)	47,198*
	359				
1	{45,858 / 45,869	(846)	46,704	(844)	47,548*
	359				
2	{46,218 / 46,227	(839)	47,057	(832)	47,889*
	356				
3	46,574				
	351				
4	46,925				

* Measured by Chow.

cm⁻¹ is clearly visible on the records given in Chow's paper. It is predominant further to the ultraviolet, according to Herreng,[7] and to not yet published results obtained in our laboratory by P. Migeotte.**

For the system of Table III, the ν_1' series are much more developed than for the system of Table II corresponding to the decreasing ν_1'/ν_1'' ratio.

TABLE V. Absorption bands of SO_2 arising from excited vibrational levels of the ground state.

ν	Arising from:	Corresponding band arising from (0″0″0″)	$\Delta\nu$
{41,620 / 41,633	(2″0″0″)	{43,919 / 43,930	2,299 / 2,297
41,807	(1″0″0″)	42,955	1,148
{41,987 / 41,998	(1″0″0″) / (1″0″0″)	{43,138 / 43,149	1,151 / 1,151
{42,059 / 42,073	(0″1″0″) / (0″1″0″)	{42,576 / 42,589	517 / 516
{42,249 / 42,387	(1″1″0″) / (1″0″0″)	43,919 / 43,539	1,670 / 1,152
{42,766 / 42,776	(1″0″0″) / (1″0″0″)	{43,919 / 43,930	1,153 / 1,154
43,020	(0″1″0″)	43,539	519

Mean values: $\nu_1'' = 1,151.5$ cm⁻¹ from infra-red[8] $\nu_1'' = 1,151.38$
  $\nu_2'' = 517.3$ $\nu_2'' = 517.84$

[7] P. Herreng, Rev. d'optique 15, 413 (1936).
** According to preliminary results of P. Migeotte, it seems probable that a new electronic transition is responsible for bands in the 1900–1800A region.

The two schemes of Tables II and III contain nearly all the strong bands observed by us and by Chow, with the exception of the bands denoted α_3 in the Table I. On account of their great relative intensity, it is difficult to correlate the latter with an asymmetrical frequency. For this reason, the possibility that they belong to a third electronic system must be taken into consideration. For this hypothetical third system, the scheme of Table IV with $\nu_1' = 845$ and $\nu_2' = 360$ cm^{-1} seems to be the most probable one.

The third column of Table IV corresponds to bands observed by Chow only. They cannot be explained as arising from excited vibrational levels of the ground state. A study further to the ultraviolet is of course necessary before reaching definite conclusions concerning the reality of this system.

Under the conditions of our experiments, bands corresponding to excited vibrational levels of the ground state are practically lacking at $-80°$, but they are easily observed at $20°$. An accurate measure of these bands is possible only on the long wave-length side of the $(0'0'0')$ $-(0''0''0'')$ band of the α_1 system, and the mean values obtained for several bands at temperatures ranging up to $335°$ are given in Table V. For ν_1'' and ν_2'' the mean values obtained are in good agreement with the values given by Barker[8] on the basis of infra-red analysis. $\Delta\nu$ values for the first two bands of Table V indicate a small but definite anharmonicity for ν_1''.

ROTATIONAL STRUCTURE

The dispersion used did not allow a complete resolution of the fine structure, but some very characteristic features of this structure were observed. For instance, the coarse K-structure was analyzed for several bands situated at the long wave-length end of the spectrum, where blendings are less frequent than in other parts of the spectrum.

It can be seen easily that the structure of all bands in the first two columns of Table II is similar, thus reinforcing our previous assumption that these bands belong to the same electronic transition. On the other hand, we have observed two series of sub-bands (p and r) in the K-

structure of several α_1 bands; this indicates that they belong to the perpendicular type. Using the second differences, we obtain $C' - C'' = -0.7$ ± 0.10 cm^{-1}. Taking into account the value $C'' = 1.8$ cm^{-1}[***] and the fact that the K-structure is degraded towards the red, it can be stated that $C' = 1.1 \pm 0.10$ cm^{-1}.

With the dispersion used, the J-structure remains completely unresolved, but there are indications that the convergence is slow.

For this reason, it can be reasonably admitted that the change of B correlated with the electronic transition is small; even the sense of the degradation in the J-structure is not clear, but it seems to be rather degraded in the same direction as the K-structure, i.e., toward the red. This statement is enhanced by the lack of marked absorption on the short wave-length side of the K-heads, even at high pressure.

It should be of great interest to resolve the fine structure of the α_2 bands given in the first two columns of Table III. All that can be said for the time being is that it seems to be very different from the structure of the α_1 bands (Table II). Our previous arguments in favor of separating the observed bands into at least two electronic systems are thus reinforced.[†]

INTERPRETATION OF THE RESULTS

The molecular orbitals for C_{2v} symmetry are distributed among four classes, following the symmetry of the wave functions with respect to the planes of symmetry of the molecule. These classes have been described by Mulliken as a_1, a_2, b_1, and b_2. On this basis and by the application of the molecular orbital theory, Mulliken[9] has proposed a scheme of the electronic levels of angular molecules and particularly of SO_2. He has given a preliminary interpretation of the observed electronic spectra of this molecule and

[***] In our previous letter (Nature 157, 692 (1946)) we had erroneously given the value $C'' = 1.6$ cm^{-1}. This error does not affect our results.

[†] It must be stated, however, that the alternative arrangement, according to which the bands of Table II and Table III form a single electronic system, though rather improbable cannot be definitely ruled out. In fact, from a strictly numerical point of view it would be possible to consider the first two columns of Table II and the columns of Table III as consecutive v' series with ν_1' increasing from 965 ± 380 to 1062 ± 375 and reaching 1150 ± 370 cm for $\nu_1' = 2$.

[9] R. S. Mulliken, Rev. Mod. Phys. 14, 204 (1942).

[8] E. F. Barker, Rev. Mod. Phys. 14, 198 (1942).

has considered the a-system as resulting from an allowed transition $3b_2 \rightarrow 5a_1$.

In the first part of this paper we have explained that the "a-system" must be divided into at least 2 electronic transitions corresponding to Tables II and III and described, respectively, as α_1 and α_2.

The molecular constants of the upper state of the two systems are the following:

$\alpha_1 \cdots \nu_1' = 963$ cm^{-1}, $\nu_2' = 379$ cm^{-1},

$\qquad x'\nu_2' = 2$ cm^{-1}, $\nu_0 = 42{,}170$ cm^{-1}.

$\alpha_2 \cdots \nu_1' = 775$ cm^{-1}, $\nu_2' = 375$ cm^{-1},

$\qquad\qquad\qquad \nu_0 = 44{,}236$ cm^{-1}.

The high transition probability for both systems and the lack of antisymmetrical vibrations indicate that they are presumably due to allowed transitions; it must be stated however that the α_2 bands are much more intense than the α_1 bands. As already remarked, the α_1 bands appear to be of perpendicular type; according to group theoretical rules they must thus correspond to one of the three transitions: $a_1 - a_1$, $a_1 - b_1$, and $a_2 - b_2$. The first assignment is partially in agreement with the theoretical scheme proposed by Mulliken.†† In fact this scheme predicts two transitions in the 2000A region, one of them corresponding to $4a_1 - 5a_1$ ($\perp$ type), the other to $3b_2 - 5a_1$ ($\parallel$ type). It seems thus possible to correlate α_1 with the first and α_2 with the second one. The relative intensities of both systems are also in agreement with Mulliken's prediction. This interpretation, however, cannot be definitely accepted because Mulliken predicts $\Delta\alpha > 0$ for the $4a_1 - 5a_1$ transition, while, as we shall see below, we have deduced $\Delta\alpha < 0$ from our analysis of rotational structure.

It is also to be noticed that, while the α_1 system is weak relatively to α_2, it is much stronger than the b-system at 3000A, corresponding to $1a_2 - 2b_1$; this seems also contrary to Mulliken's predictions.

For this reason, the other possibilities mentioned above cannot be disregarded.

As the transition $a_1 - b_1$ has already been correlated with the c-system (λ max $\sim$3700A),[9] we have to emphasize only the third one, i.e.,

$1a_2 - 4b_2$. However this would require, according to Mulliken's scheme, 10 ev, instead of about 5 ev, according to our analysis. But it must be noted that even the energetic position of $3b_2$ has not been determined with certainty experimentally and that according to Mulliken all the calculations have not much more than a qualitative meaning. If α_1 corresponds really to $1a_2 - 4b_2$, it should be necessary to reconsider theoretically the variation of $4b_2$ with respect to the apex angle α of the molecule.

On the other hand, we have said that B' must be nearly equal to B'' while C' is very different from C''. If so, we have a case already discussed by Metropolis[10] and related to $\Delta\alpha < 0$ and $\Delta r \sim 0$. Then from the variation of C and B, we can conclude that the angle α has decreased by about 20°, while r_e has slightly increased by excitation.

These conclusions are in complete agreement with the general considerations of Metropolis[10] and would explain the fact that the α_1 system is not well developed toward high ν_1' values.

For the α_2 system, the lack of rotational data prevents a more extensive analysis. A transition such as $3b_2 \rightarrow 5a_1$, as proposed by Mulliken for the whole a-system, seems not to be excluded and would give rise to parallel bands. In any event, the angle α cannot be determined by the analysis of the vibrational potential function of the excited state as it has been done by Metropolis[11] for the b-system. The reason lies in the fact that the value of α is very sensitive to the cross terms for angular molecules and, as it has been proved by one of us,[12] the cross terms cannot be neglected in such molecules. Furthermore, as the parallel character of the bands in the b-system must be considered with caution, we shall understand that the assigned transition ($1a_2 \rightarrow 2b_1$) cannot be considered as being established with certainty. The full discussion of the scheme proposed by Mulliken must thus be postponed until new experimental data farther to the ultraviolet will be available. On the other hand, it seems that the α_2 system is much more developed in the sense of high ν_1' values than the α_1 system, and this indicates that in the

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†† We are very indebted to Professor Mulliken for his valuable suggestion concerning this possibility, erroneously neglected by us in our previous letter (Nature **157**, 692 (1946)).

[10] N. Metropolis, Phys. Rev. **60**, 283 (1941).

[11] N. Metropolis, Phys. Rev. **60**, 295 (1941).

[12] J. Duchesne, Mémoires Soc. Roy. Sci. (Liége) 1, fasc. 2, 429 (1943).

former r_e must be modified by excitation as well as α.

Before new steps in the interpretation of the SO_2 spectrum can be undertaken, it would be important to check the reality of the third α_3 system of Table IV, to get more information concerning the distribution of intensity in the bands, and to have more reliable data concerning bands in the 2000–1800A region.

P. Migeotte in our laboratory is now engaged on such experiments.

SeO_2

Introduction

The electronic diffraction patterns of SeO_2 vapor, studied by Palmer and Elliott,[13] indicate an angular symmetrical structure of the SeO_2 molecule, with a $Se-O$ distance of 1.61A. The diffraction patterns being relatively insensitive to the apex angle, its value has not yet been determined.

The SO_2, SeO_2, and TeO_2 molecules belong to the same class of 18-electron molecules, and their comparative spectroscopic study presents, therefore, considerable interest. Up to now, three electronic systems of SeO_2 have been reported between 2000 and 5000A. Preliminary descriptions of these systems were given by several authors,[14] and in a recent paper[1] we have analyzed in some detail the vibrational structure of the b-system situated between 2300 and 3300A. In the present paper we deal with the vibrational study of the c-system situated in the visible, and we will try to develop some general conclusions regarding the electronic structure of the excited states. The analysis of the a-system in the farther ultraviolet is now in progress and will be published later.

Vibrational Analysis

For the present study we have used a two-prism Bourguel spectrograph for the visible, giving a dispersion of about 30A/mm at 4500A, and a Jobin quartz spectrograph giving a dispersion of about 15A/mm at 3000A. The source

[13] K. J. Parlmer and N. Elliott, J. Am. Chem. Soc. **60**, 1389 (1938).

[14] S. F. Evans, Nature **125**, 528 (1930); Choong-Shin Piaw, C. R. Acad. Sci. Paris **202**, 127 (1936); *ibid.* **203**, 239 (1936); Ann. de physique **10**, 191 (1938).

of background radiation was an Osram Nitra tungsten-strip filament bulb. The absorption of the SeO_2 vapor was investigated in 4-meter, 25-cm, and 2-cm absorption cells at temperatures varying between 300 and 500°C.

The SeO_2 crystals were carefully purified by repeated distillations in vacuum and introduced in a side tube sealed to the main absorption cell. This side tube could be heated independently from the furnace heating the main cell, and thus the vapor pressure could be varied in the usual manner independently of the temperature. We used pressures between 50 and 450 mm.

By varying the conditions of pressure and temperature, the SeO_2 absorption spectrum was investigated between 5000 and 3400A. In this region about 100 bands were measured, and the measurements are in general in agreement with those of Evans and of Choong-Shin Piaw.[14] These authors have reported (especially in the ultraviolet part of the spectrum) more bands than we. Some of them must probably be correlated with rotational structure, as we have already noted in the case of the b-system.[1]

The absorption in the bands of the c-system is considerably weaker than in the bands of the a- and b-systems. The number of molecules needed to reveal absorption in the visible is at least 10 times greater than the number needed to provoke absorption in the ultraviolet.

A characteristic feature of the c-system is the diffuseness of the bands in the central region and the increased sharpness toward both ends. On both extremes, the bands are relatively well defined and the majority of the heads can be measured with good precision, although errors up to 20 cm^{-1} cannot be excluded for fainter bands. In the central region, heads cannot be measured at all, and we have determined the position of the maxima of intensity on microphotometric records. Another striking feature of the c-system is provided by long series of bands extending through all the spectrum with the characteristic periodicity of about 200 cm^{-1}. These series are given in the columns of Table VI. The 200-cm^{-1} progression must surely be correlated with the bending frequency ν_2' of the excited state. The presence of long ν_2' progressions indicates a considerable change of the apex angle of the molecule. The apparent lack of

TABLE VI.

$0_1'v_2'0_3'$ \\ $v_1''0_2''0_3''$	0		1		2		3		4
0	—		20,940						
			178						
1	—		21,118	917	20,201				
			206						
2	—		21,324						
			210						
3	—		21,534*	919	20,615				
			210		205				
4	—		21,743	923	20,820				
			192		215				
5	22,855	920	21,935	900	21,035				
	203		208		203				
6	23,058	915	22,143	905	21,238				
	201		198		210				
7	23,259	918	22,341	893	21,448				
	203		199		207				
8	23,462	922	22,540	885	21,655				
	192		193		188				
9	23,650	917	22,733	890	21,843				
	184		197		207				
10	23,834	904	22,930	880	22,050*				
	190		206		190				
11	24,030	894	23,136	896	22,240				
	200		209		174				
12	24,230	885	23,345	931	22,414				
	192		165		216				
13	24,422*	912	23,510	880	22,630		21,680		
	200		194		163		192		
14	24,622	918	23,704	911	22,793	921	21,872		
	198		185		198		200		
15	24,820	931	23,889	898	22,991	919	22,072	897	21,176
	182		201		202		211		215
16	25,002	912	24,090	897	23,193	910	22,283	892	21,391
	203		204		197		199		194
17	25,205	911	24,294*	904	23,390	908	22,482	897	21,585
	185		186		182		214		198
18	25,390	910	24,480	908	23,572	876	22,696*	913	21,783*
	245		210		190		198		
19	25,635	945	24,690	928	23,672	868	22,894		
	181		212		197		208		
20	25,816	914	24,902	947	23,955	853	23,102	919	22,183
					208		208		
21					24,163	855	23,310		
					205				
22					24,368				
					196				
23					24,564*				
					211				
24					24,775				
					188				
25					24,963				

* The underlined bands correspond to intensity maxima in the series.

TABLE VII.

$\Delta G_{v_1}''$	b-system mean values	c-system weighted values
0–1	894	911
1–2	893	898
2–3	907	889
3–4	902	903
0–4	3,596	3,601

stretching frequencies means that the valency bond remains practically unchanged. It seems, however, not excluded that some fainter bands in the ultraviolet part of the spectrum are due to a weak excitation of the valence frequency.

The first column of Table VI contains the most prominent bands of the whole system, and must, therefore, undoubtedly be correlated to the zero level of the normal state. The intensity distribution in this series is regular, and the maximum occurs at about 24,500 cm^{-1}. The assignment of the other series to definite vibrational levels cannot be done without some ambiguity. This is due to lack of regularity in the intensity distribution and to frequent irregularities in the distances between neighboring bands. From a strictly numerical point of view, several arrangements are possible; however, the scheme given in Table VI seems to us to be by far the most reliable; in particular, it gives for the ground level a frequency of about 900 cm^{-1}, already assigned to the stretching frequency of normal SeO$_2$ on the basis of our analysis of the b-system.

It is important to check this last conclusion by comparing the mean values of $\Delta G''$ resulting from the study of the b- and the c-systems. The agreement of the mean $\Delta G''$ values, corresponding to both systems and given in Table VII, can be considered as satisfactory and is even improved if we consider only those bands which can be measured with good accuracy. In doing so we obtain for the symmetrical stretching frequency in the ground level of SeO$_2$ the value of $\nu_1'' = 910$ cm^{-1}.

In adopting the vibrational scheme of Table

TABLE VIII. Isotopic constitution of selenium.

Atomic weights	74	76	77	78	80	82
Abundance	0.9	9.5	8.3	24	48	9.3

VI for the c-system, we must admit that the irregularities in the progressions are due to some kind of perturbation. On the other hand, the occurrence of two intensity maxima observed in the bands of the second and third columns of Table VI (underlined bands) must be correlated either with the special form of potential energy surfaces or with the superposition of at least two series.

We have already noted that the band edges become increasingly sharper toward both ends of the spectrum; whereas on the long wave-length side the bands are shaded toward the red, they are shaded to the opposite sense at the other extremity of the spectrum. In the central part, the sense of the shading is not well defined; however the change of shading can be approximately located at 22,000 cm^{-1}.

A similar anomaly in the shading was observed by us in the TeO$_2$ bands, as will be reported in detail in the last part of this paper. On the other hand, the bands of all known SO$_2$ band systems are uniformly degraded toward the red (if we neglect the J-structure which has not been observed in the spectra of SeO$_2$ and TeO$_2$). It seems to us that the above-mentioned behavior of the SeO$_2$ and TeO$_2$ spectra must be explained as due to an isotopic shift and can be correlated with the fact that Se and Te have several abundant isotopes, whereas S has practically only one. We give in Table VIII the isotopic constitution of selenium:

Table VIII shows that the center of gravity of the isotopic group lies on the side of greater atomic weights. Thus the groups of isotopic bands are apparently shaded toward the red on the long wave-length side with respect to the origin, and toward the violet at the opposite extremity. In conformity with this point of view the change in the sense of degradation occurs at about 22,000 cm^{-1}, and coincides with the origin of the system according to the proposed vibration scheme.

Interpretation of Results

The present data do not permit stating whether the c-bands of SeO$_2$ correspond to an allowed or to a forbidden transition. The intensity distribution in the vibrational series indicates strongly that the electronic excitation does

not change appreciably the Se−O distance, whereas the apex angle is considerably modified.

We have already noted that most of the bands are rather diffuse, and this could presumably be due to the fact that the J- and K-structures are shaded in opposite directions. Not much more can be said for the moment about the structure of the molecule in the upper level.

It is worth while pointing out that no analogy can be established between this system and the c-system of the SO_2 molecule, studied by Metropolis and Beutler.[15] For the former, $\Delta r \cong 0$ and $\Delta \alpha \neq 0$, while for the latter $\Delta r \neq 0$ and $\Delta \alpha \cong 0$. On the contrary, the c-system of SO_2 is much more similar in regard to these properties to the b-system of SeO_2 for which we have previously proved[1] that r_e is the only parameter to change appreciably.

As Metropolis remarked,[10] the ratio of the moments of inertia I_c/I_b is practically constant (~ 1.17) in the normal state of a series of angular molecules such as SO_2, NO_2, and ClO_2. If we extend the validity of this rule to SeO_2, it provides an apex angle of about 130°. On the other hand, we observe that the ratio of the antisymmetrical and symmetrical frequencies of the same molecules also follows such a sort of regularity and equals approximately 1.17. Though the identity of the constants seems purely fortuitous, the extrapolation of this rule to SeO_2 gives us the possibility to locate ν_3'' at about 1060 cm^{-1}. The bending frequency ν_2'' can also be approximately estimated; in fact the apparent disappearance of this vibration in the spectrum may be explained by assuming that the fundamental frequency ν_2'' is a multiple of ν_2', the most probable value being $\nu_2'' = 400$ cm^{-1}. If this estimation is correct, the columns of Table VI could result from a superposition of several types of progressions, and the apparent lack of the 400-cm^{-1} progression, as well as the anomalies of intensity referred to above, could be satisfactorily explained.

With the three fundamental frequencies thus obtained (910, 400, and 1060 cm^{-1}) and by using a valence-deformation force field, we compute an apex angle of about 160°. The reason for the divergency with respect to 130°, which seems

much more plausible, could be explained by the neglect of the cross terms in the potential function. The introduction of a small stretch-stretch cross term (f_{12}) of about -0.4×10^5 dyne/cm is sufficient to remove the divergency. On the other hand, by taking into account a stretch-deformation cross term (g_c) only, the best value equals about $+0.4 \times 10^5$ dyne/cm, and it is impossible to obtain quite satisfactory results. However, in order to obtain such results, it is sufficient to add in the potential function a slightly negative value of f_{12}. Thus, as we have no reason to believe that f_{12} has a considerable value, while $g_c = 0$ (or the reverse), it seems established that f_{12} and g_c have opposite signs, the former being negative and the latter positive, with numerical values smaller than 0.4×10^5 dyne/cm. Furthermore, the presence of the cross terms proves that the apex angle of molecules like SeO_2 and SO_2 cannot be determined by assuming a valency force field, contrary to the assumption by Metropolis for the case of the c-system of SO_2.

TeO₂

The TeO_2 absorption bands were first studied by Choong-Shin Piaw.[16] He arranged a part of the observed bands in a vibrational scheme according to the formula:

$$\nu = 25636 + 545\nu_1' - \nu_1'^2 + 206\nu_2'$$
$$- 3\nu_2'^2 + 675\nu_3' - 2.7\nu_3'^2.$$

Several objections can be raised against this analysis:

1—It seems quite abnormal that at the high temperature used, the frequencies of the ground level do not appear in the spectrum.

2—only about 60 percent of the observed bands fit into the scheme.

3—the selection rules are not respected. It thus seemed necessary to re-investigate the TeO_2 spectrum before any attempt to compare it with the SO_2 and SeO_2 band systems could be undertaken.

Experimental Procedure

The TeO_2 vapor reacts with quartz at high temperatures necessary to obtain sufficient vapor

[15] N. Metropolis and H. Beutler, Phys. Rev. **57**, 1078 (1940).

[16] Choong-Shin Piaw, C. R. Paris **201**, 1181 (1935); Thesis, Paris (1937).

pressure. The absorption was therefore studied in thin open porcelain tubes filled with carefully purified TeO_2 crystals. The tube with TeO_2 was introduced into the electric furnace after the desired temperature was attained. We have thus operated in conditions far from equilibrium and contrary to the experiments concerning the SO_2 and SeO_2 absorption we were not able to vary the pressure independently of the temperature. In some cases, it was necessary to avoid excess oxygen and then the absorption tube was provided with water-cooled quartz windows and filled with nitrogen to prevent rapid distillation of TeO_2 outside the high temperature zone.

The dispersion used was the same as in the case of SeO_2. For the bands situated near 4000A, it was possible to use a multiple-prism Jobin spectrograph in Littrow mounting, either with 5 quartz prisms giving a dispersion of about 9A/mm, or with 5 glass prisms with a dispersion of about 2A/mm at 4000A.

Vibrational Analysis

The most characteristic band system of TeO_2 is situated in the blue and near ultraviolet, between 3000 and 4550A, with a maximum near 3550A. In the conditions of our experiments (absorbing layer of a few centimeters, rapid distillation from the middle of the furnace towards the end) it appears at about 900°. At about the same temperature, we have observed very strong absorption bands in the region of 2000A, but owing to the presence of O_2, it has been up to now impossible to investigate these in detail. It is not even excluded that this absorption is due to impurities. Choong Shin-Piaw observed in the ultraviolet above 3000A only continuous absorption. At somewhat higher temperatures (about 1000°C) very weak and diffuse absorption bands appear in the region between 2450–2650A†††). It may belong also to some impurities. At a temperature of about 1100°, some weak and very diffuse bands appear between 4650 and 5100A. We shall refer to them at the end of this paper. At still higher temperature, the TeO_2 bands gradually disappear, and they are replaced by TeO absorption bands which will be discussed in detail elsewhere. In this paper we will deal chiefly with the main system between 3000–4550A, which will be designed as the b-system.

In the b-system, the bands situated in the blue are sharp and shaded towards the red. Towards the ultraviolet they gradually become more diffuse, and even the sense of degradation is reversed in the extreme ultraviolet end of the spectrum. This change of shading is probably due to an isotopic effect in the same way as

TABLE IX. Intensity maxima in the bands of the b-system of TeO_2.

ν_{max}	ν_{max}	ν_{max}
21,950	24,680	⌠29,460
22,130	24,810	{ 29,490
22,240	25,000	⌡29,515
⌠22,380	⌠25,150	⌠29,650
{ 22,390	{ 25,170	{ 29,675
⌡22,400	⌡25,190	⌡29,700
⌠22,560	25,340	29,870
{ 22,570	25,470	29,950
⌡22,580	25,525	30,080
		30,165 a
⌠22,650	⌠25,620	30,320
{ 22,665	{ 25,640	30,400 a
⌡22,680	⌡25,660	30,515
	25,825	30,610 a
	26,000	30,750
⌠22,750	26,080	30,790
{ 22,765	26,160	30,830 a
⌡22,780	26,280	30,960 b
	26,460	31,050 a
	26,640	31,160 b
⌠22,920	26,820	31,250 a
{ 22,930	26,920	31,385 b
⌡22,940		31,450 a
	⌠27,070	31,580 b
23,060	{ 27,095	31,660 a
	⌡27,120	31,800 b
	27,260	31,865 a
23,200	27,460	32,000 b
	27,550	32,090 a
23,385	27,730	32,205 b
	⌠27,880	32,275 a
⌠23,550	{ 27,910	32,410 b
{ 23,575	⌡27,940	32,500 b
⌡23,600	28,125	32,620 b
	28,210	32,700 a
⌠23,710	⌠28,570	32,830 b
{ 23,730	{ 28,385	33,040 b
⌡23,750	⌡28,400	
	28,540	
23,870	28,860	
⌠24,000	⌠29,020	
{ 24,020	{ 29,030	
⌡24,040	⌡29,045	
24,200	29,190	
⌠24,360	29,345	
{ 24,375		
⌡24,400		
24,540		

††† The wave numbers of the band heads, which are shaded toward ultraviolet, are the following: 40740, 40260, 39760, 39400, 39260, 39060, 38920, 38740, 38580, 38420, 38240, 38080 cm^{-1}.

described for the corresponding case occurring in SeO₂. In fact, the proportion of the different isotopes of Te is such that the general character of the isotopic shift is the same in both cases.

The general character of the b-system of TeO₂ has many common features with the b-system of SeO₂. As in the case of SeO₂, it is rather difficult to locate the heads accurately, owing to the diffuse character of most bands. The spectra taken with great dispersion show a very complicated sub-structure which, even at the dispersion of 2A/mm, is not resolved into lines. The present data are not sufficient to decide whether this observed structure is due to isotopic effect or represents sub-bands in the coarse structure of the system. Probably both kinds of substructure interfere and explain the complicated character of the whole system.

The positions of the most prominent band heads are in good agreement with those given by Choong Shin-Piaw, but for the reason given above these figures must be considered with caution. For the vibrational analysis, we preferred to use chiefly the measures of the band maxima given in Table IX.

As in the case of the b-system of SeO₂, the TeO₂ b-system is characterized mainly by long series of bands with a periodicity of about 650 cm⁻¹. Several irregularities are observed in the distances between neighboring bands; these irregularities are less marked if we use band maxima instead of band heads. With small dispersion the complicated structure of the bands resolves into very characteristic doublets, with irregular doublet separation. As this doubling is presumably due to some kind of perturbations, we have used the mean values for the vibrational analysis. In the Table IX these doublets are joined by brackets. The vibrational analysis finally adopted is reproduced in Table X. Most of the bands of Table IX are fitted into this scheme with only one characteristic frequency in each state; both are to be considered as symmetrical valency frequencies $\nu_1'=670$ and $\nu_1''=810$ cm⁻¹.

It is worth while to note that the value $\nu_1''=810$ cm⁻¹ for the valency frequency of the ground state of TeO₂ is nearly equal to the vibrational frequency $\omega''=796$ of TeO given by

TABLE X. b-system of TeO₂.

(Columns indexed by ν_1' = 0–13; rows indexed by ν_2'' = 0–5. Small numbers are the differences between neighboring bands: horizontal differences lie between value columns, vertical differences between value rows.)

ν_2''	0		1		2		3		4		5		6		7		8		9		10		11		12		13
0	24,020	660	24,680	660	25,340	660	26,000	640	26,640	640	27,280	630	27,910	630	28,540	650	29,190										
	820		810		800		830		815		820		815		810		805										
1	23,200	670	23,870	670	24,540	630	25,170	655	25,825	635	26,460	635	27,095	635	27,730	655	28,385	645	29,030	645	29,675	645	30,320	640	30,960		
	810		810		810		795		825		820		815		810		835		820		815		830		795		
2	22,390	670	23,060	670	23,730	645	24,375	625	25,000	640	25,640	640	26,280	640	26,920	630	27,550	660	28,210	650	28,860	630	29,490	675	30,165	625	30,790
					800		800		800		830		810		840											
3					22,930	645	23,575	625	24,200	610	24,810	660	25,470	610	26,080											
					800		810		815																	
4					22,130	635	22,765	620	23,385																		
							815		815																	
5							21,950	620	22,570																		

Choong-Shin-Piaw.[16,‡] The same relation is correspondingly valid for the valency frequencies of SeO_2 and SO_2 (910 and 1152) as compared with those of SeO and SO (909 and 1124). Although at present, no theoretical considerations supply a basis for such a relation, it seems nevertheless that the parallelism in the behavior of the six molecules constitutes a further argument in favor of our analysis. The scheme of Table X contains nearly all bands observed between 22,000 and 30,000 cm^{-1}. In the ultraviolet end of the spectrum, however, there are two rather long series of faint bands which appear only when the absorption in the central part is complete and which cannot be fitted in the scheme. These bands are marked a and b in Table IX and form two progressions with a characteristic frequency of about 200 cm^{-1}. On the other hand, some of the weaker bands farther to the visible, which cannot be fitted in the scheme of Table X, are situated at about 200 cm^{-1} on the violet side of strong bands belonging to the main series. It seems reasonable to admit that 200 cm^{-1} represents the deformation frequency of the upper state and that each

‡ According to the new analysis of TeO bands (not yet published) by one of us, $\omega'' = 790$ cm^{-1}.

v_1' level is combined with a series of v_2' levels. This statement cannot, however, be considered as definitive, as the possibility that the 200-cm^{-1} progression belongs to a separate electronic transition cannot be ruled out. If all the bands belong to a single system, it would mean that the corresponding transition is accompanied not only by considerable change of the apex angle α but also of the Te$-$O distance.

After having established the analogy existing between the b-systems of SeO_2 and TeO_2, we have searched for a system of TeO_2 situated farther toward the red in analogy with the c-system of SeO_2. At the highest pressure obtainable, corresponding to temperature above 1100°C, some weak and diffuse bands, without marked heads, appear between 4650 and 5100A on microphotometer records; we have measured the following maxima: 21,520, 21,030, 20,560, 20,150, 19,750 cm^{-1}. These bands bear no analogy with the c-system of SeO_2.