Molecular Spectra of OCSe

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The absorption spectra of OCSe vapour have been recorded in the i.-r. $(300-5000 \text{ cm}^{-1})$ and u.-v. (2600-1350 Å) regions. Several electronic transitions were identified, which always display progressions in v'_3 and possibly v'_1 , except the first transition at 4.89 eV, where v'_2 is active: this absorption has been assigned to a bent-linear transition. An upper limit to the dissociation energy of OC—Se bond (3.1 eV) was obtained from linear extrapolation of the v'_3 progression of the second transition at 5.83 eV.

The electronic absorption spectrum of the linear molecule OCSe was previously reported by Stiles, Tyerman, Strausz and Gunning.¹ These authors recorded, between 3000 and 1900 Å, a weak transition centred around 2500 Å exhibiting little sign of structure, and a strong absorption at 2000 Å with vibrational structure and overlapped by a continuum.

In the present work the absorption of OCSe vapour between 2600 and 1350 Å is reported and discussed. Also the i.-r. spectrum in the range $300-5000 \text{ cm}^{-1}$ was recorded.

EXPERIMENTAL

OCSe was prepared by passing dry CO over molten Se² and purified by several distillations at reduced pressure. Besides the OCSe bands, CO_2 bands were observed in the i.-r. spectrum of the vapour. CO_2 was removed by pumping on the mixture of OCSe and CO_2 at -120° C for two hours. At this temperature the vapour pressure of CO₂ is about 10 times larger than that of OCSe. Spectra were photographed on a Bausch-Lomb quartz prism spectrograph at a linear inverse dispersion of about 2.5 Å/mm (2600-2100 Å) and recorded on a Jarrell-Ash 1 metre grating spectrometer, at 8 Å/mm (2100-1350 Å). A few plates were taken on a large concave grating spectrograph (6.65 m) in the region around 2500 Å. A high pressure Xe arc (450 W), and Xe and Kr microwave excited lamps provided the continuum. Iron lines from an hollow cathode lamp provided the wavelength standards in the near u.-v. Carbon atomic emission lines, present as impurity in the Xe and Kr lamps, were used to calibrate the spectrum in the far u.-v. Cells 10 and 20 cm long were employed, with pressure varying from 0.1 (far u.-v.) to 10 mmHg (near u.-v.). Owing to the photodissociation of OCSe by u.-v. radiation, in all experiments the vapour was continuously pumped through the cell. The i.-r. spectrum was recorded on a Perkin-Elmer 180 spectrophotometer, with a slitwidth of 0.3 cm^{-1} , in a 20 cm cell at 10-40 mmHg.

RESULTS AND DISCUSSION

J.-R. SPECTRUM

The i.-r. absorption bands of OCSe are reported in table 1 with their assignments. The fundamentals were previously measured by McDonald and Lord, as reported

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by Wentink.³ In addition we have observed the overtones $2v_1$, $2v_2$ and the combination $v_1 + v_3$. The band at 466 cm⁻¹ was unambiguously assigned to v_2 , being the only perpendicular band in the spectrum.

	TABLE 1.—INFRA-R	ed data for OC	CSe
$\nu/\mathrm{cm}^{-1} a$	type	intensity	assignment
465.5	1	w	<i>v</i> ₂
(466.1)			
643.0		s	<i>v</i> ₃
(642.1)			
927.1		w	$2v_2$
2022.3		vs	v ₁
(2021.2)			
2664.0		S	$v_1 + v_3$
4020.2		s	$2v_1$

^{*a*} vacuum wavenumbers (accuracy ± 0.3 cm⁻¹) refer to minimum absorption for \parallel bands and to the Q-branch for the \perp band. Values in parenthesis are from ref. (3).

U.-V. SPECTRUM

In the present investigation many electronic transitions were observed, the upper states being identified as \tilde{A} , \tilde{B} , \tilde{C} , . . . In table 2 are collected the wavenumbers of the band heads or maxima, and their assignments. The uncertainty in wavenumber measurements is about 5 cm⁻¹ for sharp and much larger (20-30 cm⁻¹) for diffuse or broad absorptions. In fig. 1 are shown the regions 1820-1730 and 1550-1380 Å, where sharp bands were observed.

Table 2.—Vacuum wavenumbers and assignments of the measured bands of OCSe in the 38 000-74 000 $\rm cm^{-1}$ range

	assignment			assignment	
	electronic	vibronic		electronic	vibronic
38 385	$ ilde{A} ext{-} ilde{X}$	000-011	55 588	$ ilde{C}- ilde{X}$	000000
340	\widetilde{A} – \widetilde{X}	000020	56 021	$ ilde{D} - ilde{X}$	000000
830	\widetilde{A} – \widetilde{X}	000001	173	$ ilde{C} extsf{-} ilde{X}$	001-000
39 015	$ ilde{A} \!\!-\!\! ilde{X}$	000-010	588	$ ilde{D}\!\!-\!\! ilde{X}$	001-000
245	\widetilde{A} – \widetilde{X}	010-001	865	$ ilde{E}\!\!-\!\! ilde{X}$	000000
480	$\widetilde{A} - \widetilde{X}$	000-000	57 157	$ ilde{D}\!\!-\!\! ilde{X}$	002-000
690	$ ilde{A} \!\!-\!\! ilde{X}$	020001	430	$ ilde{E} ext{-} ilde{X}$	001-000
925	\widetilde{A} – \widetilde{X}	010-000	713	\widetilde{D} – \widetilde{X}	003-000
40 1 30	$ ilde{A} - ilde{X}$	030-001	58 025	$ ilde{E}\!\!-\!\! ilde{X}$	002-000
340	$ ilde{A} - ilde{X}$	020-000	290		
570	$ ilde{A} \!\!-\!\! ilde{X}$	040-001	365	\widetilde{F} – \widetilde{X}	000-000
780	\widetilde{A} – \widetilde{X}	030000	565	$ ilde{E}\!\!-\!\! ilde{X}$	003-000
41 020	\widetilde{A} – \widetilde{X}	050-001	930	$ ilde{F} - ilde{X}$	001-000
210	\widetilde{A} – \widetilde{X}	040-000	59 095	$ ilde{E}\!\!-\!\! ilde{X}$	004-000
445	$ ilde{A} ext{-} ilde{X}$	060-001	505	$ ilde{F}- ilde{X}$	002-000
635	$ ilde{A} \!\!-\!\! ilde{X}$	050000	590	\widetilde{E} – \widetilde{X}	005-000
865	$ ilde{A} ext{-} ilde{X}$	070-001	60 070	$ ilde{F}\!\!-\!\! ilde{X}$	003000
42 050	$ ilde{A} ext{-} ilde{X}$	060-000	155	$ ilde{G} extsf{-} ilde{X}$	000-000
47 055	$ ilde{B}\!\!-\!\! ilde{X}$	000-000	628	$ ilde{F} - ilde{X}$	004-000
545	$\widetilde{B}\!\!-\!\!\widetilde{X}$	001-000	725	$ ilde{G} extsf{} ilde{X}$	001-000
48 005	$\widetilde{B} - \widetilde{X}$	002000	61 170	$ ilde{F}\!\!-\!\! ilde{X}$	005000
475	\widetilde{B} – \widetilde{X}	003-000	285	$ ilde{G} \!\!-\!\! ilde{X}$	002-000
94 0	$\widetilde{B} - \widetilde{X}$	004-000	690	$ ilde{F} - ilde{X}$	006-000

assignment			assignment		
	electronic	vibronic		electronic	vibronic
49 380	\widetilde{B} – \widetilde{X}	005-000	61 855	\tilde{G} – \tilde{X}	003000
825	\widetilde{B} – \widetilde{X}	006-000	62 250	$ ilde{E} ext{-} ilde{X}$	007-000
50 280	\widetilde{B} – \widetilde{X}	007-000	395	$ ilde{G} \!\!-\!\! ilde{X}$	004-000
720	$\widetilde{B} - \widetilde{X}$	008-000	64 386	$ ilde{H}$ - $ ilde{X}$	000000
51 140	$\tilde{R}-\tilde{X}$	009-000	465		
595	$\tilde{R}_{-}\tilde{X}$	0010-000	539	$\tilde{I}_{-}\tilde{X}$	000-000
52 010	$\tilde{B}_{-}\tilde{Y}$	0011_000	745	1 21	000 000
425	$\widetilde{D} \widetilde{V}$	0011-000	073	$ ilde{H}_{-} ilde{Y}$	001_000
42J 950	$D - \Lambda$ $\tilde{D} \tilde{V}$	0012-000	65 050	$\tilde{r} \tilde{v}$	001-000
630	D - A $\widetilde{D} \widetilde{V}$	0015-000	05 050	<i>I</i> - <i>A</i>	001-000
53 240	B-X	0014-000	238	~~~~	000 000
605	B-X	0015-000	444	H-X	002-000
995	B - X	0016-000	555	I - X	002000
54 380	B-X	0017000	650		
765	$\tilde{B}-\tilde{X}$	0018-000	735		
942	$ ilde{C} \!\!-\!\! ilde{X}$	000-001	896		
55 105	$ ilde{B} \!\!-\!\! ilde{X}$	0019-000	65 952	\widetilde{H} – \widetilde{X}	003-000
66 058	$ ilde{I}\!\!-\!\! ilde{X}$	003-000	69 224	$ ilde{O}- ilde{X}$	002-000
214	$ ilde{L} - ilde{X}$	000-000	362	$\tilde{P}-\tilde{X}$	002000
298	$\overline{ ilde{\mathcal{M}}}_{-}\overline{ ilde{\mathcal{X}}}$	000-000	503	$ ilde{O}- ilde{X}$	000000
411			614	2	
545			735	$\tilde{O}_{-}\tilde{X}$	003-000
670			879	$\tilde{p}_{-}\tilde{Y}$	003-000
745	ĩĩ	001 000	70.014	ñΫ	001-000
202	$\widetilde{M} \widetilde{V}$	001-000	250	$\widetilde{D} \widetilde{V}$	000 000
007	IVI-A	001-000	235	N-A	000-000
907			515	ãΫ	002 000
934			559	$\mathcal{Q}^{-\lambda}$	002-000
6/05/			/86	<i>K</i> − <i>X</i>	001-000
165	~ ~		834	* ~	
274	$\mathcal{L} - X$	002-000	71 031	Q-X	003-000
319	M-X	002-000	310	R-X	002000
470	~ ~		810	$\tilde{R} - X$	003-000
587	$\tilde{N} - X$	000000	72 044	S-X	000000
653			547	$ ilde{S} extsf{-} ilde{X}$	001-000
792	\tilde{L} – \tilde{X}	003-000	73 059	$ ilde{S} extsf{-} ilde{X}$	002000
9 78			560	\tilde{S} – \tilde{X}	003000
68 116	$ ilde{N} ext{-} ilde{X}$	001-000			
151	$ ilde{O} \! - \! ilde{X}$	000-000			
296	$\tilde{P}-\tilde{X}$	000-000			
396					
541					
632	$\widetilde{N}_{-}\widetilde{X}$	002-000			
699	$\tilde{O}_{-}\tilde{X}$	001-000			
876	$\tilde{p}_{-}\tilde{Y}$	001_000			
020	1 - 1	001-000			
60 1/2	\tilde{N} \tilde{V}	003 000			
07 143	IV-A	000-000			

TABLE 2.—continued

 $\tilde{A}-\tilde{X}$ transition: the 20 broad bands * measured between 2650 and 2350 Å can be arranged in two progressions of 440 cm⁻¹: ($0v'_20-000$) and ($0v'_20-010$). The assignment, which implies that the \tilde{A} state is bent, is based on the observation that the hot band (000)-(010) is strong. Moreover if the progressions were due to v'_3 ,

* The bands remained diffuse in spectra taken at higher resolving power.

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approximately a C—Se stretching vibration, the frequency 440 cm⁻¹ represents a 30 % drop from the ground state value. This requires a CSe bond energy in the \tilde{A} state lower than in the \tilde{X} ground state. From the correlation diagram of fig. 2, it is clear that, if the C—Se bond energy in the \tilde{A} state is D'_{C-Se} eV, the corresponding value for the \tilde{X} state D'_{C-Se} could either be $3.4 + D'_{C-Se}$ or D'_{C-Se} depending on the states of CO+Se correlating with \tilde{A} . The latter hypothesis contrasts the observed



1 IG. 1.—Absorption of OCSe in the vacuum u.-v. region. Pressure 0.1 mmHg, path 10 cm. Only the v'_3 vibrational quantum number is given, every progression being ($00v'_3$ -000).

decrease of v'_3 , while the former yields a value of D'_{C-Se} which seems too large if compared with the dissociation energy of the C—S bond in OCS (4.3 eV).⁴ In the near u.-v. spectrum of the isoelectronic OCS molecule band structure was observed superimposed on an apparently continuous absorption.⁴⁻⁶ As in the present case, the absorption was assigned to a bent-linear transition.

 $\tilde{B}-\tilde{X}$ transition: this system, about 10 times stronger than $\tilde{A}-\tilde{X}$, is formed by a single progression of 20 very broad bands overlapped by a continuum, and with spacings decreasing from 490 to 345 cm⁻¹. The 2100 Å absorption of the isoelectronic molecule CS₂ has a similar appearance. Price and Simpson ⁷ assigned the progression of 420 cm⁻¹ to ν'_3 , and Douglas and Zanon,⁸ at higher resolving power, found that each band of the progression consists of several diffuse heads and eventually

pointed out that v'_2 was responsible for these progressions. In the present case the fairly regular intensity pattern of the progression suggests a v'_3 assignment.

The $\tilde{C}-\tilde{X}$ system consists of 3 sharp bands degraded to the red (see fig. 1). Again, the only vibration active in the spectrum is v'_3 . Also the $\tilde{D}-\tilde{X}$ transition is sharp and red degraded, and consists of a short v'_3 -progression.



FIG. 2.—Correlation between the electronic states of CO+Se and those of OCSe. On the left are given the observed states of OCSe.

Starting from 1760 Å, 3 transitions are observed with origin at 56 865 $(\tilde{E}-\tilde{X})$, 58 365 $(\tilde{F}-\tilde{X})$ and 60 155 cm⁻¹ $(\tilde{G}-\tilde{X})$. The absorption between 1760 and 1600 Å is the strongest in the frequency range here investigated. The bands are diffuse and the usual progression in v_3 is observed in every transition with v_3 having nearly the same value of about 565 cm⁻¹.

Following a region (1600-1550 Å) of negligible absorption, a strong and sharp system is observed between 1500 and 1350 Å, which appears to be similar to that recorded between 1420 and 1350 Å for OCS by Kopp,⁹ and found to be diffuse at high resolving power. In the present spectrum, recorded with a slitwidth of ~ 0.8 Å, the observed bandwidth is about 1 Å and it is likely that for these bands, like those for the $\tilde{C}-\tilde{X}$ and $\tilde{D}-\tilde{X}$ transitions, the available resolving power is not enough to obtain the true band shape, and eventually resolve the rotational structure. At least 10 different electronic transitions can be recognized between 64 000 and 74 000

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cm⁻¹. They are all similar in vibrational structure: each transition consists of a short progression in $v'_3(v'_3 \leq 3)$, the 0-0 band being usually the strongest. The frequency v'_3 is very nearly the same in all the upper states involved in these transitions.

state	T_0	<i>v</i> ₁	ν2	<i>v</i> ₃
\widetilde{X} (¹ Σ ⁺)	0	2022.3	465.5	643.0
\tilde{A} (A' or A")	39 480		440	
\widetilde{B} (¹ Σ^+ or ¹ Π)	47 055			490
\tilde{C}	55 588			585
$ ilde{D}$	56 021			567
$ ilde{E}$	56 865	(1500) †		565
$ ilde{F}$	58 365			565
\tilde{G}	60 1 5 5			570
Ĥ	64 386	(1828) †		537
Ĩ	64 539	(1750) †		511
$ ilde{L}_{-}$	66 214			531
$ ilde{M}$	66 298			510
$ ilde{N}$	67 587	(1916) †		529
Õ	68 151			548
$ ilde{P}$	68 296	(1963) †		530
<i>Õ</i>	69 503			511
<i>R</i>	70 259			527
$ ilde{S}$	72 044			503

TABLE 3.—SUMMARY OF OBSERVED STATES * OF OCSe

* all data in cm⁻¹; † see text.

A few weak bands, probably hot bands, are reported in table 2 but not assigned. An alternative assignment to that of table 2 is that the transitions ending to states \tilde{F} , \tilde{L} , \tilde{M} , \tilde{Q} , and \tilde{R} are in fact progressions in v'_3 belonging to the transitions ending to states \tilde{E} , \tilde{H} , \tilde{I} , \tilde{N} and \tilde{P} respectively, where one quantum of the v'_1 vibration is excited. The corresponding v'_1 values are given in parentheses in table 3. It is likely that the first members of Rydberg states appear in this region. As for OCS, where only by photoionization experiments ¹⁰ it was possible to measure the first ionization potential from which the Rydberg series could be identified, the spectrum of OCSe below 1500 Å is very complex and we could not identify the first Rydberg states. In table 3 are given T_0 and the vibrational frequencies for the observed transitions.

PREDISSOCIATION IN THE FIRST EXCITED STATES OF OCSe

The correlation between the first electronic states of OCSe and those of CO+Se is shown in fig. 2, drawn with the assumption that the ground electronic state of OCSe is a singlet state ${}^{1}\Sigma^{+}$ as it is for the isoelectronic molecules CO₂, OCS, CS₂. The first few observed states of OCSe are given on the left of the figure. The *A* state is likely to be the *A'* or *A"* state derived from a ${}^{1}\Delta$ state 5 and correlating with CO(${}^{3}\Pi$) + Se(${}^{3}P_{g}$), with dissociation limit 5.0 eV above that of the ground state. The predissociating state should be ${}^{1}\Pi$, converging to same limit of the ground state. The same ${}^{1}\Pi$ state could be responsible for the predissociation of the *B* state. Se(${}^{1}D_{g}$) atoms are obtained 11 from flash-photolysis of OCSe, indicating that the state responsible for the predissociation should tend to the ground state dissociation limit. By linear extrapolation of the long progression of the $\tilde{B}-\tilde{X}$ transition, and by assuming that \tilde{B} is one of the singlet states deriving from $CO({}^{3}\Pi) + Se({}^{3}P_{g})$, a value of 3.1 eV is obtained for the bond dissociation energy $D_{C-Se}^{"}$. This value obtained by extrapolation is likely to be an upper limit of the correct value.

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