

The Electronic and Vibrational Spectra of Oxalyl Bromide*¹

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(Received December 15, 1967)

The infrared and Raman spectra of oxalyl bromide have been observed. The spectral features suggest that this molecule is planar and *trans* at room temperature. An assignment has been given for all the fundamental vibrational frequencies. The ultraviolet absorption spectrum of oxalyl bromide has been studied in cyclohexane and in the vapor. The spectrum consists of four absorption systems. These were ascribed to a ${}^3A_u(n, \pi^*) \leftarrow {}^1A_g$, a ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$, the second ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ and a ${}^1B_u(\pi, \pi^*) \leftarrow {}^1A_g$ transitions, respectively. Vibrational analyses have been made for the ${}^3A_u(n, \pi^*) \leftarrow {}^1A_g$ and the first ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ systems.

The infrared and Raman spectra of oxalyl chloride have been investigated by several workers.¹⁻⁴⁾ Recently, Hencher and King⁵⁾ have shown that only the *trans*-form contributes to the observed spectra and given assignments for all the fundamental vibrational frequencies.

Saksena and Kagarise⁶⁾ have studied the near ultraviolet absorption spectrum of oxalyl chloride and found two $n \rightarrow \pi^*$ absorption systems in the 3800—2400 Å region. Sidman,⁷⁾ and Saksena and Jauhri⁸⁾ have also observed the absorption spectrum of the oxalyl chloride vapor and carried out a vibrational analysis for the first $n \rightarrow \pi^*$ system. Shimada and Kanda⁹⁾ have studied the T-S emission and absorption spectra of oxalyl chloride and ascribed these spectra to a ${}^3A_u(n, \pi^*) \leftarrow {}^1A_g$ transition.

Very few spectroscopic works have been reported for oxalyl bromide, although its molecular structure is quite similar to that of oxalyl chloride. A weak absorption spectrum of oxalyl bromide in the 4300 Å region has been observed by Shimada and Kanda and it was ascribed to a $T(n, \pi^*) \leftarrow S$ transition.¹⁰⁾ This assignment was confirmed by

Borkman and Kearns.¹¹⁾ In the present investigation, the electronic and vibrational spectra of this molecule have been studied in continuation of a previous work.

Experimental

Oxalyl bromide was synthesized with oxalyl chloride and gaseous HBr, which was produced by dropping bromine on a mixture of red phosphorus, sand and water. The crude product was distilled and a fraction which boiled at 103°C was collected. The collected distillate, which still contained free bromine, was shaken with a small quantity of mercury. After the red color of bromine disappeared, the transparent liquid was decanted and fractionally distilled repeatedly. The purified oxalyl bromide was stored in an evacuated cell. The sample was prepared in a dry room just before the measurement, because oxalyl bromide reacts quite easily with water and decomposes into CO, CO₂ and HBr.¹²⁾

The Raman spectrum of oxalyl bromide was studied at 20°C, 77°K and 4.2°K with a two-prism spectrograph described previously.¹³⁾ An aqueous solution of K₂Cr₂O₇ was used as a filter in order to eliminate exciting light shorter in wavelength than 5460 Å (Hg-c line). Concentration of the filter solution was 0.2% and the optical path was 1 cm. Exposure time ranged from 12 to 48 hr with a slit-width of 50 μ and Eastman Kodak 103a-F plates. The slit was widened up to 300 μ for the low temperature measurement. The liquid sample was replaced with new one for every three hours, since prolonged strong irradiation decomposes oxalyl bromide¹²⁾ and turns the sample reddish brown. A Wollaston prism was used for the study of the depolarization factor.

The infrared spectrum of oxalyl bromide was studied in the crystal at 77°K, in the liquid at 20°C, in CCl₄ and CS₂ solutions at 20°C and in the vapor at various temperatures ranging from 20 to 200°C without

*¹ Preliminary part of this paper was presented at the Proc. Intern. Symp. Mol. Struct. Spectry., Tokyo (1962).

1) B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 987 (1951).

2) R. E. Kagarise, *ibid.*, **21**, 1615 (1953).

3) J. S. Ziomek, A. G. Meister, F. F. Cleveland and C. E. Decker, *ibid.*, **21**, 90 (1953).

4) B. D. Saksena, R. E. Kagarise and D. H. Rank, *ibid.*, **21**, 1613 (1953).

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6) B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 999 (1951).

7) J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 1527 (1956).

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9) H. Shimada, R. Shimada and Y. Kanda, *Spectrochim. Acta*, **23A**, 2821 (1967).

10) Y. Kanda, R. Shimada, H. Shimada, H. Kaseda and T. Matsumura, Proc. Intern. Symp. Mol. Struct. Spectry., Tokyo (1962).

11) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **46**, 2333 (1967).

12) H. Staudinger and E. Anthes, *Ber.*, **46**, 1426 (1913).

13) M. Ito, *J. Chem. Phys.*, **41**, 1255 (1964).

altering the total number of molecules in the vapor cell with a Hitachi Infrared Spectrophotometer, type EPI-2. Since oxalyl bromide is not stable at high temperature,¹²⁾ the vapor cell was heated rapidly up to an appropriate temperature and the spectrum was scanned very quickly. The sample was replaced with new one for every run. The cell thickness was 10 cm for the vapor and 0.1 cm for solutions. A thin layer sample was used for studying the liquid phase. The spectrum of the crystal at 77°K was observed in the same way as described previously.¹⁴⁾

The ultraviolet absorption spectrum was observed in cyclohexane solution at 20°C with a Hitachi Recording Spectrophotometer, type EPS-3, and in the vapor with a Shimadzu Large Quartz Spectrograph, type QL-170. Vapor pressure of oxalyl bromide in a vapor cell of 40 cm in length was controlled by changing the temperature of the cell from -20 to 50°C. A 1 m vapor cell was used for the observation of the T-S absorption. The vapor spectrum was also studied at various temperatures ranging from 20 to 200°C with keeping the total number of molecules constant in the cell. The same care was taken to prevent the sample from decomposition by heating as that taken for the infrared spectrum.

Results and Discussion

Rotational Isomerism. Since oxalyl bromide contains two CoBr groups connected with a C-C bond, one can expect the existence of rotational isomers, that is, *trans*-, *cis*- and *staggered*-isomers. Among them, the first isomer is expected to be most stable, because (1) the resonance energy of π -electrons is greater in the *trans*- and *cis*-isomers than in the

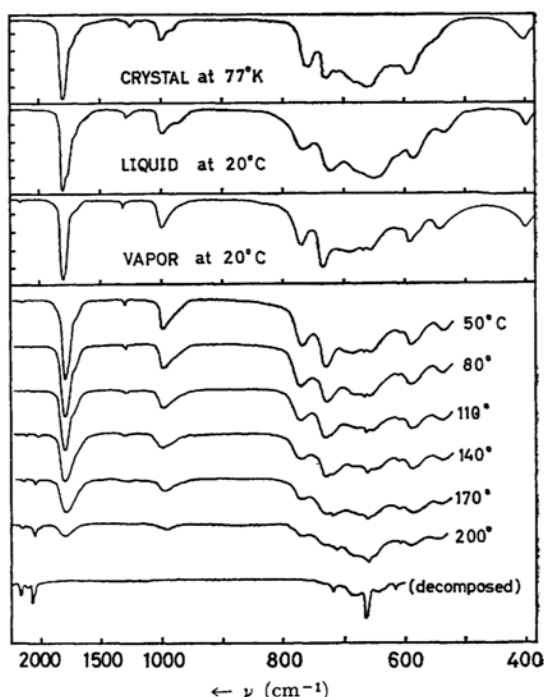


Fig. 1. Infrared spectrum of oxalyl bromide.

Upper half: in various phases.

Lower half: at various temperatures in the vapor phase.

staggered-isomer, (2) the electrostatic potential is lower in the *trans*-isomer than in the *cis*-isomer, and

TABLE I. VIBRATIONAL ANALYSIS OF THE INFRARED SPECTRUM OF OXALYL BROMIDE

Crystal (77°K) ν , cm^{-1}	Liquid (20°C) ν , cm^{-1}	Solution (20°C) ν , cm^{-1}	Vapor (20°C) ν , cm^{-1}	Assignment
405 w	405 w	405 w	405 w	ν_{11} (b_u) COBr scissoring
	540 w	535 w	545 w	$\nu_{10}-\nu_5$
594 m	592 m	588 m	595 m	$\nu_3+\nu_{11}$
664 ^s br	660 ^s br	656 ^s br	661 m	$\nu_4+\nu_6$
			670 m	CO ₂
685 ^m br	690 ^m br	690 ^m br	690 ^m br	$\nu_5+\nu_7+\nu_8$ OR $\nu_7+\nu_{11}+\nu_{12}$
714 vw				CO ₂
729 s	728 s	728 s	731 s	ν_{10} (b_u) C-Br stretching
762 m	772 m	770 m	773 m	$\nu_3+\nu_{12}$
980 ^{vw} sh	975 ^{vw} sh	972 ^{vw} sh		$\nu_3+\nu_8$
1013 m	1004 m	1002 m	1007 m	$\nu_3+\nu_{11}$
1290 w	1295 w	1302 w	1324 w	$\nu_3+\nu_{10}$
1720 vw	1723 vw	1725 vw	1733 vw	$\nu_3+\nu_4+\nu_{10}$
	1780 ^w sh	1785 ^m sh		$\nu_2+\nu_{10}$?
1815 vs	1807 vs	1807 vs	1818 vs	ν_9 (b_u) C=O stretching

s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad

14) T. Omori and Y. Kanda, *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **6**, 29 (1967).

(3) the steric repulsion between the Br and O atoms is smaller than that between the two Br atoms.

In order to seek the possible evidences for the existence of rotational isomers in oxalyl bromide, we studied the temperature dependences of the Raman, infrared and ultraviolet absorption spectra of this molecule. The infrared spectra observed in various phases and at various temperatures are shown in Fig. 1 and the spectral data are given in Table 1. The Raman spectral datum observed in the liquid is given in Table 2. The observation of the Raman spectrum of the oxalyl bromide crystal was unsuccessful owing to quite weak scat-

tering from the crystal and only a few bands were obtained. These are given in Table 2. The temperature dependence of the ultraviolet absorption spectrum is shown in the upper right of Fig. 3. It can be seen from these figures and tables that:

(1) Each band in the infrared spectrum observed in the vapor becomes broader with increasing temperature but the essential spectral structure remains unchanged except for a few bands which increase in intensity at high temperature and become quite prominent in the spectrum at 200°C. The infrared spectrum of the "oxalyl bromide"

TABLE 2. VIBRATIONAL ANALYSIS OF THE RAMAN SPECTRUM OF OXALYL BROMIDE

Liquid (20°C)			Crystal		Assignment
ν , cm^{-1}	Rel. int.	Pol.	(77°K) ν , cm^{-1}	(4.2°K) ν , cm^{-1}	
137	2				$\nu_8 - 2\nu_7$?
191	8	p	193		ν_5 (a_g) COBr rocking
246	1				$2\nu_7$ (ν_7 : COBr twisting)
342	2 (sh)				$2\nu_{12}$ (ν_{12} : COBr rocking)
376	6	dp	364	363	ν_8 (b_g) COBr wagging
415	4	p			ν_4 (a_g) COBr scissoring
494	1				$2\nu_6$ (ν_6 : COBr wagging)
600	7	p	586	587	ν_3 (a_g) C-Br stretching
808	3	p ?			$2\nu_{11}$
870	3				$2\nu_6 + \nu_8$?
1032	4	p			ν_2 (a_g) C-C stretching
1784	10	p	1754	1752	ν_1 (a_g) C=O stretching

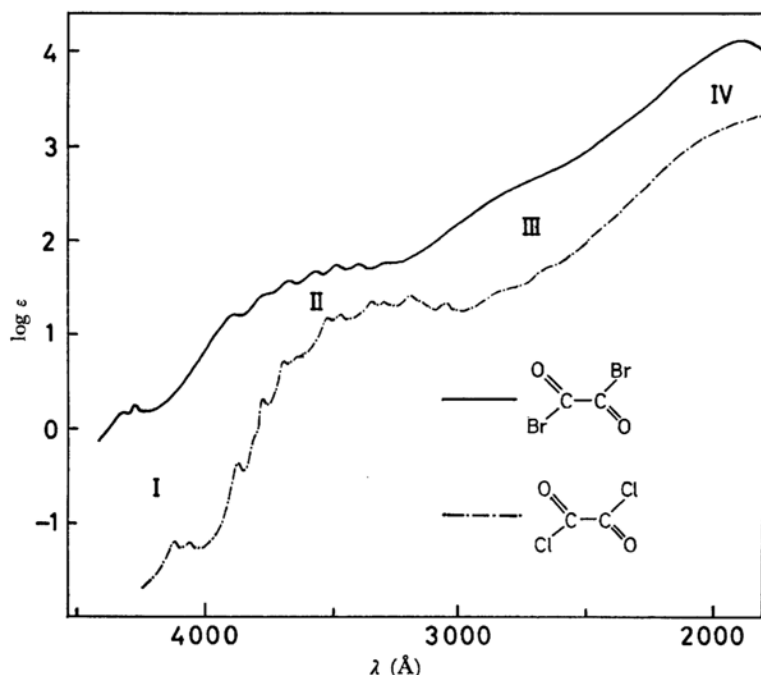


Fig. 2. Ultraviolet absorption spectra of oxalyl bromide and chloride in cyclohexane at room temperature.

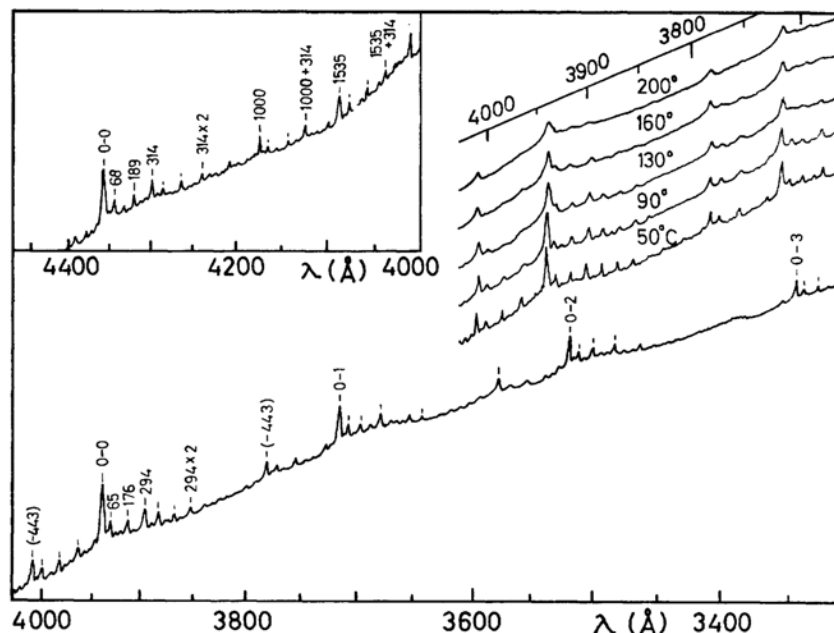


Fig. 3. Near ultraviolet absorption spectrum of the oxalyl bromide vapor.

vapor which was kept at about 220°C for about one hour and then cooled at room temperature is given in the bottom of Fig. 1. This spectrum consists of a few bands which coincide with the unusual bands observed in the high temperature spectrum. These frequencies are 2350, 2155, 2080, 720, 668 and 616 cm^{-1} . The 2155 cm^{-1} band is ascribed to the CO gas¹⁵⁾ and the others to the CO₂ gas.¹⁶⁾

(2) There are no essential structural differences in the infrared spectra observed in various phases except for the bands at about 540, 660, 714, 975 and 1780 cm^{-1} . The 540 cm^{-1} band is assigned to a difference band and this must be diminished at low temperature. The 660 cm^{-1} band, whose intensity is fairly strong in the condensed phases, is ascribed to an unresolved band of 662 and 667 cm^{-1} . The 667 cm^{-1} band and the 714 cm^{-1} band, which is observed in the crystal, are ascribed to CO₂, because slight bubbling of oxalyl bromide was inevitable during the preparation of the sample. The weak 975 cm^{-1} band, which is not observed in the vapor, is assigned to an infrared inactive band which appears in the spectrum through perturbation by the medium.

(3) A mutual exclusion relationship is found between the infrared and Raman spectra except for the strongest Raman band at 1784 cm^{-1} . The same vibrational frequency was also observed in

the infrared spectrum as a shoulder of the strongest band at 1807 cm^{-1} in the liquid and solutions, but this was not observed in the crystal nor in the vapor even at high temperature. This band is assigned to an infrared active band and will be discussed in the next section.

(4) The behavior of the temperature dependence of the ultraviolet absorption spectrum of the oxalyl bromide vapor is the same as that observed in the oxalyl chloride vapor by Sidman.⁷⁾ Although the spectral structure remains unchanged, the absorption bands, which are very sharp at room temperature, become broader and decrease in intensity with increasing temperature. At higher temperature, the discrete bands are superimposed on a continuous background and this background increases in intensity with increasing temperature. This phenomenon is reversible if heating does not exceed 130°C. Heating of the oxalyl bromide vapor above 130°C does not change the spectral structure when the sample is cooled at room temperature again, but the absorption decreases in intensity owing to the decomposition of the sample.

These experimental facts indicate that only one isomer contributes to the observed discrete spectral bands and thus it can immediately be concluded that the discrete band spectra are due to the *trans*-isomer of oxalyl bromide. A careful observation of the ultraviolet absorption spectrum of the oxalyl bromide vapor showed that the continuous background, which was assigned to the *cis*-form by Sidman,⁷⁾ was hardly detectable at room temperature. This indicates that the oxalyl bromide molecule is planar and *trans* at room temperature.

15) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Company, New York (1950), p. 62.

16) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, New York (1949), p. 272.

Vibrational Spectrum and Assignments.

For the *trans*-form of oxalyl bromide (C_{2h} point group), the twelve fundamental vibrations are classified into four symmetry species, that is, 5 vibrations into a_g species, 1 into b_g , 2 into a_u and 4 into b_u . The first six fundamentals are Raman active and the last six are infrared active.

The observed strong and polarized Raman bands of 191, 415, 600, 1032 and 1784 cm^{-1*2} are straightforwardly assigned to totally symmetric COBr rocking ν_5 , COBr scissoring ν_4 , C-Br stretching ν_3 , C-C stretching ν_2 and C=O stretching ν_1 vibrations, respectively and the strong and depolarized Raman band of 376 cm^{-1} to a COBr wagging vibration ν_8 of b_g species.

The strong infrared bands of 728 and 1807 cm^{-1} are assigned to a C-Br stretching vibration ν_{10} and a C=O stretching vibration ν_9 , both are of b_u species, respectively. A weak infrared band around 405 cm^{-1} , whose intensity could not precisely be measured because of poor reliability of our spectrophotometer in this region, can be assigned to a COBr scissoring vibration ν_{11} of b_u species. The medium strong Raman band of 808 cm^{-1} , which seems to be polarized, and the medium infrared bands of 592 and 1004 cm^{-1} can be interpreted as an overtone vibration of ν_{11} and combination vibrations of $\nu_5 + \nu_{11}$ and $\nu_3 + \nu_{11}$, respectively.

The remaining three fundamentals, that is, a COBr rocking vibration ν_{12} of b_u species, a COBr wagging vibration ν_6 of a_u species and a COBr twisting vibration ν_7 of a_u species are expected to appear in the lower frequency region than 400 cm^{-1} , which is the limit of measurement with our spectrophotometer. The weak Raman bands of 246, 342 and 494 cm^{-1} were presumed to be assigned to overtone vibrations of ν_7 , ν_{12} , and ν_6 , respectively. The medium infrared bands of 662 (a component of the unresolved 660 cm^{-1} band), 690 and 772 cm^{-1} could be interpreted as combination vibrations of $\nu_4 + \nu_6$, $\nu_5 + \nu_7 + \nu_8$ (or $\nu_7 + \nu_{11} + \nu_{12}$) and $\nu_3 + \nu_{12}$, respectively.

The weak but distinct infrared band of 1780 cm^{-1} is rather puzzling. This band was assigned to a combination vibration of $\nu_2 + \nu_{10}$, but it cannot be understood why this band is not observed in the crystal nor in the vapor. Detailed analyses of the infrared and Raman spectra are given in Tables I and 2.

Ultraviolet Absorption Spectrum. *Assignment of the Electronic Transitions.* The ultraviolet absorption spectrum of oxalyl bromide in cyclohexane is given in Fig. 2 together with that of oxalyl chloride. The spectrum consists of four absorption systems, which will be called here system I, II, III and IV.

The system I appears in the longest wavelength region and its absorption maximum is located at 4276 Å with $\epsilon=2.0$ in cyclohexane. We observed the corresponding absorption system of oxalyl chloride in the 4100 Å region with $\epsilon_{max}=0.07$ and ascribed it to a ${}^3A_u(n, \pi^*) \leftarrow {}^1A_g$ transition on the basis of a vibrational analysis and the lifetime of the corresponding emission spectrum.⁹⁾ Comparing these two absorption spectra with one another, the system I has to be assigned to the same T \leftarrow S transition as that of oxalyl chloride. A vibrational analysis of this system in the vapor spectrum, which will be described later, indicates that the transition has an allowed $n \rightarrow \pi^*$ character. This fact also supports the ${}^3A_u \leftarrow {}^1A_g$ assignment given to this system.

We tried to observe the T \rightarrow S emission of oxalyl bromide but it was too weak to be measured in any solvent. Recently, Borkman and Kearns¹¹⁾ studied the phosphorescence excitation spectrum of oxalyl bromide in rigid glass solutions containing naphthalene or phenanthrene and confirmed this assignment.

The $f_{T \leftarrow S}$ -value observed in cyclohexane solution is 3.0×10^{-6} . This is unusually large for a multiplicity forbidden transition.¹⁷⁾

The system II which appears in the $4000\text{--}3200\text{ Å}$ region with $\epsilon_{max}=50$ is ascribed to a ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ transition on the analogy of the corresponding absorption system of oxalyl chloride.⁶⁾ We observed the rotational spectrum of the 0-0 band of this system under high resolution condition and found that this band has a typical parallel type structure. This fact indicates that the transition moment of the 0-0 band is perpendicular to the molecular plane and this definitely confirms the above assignment. A detailed report on the rotational spectrum will be given elsewhere. The f -value observed in cyclohexane is 7×10^{-4} .

The system III which appears in the $3000\text{--}2500\text{ Å}$ region with $\epsilon \approx 500$ is very diffuse and was attributed to the second ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ transition by analogy with the assignment given for the corresponding absorption system of oxalyl chloride.⁶⁾

The onset of the system IV overlaps on a tail of the system III and a broad absorption appears to the shorter wavelengths with increasing intensity. Although the exact absorption maximum was not determined because of poor reliability of our spectrophotometer in this region, the apparent maximum is located around 1900 Å with $\epsilon \approx 10^4$. Sidman¹⁸⁾ calculated the energy of the first ${}^1B_u(\pi, \pi^*) \leftarrow {}^1A_g$ transition in glyoxal and obtained 7.4 eV for this energy, which corresponds to about 1680 Å . From the very strong intensity of this system and the general prediction that a bromine substitution causes a red shift for a $\pi \rightarrow \pi^*$ transition, we ascribed this system to a ${}^1B_u(\pi, \pi^*) \leftarrow {}^1A_g$

*2 The Raman and infrared frequencies observed in the liquid at room temperature are used in this discussion.

17) H. Shimada and Y. Kanda, This Bulletin, **40**, 2742 (1967).

18) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

TABLE 3. VIBRATIONAL ANALYSIS OF THE ULTRAVIOLET ABSORPTION SPECTRUM OF THE OXALYL BROMIDE VAPOR

ν , cm^{-1}	Assignment	ν , cm^{-1}	Assignment
22760 w	A - 183	25615 m	
22828 w		25667 s	B + 294
22916 vw		25735 m	B + 294 + 65
22943 m	0-0 of the T \leftarrow S(A)	25796 w	
22975 vw		25847 m	B + 294 + 176
23011 w	A + 68	25963 m	B + 294 \times 2
23074 vw	A + 314 - 183	25994 w	
23132 w	A + 189	26190 w	
23193 w		26433 w	
23226 w		26465 s	B + 1537 - 443
23257 m	A + 314	26498 w	
23297 vw		26532 m	B + 1537 - 443 + 65
23320 vw	A + 314 + 68	26568 w	
23414 vw		26640 m	B + 1537 - 443 + 176
23440 w	A + 314 + 189	26725 w	B + 1537 - 180
23505 vw		26840 w	
23545 vw		26910 vs	B + 1537
23573 w	A + 314 \times 2	26940 w	
23606 vw		26975 s	B + 1537 + 65
23650 vw	A + 314 \times 2 + 68	27014 w	
23670 vw		27081 m	B + 1537 + 176
23760 vw	A + 1000 - 183	27146 w	
23792 vw		27206 s	B + 1537 + 294
23825 vw		27274 w	B + 1537 + 294 + 65
23943 w	A + 1000	27377 m	B + 1537 + 294 + 176
23970 vw		27856 w	
24010 vw	A + 1000 + 68	27970 m	B + 1537 \times 2 - 443
24042 vw		27980 w	
24208 vw		28234 w	B + 1537 \times 2 - 180
24258 w	A + 1000 + 314	28353 w	
24295 vw	A + 1535 - 183	28410 s	B + 1537 \times 2
24325 vw		28445 w	
24452 vw		28473 m	B + 1537 \times 2 + 65
24478 m	A + 1535	28587 m	B + 1537 \times 2 + 176
24512 vw		28655 w	
24608 vw		28714 m	B + 1537 \times 2 + 294
24664 vw	A + 1535 + 189	28780 w	B + 1537 \times 2 + 294 + 65
24790 vw	A + 1535 + 314	28888 w	B + 1537 \times 2 + 294 + 176
24857 vw		28960 vw	
24930 s	B - 443	29013 w	B + 1537 \times 2 + 294 \times 2
24995 m	B - 443 + 65	29838 w	
25096 w		29890 s	B + 1537 \times 3
25113 w	B - 443 + 176	29925 vw	
25135 w		29955 m	B + 1537 \times 3 + 65
25193 w	B - 180	30069 m	B + 1537 \times 3 + 176
25227 m	B - 443 + 294	30112 w	
25325 vw		30136 w	
25373 vs	0-0 of the S' \leftarrow S(B)	30191 m	B + 1537 \times 3 + 294
25408 w		30257 vw	
25438 s	B + 65	31347 m	B + 1537 \times 4
25470 w		31537 vw	
25549 m	B + 176		

s: strong, m: medium, w: weak, v: very

transition.

Vibrational Analysis of the Absorption Spectrum. The absorption spectrum of the oxalyl bromide vapor due to the first ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ transition consists of a number of sharp bands and its spectral structure quite resembles to that of oxalyl chloride.⁷⁾ The spectrum and the spectral data for this system are shown in Fig. 3 and Table 3, respectively.

The strongest band at 25373 cm^{-1} was taken as the 0-0 band of this system. The prominent feature of the spectrum is the interval of 1537 cm^{-1} , which produces a main progression starting from the 0-0 band. This frequency can be assigned to the totally symmetric C-O stretching vibration ν_1 in the excited state.

The next prominent feature is the interval of 443 cm^{-1} which appears in the longer wavelength side of the individual bands of the main progression. Temperature dependence of the 24930 cm^{-1} band, which is separated by 443 cm^{-1} from the 0-0 band, clearly shows a characteristic behavior of a hot band (see Fig. 3). We therefore, assigned the interval of 443 cm^{-1} to the ground state frequency of ν_4 . The corresponding Raman frequency observed in the liquid is 415 cm^{-1} . The discrepancy between two frequencies is fairly large. The similar frequency shifts were also observed in the Raman spectrum by changing the phase from the liquid to the crystal (see Table 2). These observations may suggest that the modes of these vibrations are sensitive to a change of the phase in this molecule. The band at $26,465\text{ cm}^{-1}$ is separated by 445 cm^{-1} from the 0-1 band and by 1092 cm^{-1} from the 0-0 band. Although the interval of 1092 cm^{-1} might be assigned to the excited state frequency of the totally symmetric C-C stretching vibration ν_2 , the behavior of the temperature dependence of the 26465 cm^{-1} band is the same as that of the 24930 cm^{-1} band. This fact denies the ν_2 assignment.

There are another prominent interval of 294 cm^{-1} which appears in the shorter wavelength side of the individual bands of the main progression. This interval very probably corresponds to the excited state frequency of ν_4 , because the band structure of the 294 cm^{-1} band resembles to that of the 443 cm^{-1} band and the overtone of this frequency is

also observed in the spectrum. Other intervals of 65 and 176 cm^{-1} are also quite prominent. All strong bands mentioned above are accompanied by these two subbands in their shorter wavelength side.

The absorption spectrum of the oxalyl bromide vapor due to the ${}^3A_u(n, \pi^*) \leftarrow {}^1A_g$ transition consists of a number of sharp bands. A microphotometer tracing of the spectrum and the spectral data are presented in the upper left of Fig. 3 and Table 3, respectively. The spectral structure is quite similar to that of the ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ absorption system.

The strongest band at 22943 cm^{-1} was taken as the 0-0 band of this system. The totally symmetric C-O stretching vibration seems to constitute a main progression, but the tail of this system overlaps on the onset of the strong $S' \leftarrow S$ absorption system and, therefore, only one quantum of this vibration could be observed. A strong band at 24478 cm^{-1} , which is separated by 1535 cm^{-1} from the 0-0 band, is the first member of this progression. There is a sharp and distinct band at 23943 cm^{-1} , which is separated by 1000 cm^{-1} from the 0-0 band and by 535 cm^{-1} from the 0-1 band. The interval of 1000 cm^{-1} was assigned to the triplet state frequency of the C-C stretching vibration ν_2 , because the interval of 535 cm^{-1} is too large to be assigned to the ground state frequency of ν_4 . There are prominent intervals of 68, 189 and 314 cm^{-1} which appear in the shorter wavelength side of three strong bands mentioned above. The interval of 314 cm^{-1} very probably corresponds to the triplet state frequency of ν_4 .

The fact that the spectral structure of this system quite resembles to that of the first ${}^1A_u(n, \pi^*) \leftarrow {}^1A_g$ absorption system (see Fig. 3) suggests that the system I is caused by an $n \rightarrow \pi^*$ promotion. The allowed $n \rightarrow \pi^*$ character of this transition definitely indicates that the triplet state involved in this transition is a ${}^3A_u(n, \pi^*)$ state.

Detailed vibrational analyses of both the systems I and II are given in Table 3.

The authors indebted to the Ministry of Education for grants-in-aid out of the Scientific Research Expenditure.