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THE ULTRAVIOLET ABSORPTION SPECTRUM OF SULFUR DIOXIDE

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Abstract

Measurements of spectrograms of the ultraviolet SO_2 absorption bands taken at different pressures, tube lengths and temperatures together with known infrared and Raman frequencies serve to locate the three fundamental vibrational series. Tables giving the band assignments to these sequences are included. The three lower state frequencies for infinitesimal amplitude are 1369, 1164 and 610 cm^{-1}, while for the excited state the corresponding frequencies are 341, 387 and 290 cm^{-1}. The types of addition series are discussed.

The excited state $\Delta\nu_v:v$ curves for $v<4$ have a positive slope, while for $v>4$ there is a sudden reversal to the usual negative anharmonic coefficient. The three ground state frequencies indicate a value of 34° for the half-angle at the apex of the SO_2 triangular model. Comparisons of the heats of dissociation estimated from the extended areas under the $\Delta\nu_v:v$ curves with thermal and spectroscopic data suggest the process $SO_2 \rightarrow S+O_2$ for the two symmetrical vibrations and $SO_2 \rightarrow SO+O$ for the asymmetrical vibration. The dissociation products appear to be the same in the two electronic states.

Introduction

UP TO the present time there has been but very little investigation of the details of the ultra-violet band systems of triatomic molecules. Great advances have been made in the study of diatomic molecular spectra with the aid of the quantum theory, but owing to their quite evident complexity, the spectra of polyatomic molecules have been avoided. Many of the ideas of molecular dynamics developed for diatomic molecules should be applicable to more complex molecules, however, and in addition there is now available much information on the fundamental vibrational frequencies of these molecules from their infrared and Raman spectra. Without this previous knowledge of the three fundamental frequencies of the ground state for molecules such as SO_2 and CS_2, the vibrational quantum analysis of their complex electronic band systems would be all but impossible.

The infrared vibration-rotation absorption bands of sulfur dioxide have recently been measured by Bailey, Cassie, and Angus.[1] Their work shows that the three fundamental bands are at 1361 cm^{-1}, 1152 cm^{-1}, and 606 cm^{-1}, but since a sufficient number of harmonic bands were not observed, the fundamental frequencies for infinitesimal amplitude of vibration could not be computed. The first and third of these frequencies correspond to a vibrating electric doublet lying along the bisector of the vertical angle of the triangular structure, while the middle frequency corresponds to an effective electric

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[1] C. R. Bailey, A. B. D. Cassie, and W. R. Angus, Proc. Roy. Soc. **A130**, 142 (1930).

doublet in a direction perpendicular to this bisector and in the plane of the triangle. Both the existence of a rather large permanent dipole moment and the indicated structure and intensity of these infrared bands lead to the conclusion that the SO_2 molecule is definitely triangular in shape with an acute angle at the apex. The Raman spectrum of gaseous SO_2 has been investigated by Bhagavantam[2] who found but one line at 1154 cm^{-1}, whereas for liquid SO_2 Dickinson and West[3] find the three lines 1145.9 cm^{-1} (strong), 1340.1 cm^{-1} (medium, diffuse) and 524.3 cm^{-1} (weak, diffuse). The last line is explained by Bailey, Cassie, and Angus as the difference 1152–606.

The ultraviolet absorption bands of sulfur dioxide have been referred to by Henri[4] and others. The apparent predissociation limit at about λ 2525 (112,000 cal.) has been assumed by Henri[5] to correspond to $SO_2 \rightarrow SO+O$, and on this basis he develops an energy equation with other known data to give the heat of dissociation of O_2 as 126,400 cal. (5.5 volts). This calculation has been discussed by Herzberg[6]; and we return to the question in our discussion below.

Description of Spectrum

The ultraviolet absorption band systems of sulfur dioxide have been photographed with a Hilger E_1 quartz spectrograph, the gas being contained in a glass absorption tube 111 cm long, closed at the ends with quartz windows. The SO_2 was prepared by dropping HCl on to $NaHSO_3$, and was dried by passing through a long P_2O_5 tube. The source of continuous radiation for the background was the usual hydrogen discharge tube. The spectrograms with this 111 cm absorption cell were all taken with the gas at room temperature and at pressures varying from 80 cm to less than 1 mm Hg. Spectrograms were also obtained with a 27 cm absorption cell with the SO_2 at 1 cm Hg pressure and at the temperature of a solid CO_2-acetone mixture.

Fig. 1 is a reproduction of a series of spectrograms taken at various gas pressures with the longer absorption tube. To be noted are the evident strong series of band groups in the main absorption region, and the appearance of new bands at the long wave-length end at the higher pressures. These latter bands do not form a separate band system, as has been suggested by Henri[5]; but are associated with the main absorption system and represent transitions from vibrational levels with $v=1$, 2 and 3 of the ground electronic state. At the lower temperature the very weak band at 30961 cm^{-1} is clearly the band of longest wave-length, suggesting that it is a 0,0 band, and there is considerable simplification in the region of strongest absorption. At the high frequency end of this system, absorption ceases at the lower pressures at about λ2500, the last bands being rather diffuse but with no continuous absorption in evidence. Another SO_2 band system which we have not investigated extends from about λ2350 farther into the ultraviolet. At pressures greater than

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[2] S. Bhagavantam, Nature **126**, 995 (1930).

[3] R. G. Dickinson and S. S. West, Phys. Rev. **35**, 1126 (1930).

[4] V. Henri, Structure des Molecules.

[5] V. Henri, Nature **125**, 272 (1930).

[6] G. Herzberg, Zeitz. f. Physikal. Chemie **B10**, 189 (1930).

1 cm these two band systems are fused together, the absorption being continuous from the limit of the discrete bands to be seen in Fig. 1 to some point in the vacuum ultraviolet region.

Some of the stronger and more isolated bands at about λ3300 were photographed at high dispersion with a 21-foot concave grating, but these spectrograms fail to resolve any of the rotational structure. Furthermore these SO_2 bands do not have a sharp head, but rather seem to fade out on both sides. In the measurement of the lower dispersion spectrograms, then, we could only set the cross-hair on the estimated center of the band or, in the case of broad bands produced by overlapping, the overall width was measured. This of course limits the accuracy of the measurements, and entails a possible error in the interval between any two successive bands in the series referred to below, of say, 9 or 10 cm^{-1}.

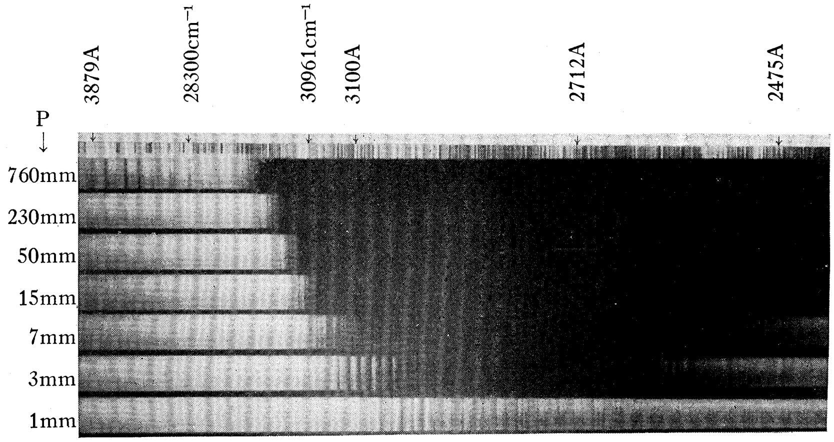

Fig. 1. Spectrograms of the ultraviolet SO_2 absorption bands taken with the Hilger E_3 spectrograph. The absorption path was 1 m, and the pressures were as indicated. To be noted are the group of bands at the red end of the high pressure spectrograms and the evident excited state sequences proceeding towards higher frequencies from 30961 at the lower pressures. Higher dispersion plates show that many of these apparently single bands are in reality groups of bands.

VIBRATIONAL ANALYSIS

The regular and intense series of bands observable in the region from λ3200 to λ2900 on the spectrograms for the lowest SO_2 pressures can only be vibrational sequences in the excited electronic state. These and other series terminate on the long wave-length end at about λ3230 in a region of bands of very low intensity, suggesting that the origin of the system is at about this frequency. Now in the high-pressure group to the red of this point the first strong band to appear with increasing gas pressure is at 28300 cm^{-1}. Assuming that this represents a transition from a lower vibrational level other than 0 of the symmetrical mode of vibration, another band is found at 29621, 1321 cm^{-1} to the high frequency side, from which the interval to 30961, which is the long wave-length end of the strongest excited state sequence, is 1340 cm^{-1}. From these regularities as a starting point, the double array of bands originating in this (v_1', v_1'') mode of vibration as presented in Table I were found. Measurement towards the violet from the 28,300 band with differences characteristic of the asymmetric mode of vibration (1150 cm^{-1}), however, does not produce any correlation.

TABLE I. *Fundamental series corresponding to the* 1369 $\textit{cm}^{-1}$ *vibration.*

v_1'' / v_1'	0	1	2	3	Average $\Delta\nu$
0	30961	29621	28300	27002	
1	31327	29979		27359	360
2	31719	30365	29043		389
3	32145	30801	29472		430
4	32619	31270	29942		471
5	33103	31757	30432		487
6	33571	32230	30895		468
7	34026	32683	31361		458
8	34461	33118	31793		434
9	34888	33539	32218		424
10	35318	33969	32638		423
11	35738	34390	33058		420
12	36130	34774	33451		390
13	36514	35156	33836		384
14	36876	35522	34193		362
15	37230				354
16	37574				344
17	37903				329
Average $\Delta\nu$		1348	1326		

It was then to be assumed that the next strongest series of bands proceeding to the high frequency side of the origin is the $v_2''=0$ sequence belonging to the asymmetrical (1150 cm^{-1}) vibrational frequency. There is indeed a band at about this interval on the red side of each of these bands of the $v_2''=0$ sequence, and in this way the fundamental sequences given in Table II were developed. Now it is impossible to have these two double arrays of bands proceed from the same 0,0 band, although they must correspond to the same electronic energy change in the molecule. But if the two sets of frequencies are represented by an equation such as (1) with half-integral vibrational quantum numbers, they both yield the same electronic frequency $\nu_e=31468$.

TABLE II. *Fundamental series for the* 1164 cm^{-1} *vibration.*

v_2' \ v_2''	0	1	2	Average $\Delta\nu$
0	31074	29932	28802	413
1	31498	30343	29208	435
2	31928	30779	29648	462
3	32393	31241	30108	475
4	32865	31719	30584	454
5	33324	32169	31036	456
6	33771	32628	31498	433
7	34210	33058	31929	432
8	34634	33491	32367	413
9	35048	33901	32781	401
10	35438	34312	33183	
Average $\Delta\nu$	1148	1130		

TABLE III. *Fundamental series for the* 606 cm^{-1} *vibration.*

v_3' \ v_3''	0	1	2	3	Average $\Delta\nu$
0	31308	30700	30103	29499	298
1	31607	30999	30394	29798	303
2	31910	31298	30700	30103	308
3	32218	31607	31008	30412	298
4	32513	31907	31308		285
5	32797	32193	31592	30999	272
6	33071	32463	31864	31270	254
7	33328	32719	32116	31521	253
8	33578	32977	32367		228
9	33802	33204	32601		221
10	34026	33423	32820		215
11	34242	33640	33037		207
12	34449	33846	33246		181
13	34634	34026	33423		169
14	34805	34193	33591		170
15	34971	34367	33759		
Average $\Delta\nu$	605.5	601	596		

This affords experimental proof of the existence of zero-point vibrational energy. It is therefore not possible to represent these SO_2 bands by a double vibrational formula such as found by Henri and Howell[7] for the ultraviolet absorption bands of phosgene.

Knowing the ν_e frequency and the third fundamental vibration frequency 606 cm^{-1}, for the lowest electronic state, it was possible to predict the 0,0 band frequency for this mode of vibration to within about 100 cm^{-1} by assuming that the corresponding excited state frequency must lie within the limits 150 to 350 cm^{-1}. Investigation showed that for but one band, 31308, in this predicted interval did another band lie 606 cm^{-1} to the red with still another spaced 600 cm^{-1} further to the red. Placing this 31308 in Eq. (1) with $v_3' = v_3'' = 0$ the excited state vibrational interval was computed to be very closely 300 cm^{-1}. This proved to be correct, and the other bands in this third double array as given in Table III were easily arranged. This $v_3'' = 0$ sequence is not obvious from inspection of the spectrograms as for the other two $v'' = 0$ sequences. However, this is in agreement with the fact that the 606 cm^{-1} fundamental absorption band in the infrared is much weaker than the other two.[1]

These three sets of fundamental vibration progressions can be represented by an equation of the type

$$\nu = \nu_e + [a'(v' + \tfrac{1}{2}) + b'(v' + \tfrac{1}{2})^2] - [a''(v'' + \tfrac{1}{2}) + b''(v'' + \tfrac{1}{2})^2] \quad (1)$$

with $\nu_e = 31468$. For all three sets of progressions, however, the excited state differences first increase to a maximum at about $v' = 4$, after which they decrease in the regular manner (see discussion below). It is therefore necessary to use different a' and b' constants for the low and high values of v'. The mean values of the a and b constants which fit the three sets of band progressions are given in Table IV.

TABLE IV. *Fundamental vibrational constants for SO_2 (cm^{-1} units).*

	v_1	v_2	v_3
a''	1369	1164	610
b''	-11	-9	-2.3
a' b'	$\left.\begin{matrix}+341\\+14\end{matrix}\right\}v_1 \leqq 4$	$\left.\begin{matrix}+387\\+12\end{matrix}\right\}v_2 \leqq 3$	$\left.\begin{matrix}+290\\+3\end{matrix}\right\}v_3 \leqq 3$
a' b'	$\left.\begin{matrix}+556\\-7\end{matrix}\right\}v_1 > 4$	$\left.\begin{matrix}+524\\-6\end{matrix}\right\}v_2 > 3$	$\left.\begin{matrix}+350\\-7\end{matrix}\right\}v_3 > 3$

All of the sequences in Tables I to III could be extended farther towards higher frequencies, but our accurate measurements do not extend into this region. However, it is obvious that these series account for only some 20 percent of the observed bands of which there are well over six hundred. Now only three fundamental frequencies are possible for a triatomic molecule, but we know from the study of the infrared bands of polyatomic molecules that addition frequencies occur. We have made plausible assignments of most of the

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[7] V. Henri and O. R. Howell, Proc. Roy. Soc. **A128,** 192 (1930).

remaining bands to various forms of addition series based on the three fundamental series, but these assignments are not unambiguous in many cases because of the density of bands and because of the lack of any guide such as the greater intensity of the $v''=0$ sequences of the main series. Our analysis shows however that there are addition bands present of the type for which addition of one or two quanta of any one of the three modes of vibration happens simultaneously in both electronic states to either of the other two main series. Some of the weaker bands are probably also due to an S isotope effect, but we have not been able to make any assignments on this basis.

Discussion of Results

Fig. 2 is a plot of the course of the vibrational energy level differences in the three sets of excited state levels as a function of v. The unusual feature of these curves is the initial positive slope. During the accretion of these first quanta of vibrational energy, the molecule, as it were, increases in stability, and then some rearrangement occurs after which the usual negative anharmonic term is operative. This phenomenon has been noted in only one instance for diatomic molecules, in the LiH spectrum[8]; but it is possibly of rather common occurrence for polyatomic molecules.[9]

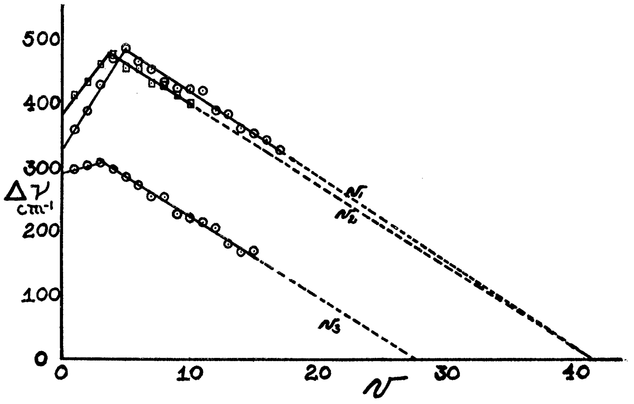

Fig. 2. Diagrams of the spacings of the excited state vibrational levels for the three fundamental modes of vibration. The interesting feature is the initial positive slope for each of the curves.

In the ground electronic state of SO_2 the vibrational frequencies decrease in the usual manner with increasing v''. But since this spectrum originates in absorption by a cold gas, only the levels $v''=0$, 1 and 2 are represented. The anharmonic coefficients b can therefore not be determined with great accuracy, but they do allow an approximate determination of the vibrational

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[8] G. Nakamura, Zeits. f. Physik **59**, 218 (1930)

[9] Positive slopes of the $\Delta\nu$:v curves, but without the maximum and subsequent negative slope, have been reported by H. D. Smyth and T. C. Chow (Abstract, Phys. Rev. **37**, 1023 (1931)) for CO_2 and by G. B. Kistiakowsky (Phys. Rev. **37**, 276, 1931) for C_2H_2.

frequencies for infinitesimal amplitude (the a'' constant in Eq. (1)) which could not be computed from the infrared absorption data.[1] Substitution of these three a'' frequencies in the determinant equation for the vibrational energy of a symmetrical triatomic molecule as given by Dennison[10], yields for α the half-angle at the apex of the isosceles triangle (cf. Fig. 3), the approximate values of 34° and 51°. Owing to the intensity relations in the infrared bands requiring an acute angle,[1] the lower of these two values is to be chosen. The vibrational frequencies a' of the excited state, however, give only imaginary solutions for this angle when placed in this equation.

Some conception of the values of the heats of dissociation for the SO_2 molecule can be obtained from the determination of the areas under the $\Delta\nu_v:v$ curves extrapolated to the convergence limit. The areas under the extrapolations are a rather large part of the whole energy, thereby limiting the accuracy of the calculation. This is particularly true of the lower electronic state values, but nevertheless the results of the computation are of some interest. One obtains the following heats of dissociation (excited state values are the sum of the areas under the curves of Fig. 2 and $\nu_e = 3.9$ volts):

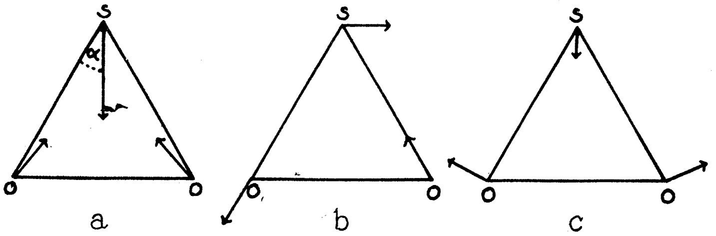

Fig. 3. Representation of the three fundamental SO_2 vibrations. *a*, the symmetrical 1369 cm^{-1} frequency; *b*, the asymmetrical 1164 cm^{-1} frequency; *c*, the symmetrical 610 cm^{-1} frequency. These three frequencies indicate α to be approximately 34°.

Lower state: $H_{v_1} = 5.3$ volts (121,000 cal.)
$H_{v_2} = 4.7$ " (107,000 cal.)
$H_{v_3} = 5.1$ " (118,000 cal.)
Excited state: $H_{v_1} = 5.2$ " (120,000 cal.)
$H_{v_2} = 5.3$ " (121,000 cal.)
$H_{v_3} = 4.3$ " (99,000 cal.)

We picture the vibrations occurring after the manner of Fig. 3. For the two symmetric modes of vibration the dissociation products would be an S atom plus an O_2 molecule. One might expect a measure of agreement between these values and that obtained from thermal data. The heat of formation of SO_2 from sulfur vapor S_2 and O_2 is given as 69,260 calories. The heat of dissociations of S_2 is known from spectroscopic data to be 102,200 calories.[5] Hence

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[10] D. M. Dennison, Phil. Mag. **1**, 203 (1926).

$$SO_2 \rightarrow \tfrac{1}{2}(S_2) + O_2 - \frac{102200}{2} - 69260 = \tfrac{1}{2}(S_2) + O_2 - 120360.$$

The agreement with our lower state H_{v_1} and H_{v_3} values is better than could be expected.

For the asymmetric mode of vibration the dissociation is probably into SO+O. Now the heat of dissociation of SO has been determined for the normal state of the ultraviolet SO band system by Henri and Wolff[11] as 148,000 cal. The value for O_2 should be approximately 5.1 volts.[6] Therefore one can write the energy equation

$$\begin{aligned} SO_2 \rightarrow SO + O - H_{v_2} &= S + O + O - 148{,}000 - H_{v_2} \\ &= \tfrac{1}{2}(S_2) + O_2 - 69260 - \frac{102200}{2} - 117300. \end{aligned}$$

This requires H_{v_2} to be about 90,000 cal. as against our value of 107,000 cal. The discrepancy may be in part due to the fact that the SO radical after the dissociation has a considerable amount of vibrational energy. In fact, the distortion in the dissociation process should most certainly produce some vibration of the SO, the energy of which should be subtracted from our extrapolated H_{v_2} value to give the true heat of dissociation.[12]

Judging from the relative values of the computed heats of dissociation for the two electronic states of SO_2 involved, apparently the dissociation products are in both states the same. But because of the possibility of a considerable error in these values due to the large extrapolation, this statement should be made with reservations.

A considerable amount of information may be expected from the study of the ultraviolet band systems of the simpler polyatomic molecules. When the bands have sharp heads, as for example in the CS_2 system on the analysis of which we are now engaged, the accuracy of the measurements can be considerably improved. For absorption bands the rotational fine structure may not be resolvable even at the highest dispersion. But if obtained as emission bands, the theoretical resolving power of a large grating can be more nearly approached, and the rotational line pattern of some of the simpler polyatomic bands may be obtained. In that event the needed test of the theoretical treatment of the rotator with three different moments of inertia as given by Kramers and Ittmann[13] and others may be made.

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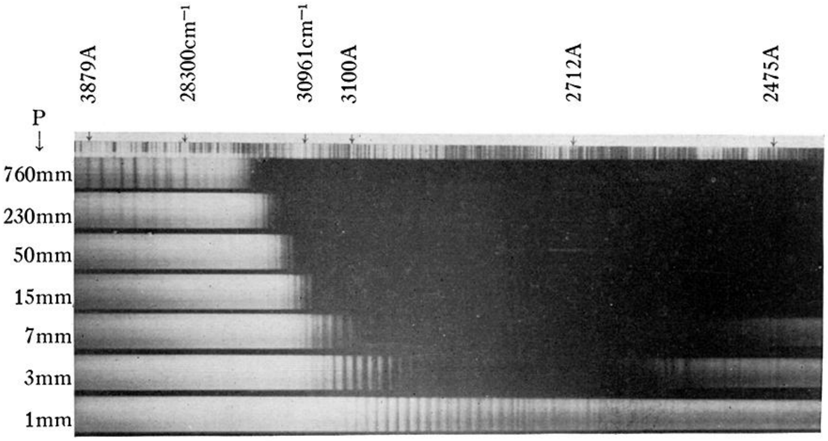
[11] V. Henri and F. Wolff, Jour. de Phys. et Rad. **10,** 81 (1929).

[12] R. M. Badger and J. L. Binder, Phys. Rev. **37,** 800 (1931) have suggested this explanation for a similar discrepancy in the case of the HCN infrared bands.

[13] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **58,** 217 (1929).



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