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discussion of the failure of the theory of small vibrations in the case of argon, pointing out that the relatively large amplitudes deducible from experimental data should give rise to appreciable anharmonicities in the vibration. With this in view, it is not surprising that small changes are necessary in the Θ -factor; in fact the surprising thing is that our bold assumption that the Θ 's can be obtained by a dimensional analysis of the mechanical system works as well as it does. This difficulty might also conceivably cause deviations of type (3).

(C) Pitzer's assumption V that the four substances have the same reduced E_p curve may not

be strictly true. Guggenheim² noted that this assumption should be accurate for large values of r , where the intermolecular potential energy ϵ is proportional to $-r^{-6}$, but that there was good reason to suppose that it does not hold accurately in general. He further stated that many macroscopic properties were insensitive to the precise form of the relation between ϵ and r for small r . The fact that argon, krypton, and xenon obey the principle of corresponding states as liquids is consistent with these considerations. In the solid state, however, it seems likely that the properties are considerably more sensitive to the shape of the potential energy curve.

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On the Ultraviolet Absorption Spectrum of Ozone†

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The absorption spectrum of ozone has been investigated in the near ultraviolet from $\lambda 3439$ to 3850\AA at two temperatures. The bands observed have been interpreted as arising in part from transitions from the vibrationless ground electronic state and in part from transitions from excited vibrational levels of the ground electronic state. The distinction between the two groups is based primarily on the relatively large temperature sensitivity of the intensity of the bands ascribed to transitions from excited vibrational states. A partial analysis gives strong support to the assignment of the frequency 1043 cm^{-1} to a fundamental vibration of the molecule. Moreover, it appears quite unlikely that the frequency 710 cm^{-1} can be eliminated as one of the fundamental frequencies. No information concerning the third fundamental frequency was obtained.

THE spectroscopic evidence on the structure of ozone has recently been critically examined by Simpson,¹ who gives a new assignment of the fundamental vibration frequencies of the ozone molecule. This assignment leads to a configuration in which the oxygen atoms are arranged in the form of an obtuse isosceles triangle with apical angle 125° and bond length 1.17\AA , in fair agreement with the electron diffraction results² which give an apical angle of 127° and bond length 1.26\AA . However, the infra-red absorption spectrum of ozone has not been ex-

amined in sufficient detail under high enough dispersion to permit an unambiguous assignment of the three fundamental frequencies from among the four possibilities which seem most likely in view of the experimental data, namely, 710 , 1043 , 1740 , and 2105 cm^{-1} .³⁻⁶

An analysis of the effect of temperature on the vibrational structure of the band system in the ozone spectrum lying in the region $\lambda 3000$ – 3850\AA offers hope of affording additional information as to the fundamental vibrational frequencies of the normal state of the molecule. Such analysis

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⁵ A. Adel *et al.*, *Astrophys. J.* **89**, 320 (1939), **94**, 451 (1941); *Phys. Rev.* **49**, 288 (1936).

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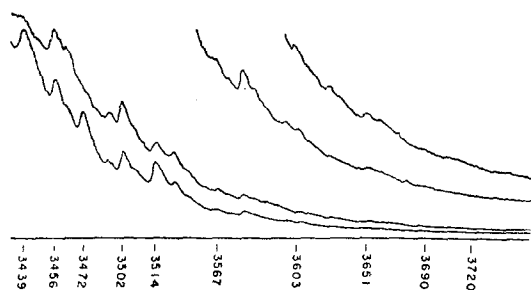


FIG. 1. Copy of microphotometer traces of a part of the near ultraviolet absorption spectrum of ozone at room temperature and at 90 degrees Centigrade. Complete description in text.

involves the finding and the interpretation of a number of bands, among the many members in the system, which originate in transitions from excited vibrational levels in the normal electronic state of the molecule. It should be possible to identify these bands by the pronounced increase with temperature of the intensity of their absorption.

The absorption spectrum of ozone in the region from $\lambda 3000$ – 3650\AA ⁷⁻¹² consists of a system of diffuse bands falling off rapidly in intensity with increasing wave-length which appear to overlie a background of continuous absorption. The intense bands in this region may be ordered in groups of partial progressions and interpreted in terms of transitions from a vibrationless ground state to an upper electronic state in which two vibrational frequencies are excited. A formula for these bands which has been suggested by Jakowlewa and Kondratjew¹¹ seems to fit the positions of the bands reasonably well:

$$\begin{aligned} \nu = & 28447 + 636.3\nu_1' - 16.0\nu_1'^2 + 351.7\nu_2' \\ & - 4.5\nu_2'^2 - 0.17\nu_2'^3 - 12.0\nu_1'\nu_2' - 1.5\nu_2'\nu_1'^2 \\ & - 0.5\nu_1'\nu_2'^2 - 1058\nu'' + 11.5\nu''^2. \quad (1) \end{aligned}$$

In addition to the bands described by this expression there exists, principally to longer wavelengths, a large number of weaker bands. These bands are strongly temperature-sensitive and may presumably be ascribed to transitions from

excited vibrational levels in the ground state. If this is the case it is to be expected that these bands may be ordered in such a way as to form progressions homologous to the temperature insensitive bands but shifted toward the red from them by constant frequency differences corresponding to the energies of the excited vibrational levels of the ground state. Four bands of such a group, based upon the frequency 1043 cm^{-1} , have been observed in work at the temperatures -78°C , room temperature, and 100°C .^{10,11} We have endeavored to extend the ultraviolet absorption spectrum of ozone to longer wavelengths in order to obtain more data on the temperature-sensitive bands, to ascertain that no temperature-insensitive bands lie beyond the proposed $(000)'' \rightarrow (000)'$ bands^{8,11} at $\lambda 3514\text{\AA}$, and to classify as many as possible of the temperature-sensitive bands in terms of vibrational frequencies of the ground state as indicated by observations in the infra-red.

The absorption was studied at room temperature and at 90°C in the region of weak absorption from $\lambda 3439$ to 3850\AA by means of a Bausch and Lomb Littrow quartz spectrograph with a dispersion of about 7\AA per mm in this region. A 500-watt tungsten projection lamp was used as a light source. The absorption cell was an 8-meter glass tube enclosed in a stainless steel jacketing tube which could be heated electrically. The ozone was prepared by passing a continuous stream of tank oxygen through two Siemens type ozonizers and then through the cell. Dry-ice traps were provided to condense N_2O_6 , which catalyzes the decomposition of ozone at the higher temperature, and might contribute to the absorption in this region if its partial pressure were not kept sufficiently low.¹³ The concentration of ozone in the cell was estimated by means of the absorption coefficients of Ny and Choong¹⁴ at $\lambda 3439\text{\AA}$ to be about 6 percent. The positions and relative intensities of the bands were determined from microphotometer traces; the weakness of the bands and the intensity of the continuous background made measurements with a visual comparator impractical. A large number

⁷ A. Fowler and G. Strutt, Proc. Roy. Soc. **93**, 729 (1917).

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¹³ E. J. Jones and O. R. Wulf, J. Chem. Phys. **5**, 873 (1937).

¹⁴ T. Z. Ny and S. P. Choong, Chinese J. Phys. **1**, 38 (1933).

of bands was observed, including all of those indicated by Chalonge and Lefebvre,⁹ and other bands at longer wave-lengths. In all, seventy-four bands were recorded, although some of these were very weak and longer ozone paths or higher concentrations would be necessary to confirm their existence and to determine their exact positions. The positions of the bands could be estimated to an accuracy of only about $\pm 1\text{\AA}$ in the region $\lambda 3439$ to 3600\AA and $\pm 2\text{\AA}$ in the region $\lambda 3600$ to 3850\AA .

A copy of microphotometer traces of a part of the spectrum is presented in Fig. 1. Two sets of traces are given which differ in the technique of microphotometering employed. The lower two traces were prepared with a narrow microphotometer slit and show the stronger bands clearly and with high resolution. The upper set of two traces was made with a wider slit for reasons of greater sensitivity in regions of the plate where the photographic density was higher. In each set the lower of the two traces corresponds to the spectrum at room temperature; the higher corresponds to that at 90 degrees C. Both traces are referred to the same base line. The wave-length of some readily identified bands is indicated on the figure. The figure does not present adequately the data at longer wave-lengths were enlarged traces made with wider microphotometer slits allow greater accuracy in measuring the bands. Moreover, comparison of measurements from several plates also lends greater confidence in the existence and position of these very weak bands than is suggested by the single figure presented. The figure shows clearly the relatively low temperature sensitivity of the bands at $\lambda 3439$, 3472 , and 3514\AA .

An approximate estimate of the absorption coefficients of the bands was made using the optical density of the photographic plate as indicated by the photometer traces and the Hurter and Driffeld curves for the plate. The ratio of these calculated coefficients for the two temperatures, 90 degrees and 25 degrees C, was used as an indication of the temperature sensitivity of the bands. Only rough quantitative significance should be attached to this ratio for the following reasons: First, the concentration of ozone at the lower temperature was known only approximately and no estimate whatsoever

was made of that at the higher temperature; most likely, it was appreciably less because of thermal decomposition. In the calculations it was assumed that these concentrations were equal. Second, the estimates were based only on the absorption of the maxima of diffuse bands and not on the integrated intensity of the bands. Moreover, since it was not possible to separate the bands from the background of overlapping bands, the estimate of the absorption coefficient depends not only on the particular band system for which it was calculated, but also on the underlying, very temperature-sensitive background. It was found that the ratio of the absorption coefficients at the two temperatures for bands assigned to transitions of the type $(000)'' \rightarrow (v_1 v_2 0)'$ was considerably less than that for bands believed to be caused by transitions from excited vibrational levels in the lower electronic state. That the "temperature-insensitive" bands vary at all with temperature is probably due to the overlapping of portions of adjacent temperature-sensitive bands. In particular, of all the bands here studied, only those at $\lambda 3439$, 3472 , and 3514\AA were relatively insensitive to temperature change; all other bands in this spectral region increased more rapidly in intensity on heating than these. Thus, the data seem to confirm quite well the assignment of the band at $\lambda 3514\text{\AA}$ to the transition $(000)'' \rightarrow (000)'$.

An attempt was made to classify the remaining temperature-sensitive bands in the following fashion. The intense bands previously reported^{8,12} and arranged in array of partial progressions were assumed to be caused by transitions from the vibrationless ground state. (A convenient tabulation of these bands is given by Melcher, reference 12.) Energies corresponding to assumed vibrational levels were subtracted from the energies associated with these temperature-insensitive bands, and the tabulated data were searched for bands with frequencies corresponding to those calculated by this method. Because of the diffuse character of the bands, the accuracy of the measurements limited the precision obtainable in matching the calculated and observed frequencies, and agreement to within about 15 cm^{-1} was considered acceptable. Attempts were made to classify the bands in terms of the assumed fundamental frequencies

TABLE I. Summary of the bands observed and their possible assignment $\nu_1''=1043$, $\nu_2''=710$, $\nu_3''=2105$.

		Upper state Lower state	$(\nu_1' \nu_2' 0)$ $(\nu_1'' 0 0)$			$(\nu_1' \nu_2' 0)$ $(0 \nu_2'' 0)$			$(\nu_1' \nu_2' 0)$ $(0 0 \nu_3'')$			$(\nu_1' \nu_2' 0)$ $(1 1 0)''$		$(\nu_1' \nu_2' 0)$ $(1 2 0)''$	
Band		$\frac{\alpha_{90}^{00}}{\alpha_{25}^{00}}$	ν_1''	ν_1'	ν_2'	ν_2''	ν_1'	ν_2'	ν_3''	ν_1'	ν_2'	ν_1'	ν_2'	ν_1'	ν_2'
3439A	29070 ± 5 cm ⁻¹	1.07	0	1	0										
3448	28994	1.24				1	1	2							
3452	28960	1.25	1	1	3										
3456	28927	1.24	1	2	1	1	2	0							
3463	28868	1.22				2	2	2							
3472	28794	1.16	0	0	1										
3481	28719	1.34													
3486	28678	1.48	1	1	2	1	1	1							
3488	28662	1.46													
3495	28604	1.40	1	2	0	2	1	3	1	4	0				
3498	28580	1.43				2	2	1							
3502	28547	1.53				3	2	3							
3506	28514	1.48										2	2		
3509	28490	1.50	3	4	3										
3514	28442	1.23	0	0	0							3	0		
3518	28417	1.37	1	0	3	1	0	2							
3526	28353	1.44	1	1	1	1	1	0						3	2
3529	28329	1.44				2	1	2							
3533	28297	1.44												4	0
3537	28265	1.40	3	4	2	2	2	0				1	3		
3538	28256	1.42	2	2	2	3	2	2							
3545	28201	1.59										2	1		
3553	28137	1.51												2	3
3560	28082	1.69	1	0	2	2	0	3;	1	3	0			3	1
						1	0	1							
3567	28027	1.47	1	1	0	2	1	1							
3571	27995	1.42	3	4	1										
3575	27964	1.47				3	1	3				1	2		
3580	27925	1.53	2	2	1	3	2	1							
3583	27902	1.52										2	0		
3590	27847	1.45												2	2
3596	27801	1.40	3	3	2										
3603	27747	1.36	1	0	1	2	0	2;						3	0
						1	0	0							
3606	27724	1.32	3	4	0										
3608	27708	1.34				2	1	0				0	3		
3614	27662	1.31	2	1	2	3	1	2							
3620	27616	1.36	2	2	0	3	2	0							
3624	27586	1.40	3	2	3							1	1		
3627	27563	1.37				4	3	0	1	2	0			1	3
3630	27541	1.47													

710, 1043, 1740, and 2105 cm⁻¹, which appear as reasonable possibilities in the light of previous investigations of both the ultraviolet and the infra-red spectrum of ozone.^{1, 6}

Table I summarizes the positions of the bands observed and the transitions assigned to them. Only two frequencies were employed in the upper state, according to Eq. (1), since the data did not seem to justify the assumption of a third. Because of the lack of resolution, the two frequencies 1740 cm⁻¹, assumed as a possible fundamental, and 1753 cm⁻¹, corresponding to (710 + 1043) cm⁻¹, are tabulated together; the data do not allow of a distinction between these two possibilities.

Table II was prepared to show the compara-

tive number of bands which can be fitted by various assumed combinations of fundamental frequencies. The assumed lower state frequencies and their combinations are indicated at the head of the columns of the table, namely, 1043, 710, 1740, 1043 + 710, 1043 + 2 \times 710, and 2105 cm⁻¹. From the columns of Table I it is readily possible to count the number of bands fitted by each of these frequencies. The maximum number of bands fitted by the frequency at the head of the column is given in the last row of the table regardless of whether it is possible to account for some of the bands by other assumed frequencies. However, since some of the bands may be described in more than one way, it is necessary in evaluating the assignment of vibrational fre-

TABLE I.—Continued.

Band	$\frac{\alpha_{90^\circ}}{\alpha_{25^\circ}}$	ν_1''	ν_1'	ν_2'	ν_2''	ν_1'	ν_2'	ν_3''	ν_1'	ν_2'	ν_1'	ν_2'	ν_1'	ν_2'
3633A	27518 \pm 5 cm ⁻¹	1.41	3	3	1								2	1
3637	27487	1.47												
3648	27405	1.35	1	0	0	2	0	1						
3651	27381	1.37									0	2		
3655	27352	1.33	2	1	1	4	1	3;						
						3	1	1						
3657	27337	1.35				4	2	1			1	0		
3664	27285		3	2	2								1	2
3667	27262													
3672	27225	1.36											2	0
3674	27211		3	3	0									
3676	27196													
3678	27181													
3681	27159													
3683	27144	1.32												
3688	27107													
3690	27093		2	0	2	3	0	2						
3693	27071					4	1	2;						
						3	1	0;						
						2	0	0						
3700	27019	1.32	3	1	3;	4	2	0			0	1	0	3
			2	1	0									
3706	26976		3	2	1									
3708	26961								1	1	0		1	1
3718	26889													
3720	26874													
3725	26838					4	0	3						
3734	26773	1.31				4	1	1;						
						3	0	1						
3738	26745		2	0	1									
3743	26709		3	1	2						0	0	0	2
3750	26659		3	2	0									
3753	26638												1	0
3760	26587													
3777	26469		3	0	3									
3782	26434					4	1	0;						
						3	0	0						
3786	26406		3	1	1;	4	0	2						
			2	0	0									
3795	26343	1.33							1	0	0		0	1
3824	26143												0	0
3840	26034		3	0	2	4	0	1						

* Since the ratio of absorption coefficients for bands at λ greater than $\lambda 3650\text{\AA}$ differed so little from that of the background, this ratio was not calculated for individual bands at wave-lengths greater than $\lambda 3680\text{\AA}$. The values given are for the region of the spectrum, not individual bands.

quencies to consider the relative value of various sets of assumed frequencies in fitting the entire band system. Accordingly, certain sets of frequencies have been chosen which are enumerated in the first column of the table. The number of bands described by each set is counted as follows:

Bands which can be accounted for by the first listed frequency of the set are tabulated in the column allocated to this frequency; then bands not already accounted for by the first frequency, but given independently by the second frequency are counted and entered in the corresponding frequency column, and similarly for the third frequency excluding bands ascribed to the first and second. Finally bands accounted for by

combinations or other frequencies are listed in their respective columns, but always so that no band has been counted more than once. In the tabulation, bands arising from the vibrationless ground state have been omitted. The last column of the table gives the total number of bands fitted by any particular set of assumed frequencies. Not all of the bands which are listed in Table I have been fitted into any of the schemes of Table II; twelve bands are not accounted for by any transitions based on the frequencies assumed. These bands are almost all at the long wave-length end of the band system and are very weak. Uncertainties in the measurement of their positions are large, and they may actually

TABLE II. Number of bands fitted into scheme of frequency.

Frequencies excited in lower state Order of use of frequencies	1043	710	1740 or 1043 + 710	1043 + 2 × 710	2105	Total
1043	33					
710		14	4	8	0	59
710		32				
1043	15		4	8	0	59
1740			12			
1043	29			8	0	59
710		10				
2105					5	
1043	31		4	6		59
710		13				
2105					5	
1043	31	—		—		43
1740			7			
Maximum number	33	32	12	8	5	

be spurious. It is however, not unreasonable to suppose that they arise from still higher levels in the ground state than have been employed in the calculations, and it is believed probable that these bands could be accounted for satisfactorily in that fashion. In addition, it should be pointed out that no value for ν_3' has been suggested, and it might indeed be profitable to examine the positions of the unassigned bands for such a possibility.

It will be noticed that the frequency 1043 cm^{-1} enters into all of the assumed schemes. The assumption of this frequency as a fundamental seems hardly disputable since the intensity of the bands based upon this frequency is greater by far than any other band arising from transitions of a similar type. The infra-red data¹ are also in support of this frequency as a fundamental. Transitions arising from levels of this set but higher than the first were fitted by adjusting the first anharmonic term in the expansion of the energy of the vibrational state so

as to give as accurate a fit as possible to the positions of temperature-sensitive bands in the correct neighborhood. With both this frequency and that based on 710 cm^{-1} only the square term in the expansion is given, since it is not believed that the three infra-red frequencies involved in the bands associated with the 1043 cm^{-1} separation and the four infra-red frequencies involved in the bands associated with the 710 cm^{-1} separation justify the addition of higher terms. The energy (expressed in wave numbers) corresponding to higher levels of these two vibrations fitted in the way described are represented by the following two formulas:

$$\begin{aligned}\nu_1'' &= 1066\nu_1'' - 23\nu_1''^2, \\ \nu_2'' &= 727\nu_2'' - 17\nu_2''^2.\end{aligned}$$

The point to which we wish to call particular attention is demonstrated by Table II, namely, that it is possible to ascribe almost all of the bands observed in the temperature-sensitive ultraviolet spectrum of ozone to the two fundamental frequencies 710 and 1043 cm^{-1} , and their harmonics and combinations. Some bands fit into schemes in which other fundamental frequencies are assumed, but these bands are just as well classified by the first two frequencies, which in addition explain many other bands. Moreover, the assumption of frequencies for the ground electronic state which do not include 710 cm^{-1} results in a scheme which is considerably inferior in classifying all of the bands. It accordingly seems very unlikely that 710 cm^{-1} can be eliminated as one of the fundamental frequencies of the ozone molecule.

The authors wish to express their appreciation to Dr. O. R. Wulf of the U. S. Weather Bureau for suggesting this problem, and for his encouragement and assistance in obtaining and interpreting the data. We also wish to thank Professor Badger for use of the spectrograph and for helpful criticism of the manuscript.