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Electronic Structures and Spectra of Triatomic Oxide Molecules

ROBERT S. MULLIKEN
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

Existing knowledge of the forms and the electronic spectra of a series of triatomic oxide and similar molecules BAB are briefly reviewed. The evidence (mostly from infra-red data) which establishes the acute-angled model of ozone as very probably correct is reviewed, one or two new points being added. New conclusions concerning the probable electronic structure of ozone are given. A new diagram is introduced showing the ionization energies of the various normal and excited valence-shell molecular orbitals as a function of the apex angle BAB. It is shown that this diagram, or a similar diagram, may be very useful in understanding the electronic structures and spectra of the molecules considered. The diagram makes possible a number of predictions which may be tested experimentally. The forms of the molecular orbitals of CO_2 are reviewed, with some interesting new modifications.

INTRODUCTION

FIGURE 1 shows an interesting group of triatomic oxide molecules, drawn to scale according to the best existing information. Nearly all these molecules show absorption spectra in the visible or the quartz ultraviolet.[1] Emission spectra[1] are also known for CO_2^+ (and perhaps CO_2), NO_2, and SO_2. It is an interesting problem to try to account for all these spectra in terms of molecular electronic structures and at the same time to determine the molecular dimensions. At present these are known largely from electron diffraction work, but in most of the dioxides the apex angle is subject to considerable uncertainty because electron diffraction patterns are relatively insensitive to it. For ozone, not even rough diffraction data are available, but spectroscopic evidence strongly favors the acute-angled model shown in Fig. 1.

Of the molecules shown, those with 16 outer electrons (counting all the *s* and *p* electrons of the outermost shell of each atom) are linear, while all with more than 16 outer electrons are bent. The ion CO_2^+, with 15 electrons, whose emission spectrum is dealt with by Mrozowski in the next paper, is also linear. Study of the molecules shown gains increased interest from the fact that they are prototypes of a much greater number of triatomic molecules with 16–20 outer electrons. Thus among other 16-electron molecules are NNO, $(NNN)^-$, $(NCO)^-$, NCX, and the large group of molecules MeX_2, where Me is any one of the bivalent metal atoms from Be to Hg or Ba, and X is any halogen; it is likely that all these are linear.

This is definitely known in a number of cases, for example in the mercury halides, whose zero dipole moment (in the vapor state) and the structure of whose absorption bands in the vacuum ultraviolet agree with a linear structure. Chemically stable 17-electron molecules are rare, but the halides GaX_2 and InX_2 may be mentioned. The 18-electron molecules include SeO_2, TeO_2, NO_2^-, NOX, SnX_2, and PbX_2 among others. Chemically stable 19-electron molecules are rare. The 20-electron molecules include OX_2, SX_2, SeX_2, and TeX_2; these are generally classed as chemically analogous to the 8-outer-electron hydride molecules OH_2, SH_2, and so on, but show

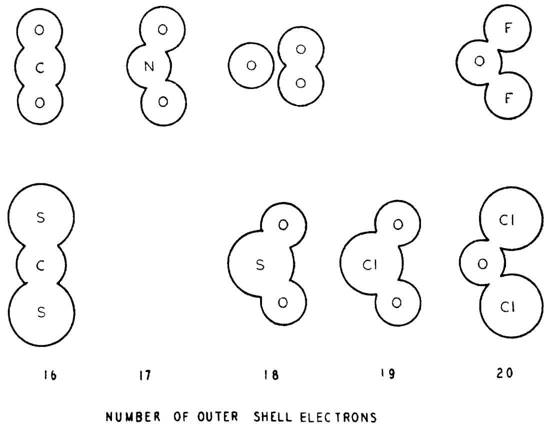

FIG. 1. The atoms have been drawn with radii somewhat greater than Pauling's single-bond radii (considerably greater in the case of F atoms). The radii used were 0.79, 0.72, 0.71, 0.74, 1.06, 1.01A for the C, N, O, F, S, and Cl atoms, respectively. The interatomic distances (drawn to scale) and the apex angles are based on the best available electron diffraction or spectroscopic evidence in each case. The degree of confluence of the atoms in any molecule pictured gives a measure of the strengths of the bonds.

absorption spectra in the visible and quartz ultraviolet which can better be understood by comparing them with the 16–19 electron molecules.[1]

As is well known, the shape of a polyatomic molecule has a very great effect on the structure of the bands in its spectrum. This holds both for the vibration and rotation spectra in the infrared and for the (mostly visible and ultraviolet) electronic spectra. The bands of *linear* molecules have structures of the same identical types as those of diatomic molecules. In general, however, the more numerous vibrational degrees of freedom lead to the appearance of more bands, often in complicated arrays.

Bent, i.e., triangular, triatomic molecules usually fall into the asymmetric top class; that is, they have three unequal moments of inertia. According to the theory, this should in general lead to very irregular, even chaotic, arrangements of quantized rotational levels, and of band lines in a band, contrasting with the relatively simple and orderly arrangements for symmetrical top and especially for linear molecules.

Fortunately it has come to be realized that the rotational level patterns and band structures for many of these asymmetric top molecules, and in particular those we are now considering, approximate those of symmetric top molecules. To see why this is, consider SO_2 as an example. Here the three moments of inertia are $I_y = 13.9$, $I_z = 83.2$, and $I_x = 97.1$, all in g $\text{cm}^2 \times 10^{-40}$. The axes used are as shown in Fig. 2. I_y is thus much smaller than I_z and I_x, while I_z and I_x are roughly equal. With these relations, the actual rotational level and band structure is on the whole not very different from that of a symmetrical top molecule with I_y as in SO_2 but having $I_z = I_x$ with a value of $1/I_z$ equal to the average of the values of $1/I_z$ and $1/I_x$ for the actual SO_2 molecule. Thus the analysis of the structures of the bands of such molecules can often, to a considerable extent, be carried out as if they were bands of symmetrical top molecules.[2] The analysis of a symmetrical top band is itself of course usually much more difficult than that of a diatomic band, but the added complexity has its rewards in that it leads to more information.

Symmetrical top bands fall into two classes, the parallel and the perpendicular types. This is true equally for vibration-rotation and for electronic bands. Parallel bands occur when the electric moment associated with the transition in question vibrates parallel to the symmetry axis, or to the axis of smallest moment of inertia in quasi-symmetric top molecules like SO_2. Perpendicular bands correspond to a transition moment vibrating perpendicular to the symmetry or quasi-symmetry axis. For parallel bands, there is a selection rule $\Delta K = 0$, for perpendicular bands $\Delta K = \pm 1$, where K is the quantum number of rotation around the symmetry or quasi-symmetry axis. This difference in selection rule results in a characteristic difference in structure, which is often obvious even with incomplete resolution. In a molecule like SO_2, K is not strictly a good quantum number, but this has relatively moderate effects in the observable band structures. In such a molecule, perpendicular bands are, strictly speaking, divided into two sub-types, according as the electric moment of the transition vibrates in the x or z direction in Fig. 2, but the structures of these differ only in those features in which the asymmetry of the molecule makes itself felt.

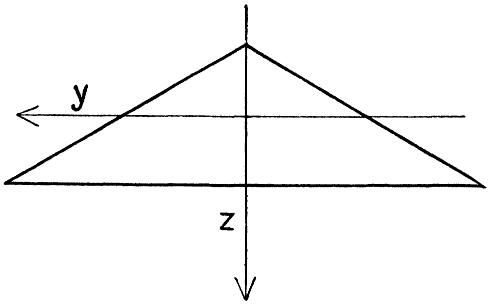

FIG. 2. Showing y and z axes; the x axis is perpendicular to the plane of the molecule.

Two examples will make clearer the difference between parallel and perpendicular band structures in electronic spectra. Figure 3 shows the λ2491 absorption band of the NO_2 molecule,[3] which is a good example of an electronic parallel band ($K' = K''$, i.e., $\Delta K = 0$). The structure consists of a series of subbands, each characterized by a definite value of K and arranged according to the law

$$\nu = \nu_0 + (C' - C'')K^2, \tag{1}$$

where the C's depend on the moments of inertia

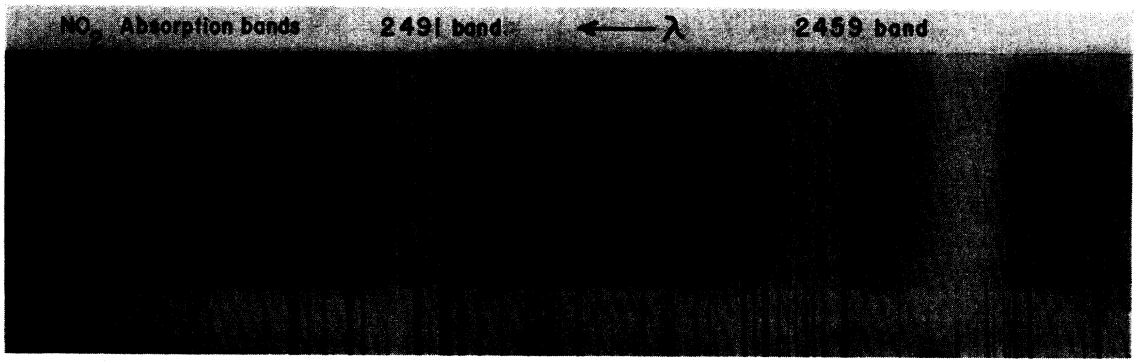

FIG. 3. Reproduced from a photograph by L. Harris with the latter's kind permission. E_1 spectrograph. The print shows two NO$_2$ absorption bands, λ2491 and λ2459. Both belong to the same electronic transition, but the structure in the former is sharp, while the latter is a very good example of predissociation.

in the upper and lower states. Within each subband there is a fine structure consisting of Q, R, and P branches, corresponding to changes $\Delta J=0$, ± 1 in the over-all rotational quantum number J. In the photograph, this J structure is incompletely resolved. In the heads of some of the subbands there is also evidence of a small spin doubling, which is expected in view of the resultant electronic spin of $\frac{1}{2}$ in NO$_2$. (In NO$_2$ λ2491, the arrangement in subbands depends on the fact that $C''-C'$ is large. When $|C'-C''|$ is small, as, e.g., in infra-red bands, the K structure collapses and only the J structure is observed, consisting of a lateral P and R branch and a central Q branch: cf., e.g., the ν_3 band of SO$_2$ as shown in Fig. 1 of the preceding paper by Professor Barker.)

We notice that a band such as this has several observable characteristics, even under incomplete resolution: (1) there is its total intensity, which may vary in different bands of a molecule by many powers of ten; (2) there is the type of polarization (here parallel); (3) there are the directions of shading of the K and of the J structure, for which there are four possible combinations (both shaded toward the red, or both toward the ultraviolet, or one each way). Finally, (4) a detailed analysis yields the rotational constants of the quantized levels of the upper and lower electronic states, from which the moments of inertia may to a large extent be deduced.

Figure 4 shows what is probably a perpendicular band. This is one of the bands of the weak absorption system of SO$_2$ near λ3800, studied by Metropolis and Beutler.[4] Again there is a series of K subbands, but now they are arranged on both sides of a central region corresponding to low K values, according to the law

$$\nu=\nu_0\pm 2C'K+(C'-C'')K^2. \qquad (2)$$

In the example shown, the K structure has a slight shading toward the ultraviolet (i.e., a slight convergence toward the red), while each subband shows evidence of J structure, notably in the presence of what are probably a Q and an R head shaded toward the red. (For an example of an infra-red perpendicular band of SO$_2$, see Fig. 1 in the preceding paper by Barker.)

Besides the *band structures*, the arrangements and intensity distribution of the various *different bands* belonging to a given electronic transition give much corroborative and additional information as to the characteristics of the molecule in the two electronic states concerned. For one thing, an analysis of the vibrational structure pattern gives more or less complete information concerning the vibrational frequencies in the two states, and from these, rough values of the apex angle and other information can be obtained. Further, the intensity distribution as a function of the vibrational quantum numbers is also closely correlated with the direction and magnitude of the changes in interatomic distances and apex angle in the electronic transition.[5] The *total absorption intensity* of the ensemble of bands, or band system, belonging to a given electronic transition is an additional important observable characteristic of the latter.

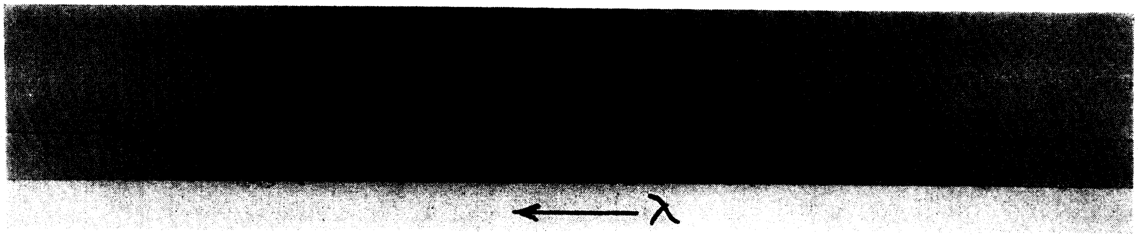

FIG. 4. The 0,0 band (λ3879) of the λ3800 absorption system of SO_2, reproduced from an original photograph by N. C. Metropolis and H. G. Beutler, with the kind permission of the authors.

ELECTRONIC STRUCTURES AND SPECTRA: SULFUR DIOXIDE

A considerable amount of work has been done toward measuring and analyzing the observable features, both rotational and vibrational, for the electronic spectra of many of the triatomic oxide molecules shown in Fig. 1. This work is now in the very interesting stage where enough is known so that an attempt can be made to draw some general conclusions, yet much more is unknown, so that the subject remains full of intriguing questions. For some time I have been trying to understand the available information concerning these molecules in terms of electronic structures, or more specifically, electron configurations. Today I have some results which I think are worth bringing forward as forming at least a tentative framework to guide further study.

Before presenting the general picture, I am going to jump ahead in order to give some idea how it can be used, and also to explain the terminology. In Fig. 5 is collected some information derived from the examination and partial analysis of the three band systems of SO_2 which are known in the region accessible with a quartz spectrograph.[1] The figure is based on a tentative explanation of these spectra in terms of electron configurations, and contains theoretical predictions both about observed and also about as yet unobserved features of these spectra, and in addition about three predicted band systems.

The electronic structure of any molecule can be considered to consist of a rather large number of shells, each occupied by two electrons. Each shell may be characterized by its term value, or by its ionization potential. Values of the latter for SO_2 are given at the right of the figure in volts, and a name for the shell is given at the left. These names correspond to the names $1s$, $2s$, $2p$, and so on used for the various electronic shells in an atom, but differ from the latter because of the different symmetry of the force field in the molecule. Whereas the symbols $1s$, $2s$, $2p$ may be called *atomic orbital* symbols, and in the wave mechanics stand for atomic orbital wave functions, the symbols $1a_2$, $3b_2$, $4a_1$, and so on, used here are *molecular orbital* symbols. Just as in atoms, the numbers 1, 2, 3, represent the deepest, second deepest, third deepest, of the given kind or species of orbital, but they do not have the additional significance of a total quantum number as in an atom. The species symbols a_1, b_1, a_2, b_2, here used[6] are those which are now standard for molecules of the symmetry possessed by SO_2, namely, the symmetry C_{2v}.

In the present figure, only the symbols for some of the outer electron shells in SO_2 are given. The molecular shells $1b_2$, $2b_2$, $1a_1$, $2a_1$, and $3a_1$, each filled with two electrons, should be thought of as also present, at levels deeper than those shown in the figure. In addition, there is the K shell for each atom. In the figure, the three molecular orbitals, $1a_2$, $3b_2$, and $4a_1$ shown by heavy horizontal lines are normally occupied each by two electrons, while the upper levels $2b_1$ and $5a_1$ shown by thin lines are normally unoccupied but are needed to explain the spectra.

An important difference as compared with atoms is the large number of distinct shells, some of them spaced rather closely on an energy scale. This is a consequence of the relatively low symmetry. With low enough symmetry (as here), there is no orbital degeneracy, i.e., there is never more than one orbital wave function for a given energy. Then, according to the Pauli principle, there cannot be more than two electrons per shell.

Now let us see how the various observed spectra are explained according to the figure. The latter assumes that the most loosely bound occupied shells are $3b_2$ and $4a_1$, each with an ionization potential of 12.5 volts. The equality of ionization potential assumed for these two shells is accidental for SO_2, and is undoubtedly not exact. The value 12.5 volts has been chosen to be in harmony with observational data on the minimum ionization potential, namely, 13.1 volts by electron impact methods, and 12.05 volts according to evidence from Rydberg series in the vacuum ultraviolet absorption spectrum of SO_2 as studied by Price.[1]

The longest wave-length band system of SO_2, whose vibrational analysis has been carried out by Metropolis and Beutler in this laboratory,[4] is here interpreted as resulting from the transition of an electron from the $4a_1$ shell to the unoccupied $2b_1$ shell. This seems to be the only interpretation capable of giving agreement between the predicted and observed characteristics of this band system. In this and other similar figures which follow, the observed characteristics are given in the left-hand column, the predicted *in parentheses* in the right-hand column, both under the wave-length value for the transition.

The wave-length given is the approximate *observed* wave-length at which the intensity in the system is a maximum; it is not the wave-length for the 0,0 or vibrationless transition. No separate predicted wave-length is given, since the heights of the various levels in the figure are based entirely on the empirical λ_{max} data. We use λ_{max} rather than λ of the 0,0 band because according to the Franck principle, this corresponds to a change of electronic state without any change in interatomic distances and because the energy levels for a fixed set of interatomic distances are the simplest to work with.

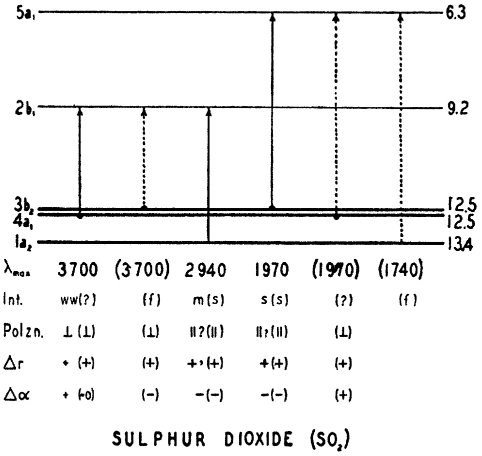

FIG. 5. Predicted and observed electronic spectra of SO_2 explainable by the valence molecular orbitals $1a_2$, $3b_2$, $4a_1$, $2b_1$, and $5a_1$; based on Fig. 6 and the known spectra of SO_2.

In the SO_2 system with $\lambda_{max}=3740$, the intensity is very low. The bands appear to be of the perpendicular type; you have already seen one of them in a previous figure. The type of shading in the bands and the vibrational intensity distribution indicate that there is a slight, but only slight, increase in the equilibrium values of both the S−O distances and the apex angle in going to the upper state.[4] All these results are in agreement with the general theoretical diagram to which we shall come shortly.

The extremely low intensity of the bands, while not directly predicted, is not at all impossible according to the theory. This low intensity at first led to attempts to interpret the λ3740 system either as the forbidden $3b_2 \rightarrow 2b_1$ singlet-singlet transition, or as the $4a_1 \rightarrow 2b_1$ singlet-triplet transition. But both these attempts led to contradictions in trying to understand the other systems of SO_2 and those of other molecules by means of electron configurations in a rational theoretical scheme.

The present scheme is in harmony with the available incomplete information on the well-known SO_2 absorption systems near λ3000 and near λ2000, as will be seen on comparing the observed and predicted characteristics of these systems in the figure. It also accounts in a reasonable way for the failure to observe three additional predicted systems: two of them are "forbidden" and should actually be very weak, while the third is also predicted to be weak but to fall in the region of the very strong λ2000 system, where, if present, it would not easily be seen. On adding one more excited level $4b_2$ (see Fig. 6), Fig. 5 also can account reasonably for the systems observed by Price[1] with $\lambda_{max}=1558$, 1330, and 1260.

ENERGY-ANGLE GRAPH FOR MOLECULAR ORBITALS

Let us turn now to Fig. 6, which embodies the main new results of the present work. This figure

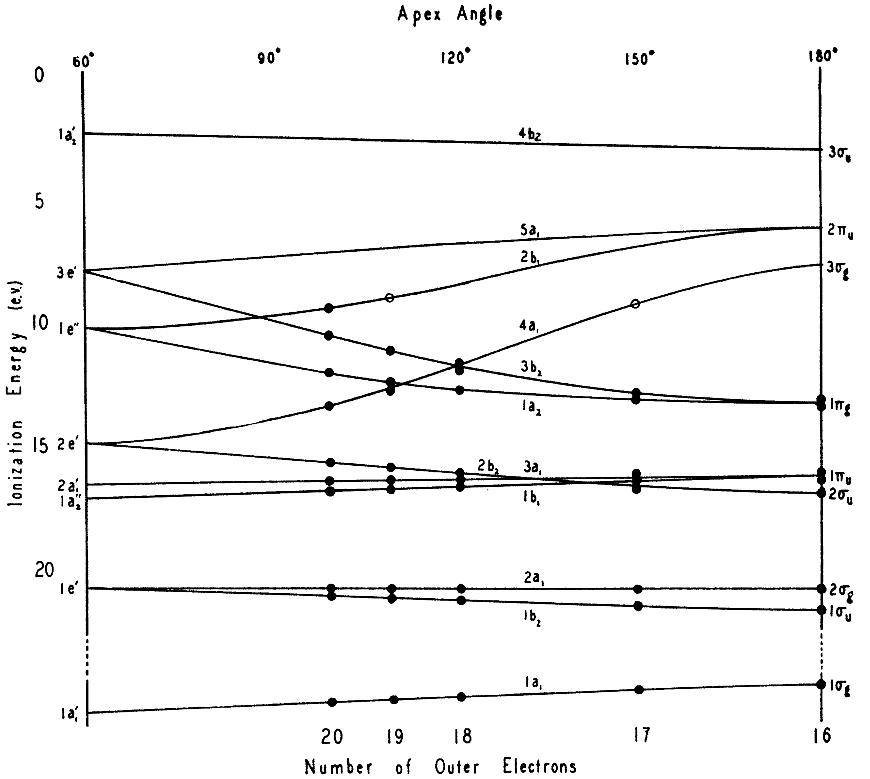

FIG. 6. General scheme for ionization energy as a function of apex angle for an "average" molecule of the AO_2 type. A fixed (but unspecified) A–O distance is assumed throughout. The figure is no more than very roughly quantitative.

is applicable to a sort of average molecule of the kind we are considering, for some fixed average value of the distance from the central to the two outer atoms. Of course the actual molecules differ in their dimensions, but since the figure is supposed to represent a sort of average molecule, it is not expected to be quantitatively correct. In fact, however, it seems to be not far from being exact for several of the molecules in which we are interested.

The figure is designed to show how the ionization energies of all the occupied and some of the unoccupied molecular orbitals vary with the apex angle, over the range from 180° to 60°. It is based on a combination of theoretical considerations and empirical evidence. At 180°, the CO_2 and CS_2 molecules give us a considerable amount of empirical information. From a study of Rydberg series in the far ultraviolet spectra of these molecules, together with the analysis of the emission spectrum of ionized CO_2, the ionization potentials for the three outer shells of CO_2 are known. The outermost occupied shell is the $1\pi_g$ shell, which has twofold degeneracy and so holds four electrons. Its ionization potential is 13.7 volts. Because $1\pi_g$ is essentially a nonbonding orbital confined almost entirely to the two oxygen atoms, its ionization potential should remain nearly the same in other oxide molecules such as NO_2, O_3, SO_2, and ClO_2 if they had a 180° apex angle. This justifies the selection of the value 13.5 volts in the figure as the ionization potential for $1\pi_g$ in our average molecule.

The twofold degeneracy of $1\pi_g$ is possible only because of the high symmetry which exists at 180°, and theory shows that $1\pi_g$ must split into the two molecular orbitals $1a_2$ and $3b_2$ if the molecule departs from linearity.[7] These two molecular orbitals are among those we have already used in explaining the SO_2 spectrum.

In addition to $1\pi_g$, the ionization energies of $1\pi_u$ and $2\sigma_u$ are known for CO_2, and this helps greatly in estimating their values for our average molecule. As the apex angle departs from 180°, $1\pi_u$, being degenerate, has to split, while $2\sigma_u$, being non-degenerate, does not. The energies of other molecular orbitals, both occupied and unoccupied in CO_2, may be estimated, although with considerable uncertainty, from theoretical considerations combined with evidence (see below) from the CO_2 and CS_2 spectra.

Although the detailed forms of the molecular orbitals which appear in Fig. 6 will not be discussed extensively here, it may be helpful to indicate their nature for the relatively simple 180° angle case. This has been discussed in an earlier paper,[8] and is here reviewed, taking CO_2 as a specific example, with some improvements based on increased knowledge.

So far as can be judged from theory combined with existing empirical evidence, the CO_2 molecular orbitals named below can be approximated by linear combinations of atomic orbitals more or less as follows:

$$\begin{aligned}
&2\sigma_u = a(\sigma-\alpha s)-b\sigma_C-a(\sigma'-\alpha s'),\ \alpha<1,\\
&1\pi_u = a\pi+b\pi_C+a\pi',\\
&1\pi_g = a\pi+b\pi_C{}^*-a\pi',\ a\gg b,\\
&3\sigma_g = a\sigma-bs_C+a\sigma',\\
&2\pi_u = a\pi-b\pi_C+a\pi',\\
&3\sigma_u = a\sigma+b\sigma_C-a\sigma'.
\end{aligned}\tag{3}$$

The a's and b's are all different but all of the same order of magnitude except in $1\pi_g$, and are all positive. The symbols σ, s, and so on, stand for atomic orbitals as follows: s, σ, π refer to $2s$, $2p\sigma$, $2p\pi$ orbitals of one oxygen atom, s', σ', π' to corresponding orbitals of the other; the σ and σ' orbitals are taken to be defined with their positive parts toward the central carbon atom. Similarly s_C, σ_C, π_C refer to carbon atom orbitals; σ_C is defined so as to have its positive part toward the second (O′) oxygen atom; $\pi_C{}^*$ represents a $3d\pi$ carbon atom orbital.

Data on the C−O distance in the three known electronic states of CO_2^+ (see references in the following paper by Mrozowski), as compared with this distance in normal CO_2 (see paper on l doubling in this issue by Herzberg), give interesting information about the bonding properties of the $2\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals. The C−O distance in normal CO_2 is 1.163A. On removal of a $1\pi_g$ electron to form the $^2\Pi_g$ normal state of CO_2^+, it becomes 1.177A, indicating that $1\Pi_g$ is slightly bonding. This could not be explained with $1\pi_g$ formulated in the usual way[8] simply as $a(\pi-\pi')$, which should be non-bonding or slightly antibonding. A slight excitation of carbon $3d$ valence (presence of $b\pi_C{}^*$ with $a\gg b>0$) is the only obvious way to account for the slightly bonding behavior of $1\pi_g$. That $1\pi_u$ is *strongly* bonding, as expected, is shown by the fact that on removal of a $1\pi_u$ electron to form the $^2\Pi_u$ state of CO_2^+, the C−O distance becomes 1.228A.

For $\alpha\ll 1$ in Eqs. (3), $2\sigma_u$ should be strongly bonding, and removal of a $2\sigma_u$ electron to form the known $^2\Sigma^+{}_u$ state of CO_2^+ would be expected to lead, as for removal of a $1\pi_u$ electron, to a considerably increased C−O distance. Actually, the C−O distance is increased only to 1.180A. It is difficult to see any way of explaining this except by concluding that there is strong $s-p$ mixing in the σ orbitals of oxygen in $2\sigma_u$, i.e., that α approaches 1.

If this is correct, the same may also be true (although this has not been indicated in Eqs. (3)) for $3\sigma_g$ and $3\sigma_u$; in any event, *some* s, p mixing must be present in σ and σ' of these. Empirically, $3\sigma_g$, $2\pi_u$, and $3\sigma_u$ are high above $1\pi_g$ in energy in CO_2 (and fairly high also in CS_2), which can be understood only if the b's for these orbitals are not small compared with the a's. This in turn means that these three excited orbitals must be strongly antibonding.

In seeking to determine the curves of ionization energy against apex angle for the various molecular orbitals, we first use the fact that each of these curves must have either a maximum or a minimum at 180°, since angles equally greater and smaller than this are physically equivalent. The *total* energy of the molecule must likewise, of course, be either a maximum or a minimum at 180°, the former if the molecule in its normal state is triangular, the latter if it is linear.

A comparative study of the force constants for the bending vibration in various electronic states of such linear molecules as CO_2, CO_2^+, and CS_2 would give much information as to the way in which the curves of molecular orbital energy against angle start off from 180°. At present our information about these force constants is confined to the normal states of CO_2 and CS_2; a continuation of the work on CO_2^+ discussed by Dr. Mrozowski in the next paper would offer much promise for progress in this direction.

The course of the energy curves can be determined to a considerable extent by plotting the energies at 60° as well as at 180°, and interpolating. If the three atoms are all equal, as in O_3, the relatively high symmetry at 60°(D_{3h}) permits twofold degenerate orbitals as at 180°.[6] This reduces the total number of energy levels and makes it possible to say a good deal about their arrangement from theoretical considerations. Even though in most cases the central atom actually is different from the outer two, this probably does not radically alter the curves obtained. In constructing the figure, not alone qualitative considerations have been used, but rough quantitative computations also have been made for 60°, 180°, and to some extent for 120°. These were based on assumed values of certain exchange integrals which were adjusted to fit the empirical evidence. Thus the forms of most of the curves have more than a purely empirical foundation. I shall not, however, discuss the computations at this time.

It may be well to mention that there is one extremely important curve in the figure, the $3\sigma_g - 4a_1$ curve, whose rapid downward course between 180° and 120° is based wholly on empirical evidence. While the striking behavior of this curve does not contradict the theory, nevertheless I have not found any way of predicting it with the use of simple approximations. Empirically, it would seem that b/a in Eq. (3) for $3\sigma_g$ must decrease markedly with decreasing apex angle; the orbital must then also become less antibonding.

STRUCTURES OF 16-20-ELECTRON MOLECULES

The black dots at various places on the curves in Fig. 6 are supposed to represent pairs of electrons. Each *open* circle represents a single unpaired electron. In the molecules with 16 outer electrons, like CO_2, the apex angle is 180°, and the 16 electrons are distributed among various orbitals as indicated in the figure. The stability of the 180° angle must mean that on the whole the energy curves of the occupied orbitals turn upward more than downward for angles differing from 180°.

For molecules with 17 outer electrons, such as NO_2, the seventeenth or odd electron has to go in the normal state into an orbital whose curve goes rapidly downward from 180°, evidently sufficiently so to overbalance the effect of the preceding 16 electrons which tend to stabilize the 180° arrangement, since normal NO_2 is known to be bent. However, the effect of this orbital, which is the remarkable $4a_1$ orbital already mentioned, becomes balanced at probably[3] about 150° by a steadily accelerated rise of the curves of some of the other occupied orbitals.

In a molecule like SO_2, with 18 outer electrons, the *two* electrons now present in the $4a_1$ orbital in the normal state cause a further decrease in the angle to about 120°. In the case of O_3, which one might have expected to have approximately a 120° angle like SO_2, spectroscopic evidence points almost certainly to an angle of about 40° (see below). This does not in itself contradict Fig. 6, but may mean merely that the energy has a second minimum at 40° with lower energy than near 120°. However, the acute-angled ozone model assumes that the apex atom is considerably farther from the two base atoms than it would be for a 120° model (cf. Fig. 1).

Why a 120° model should be more stable in SO_2 than in O_3 is not clear. Perhaps *3d* valence acts to stabilize the obtuse-angled model, and does so much more in SO_2 and ClO_2 than in O_3, since the *3d* shell is much closer in energy to the *3p* valence shells in these molecules than it is to the *2p* shells in O_3 or NO_2 or CO_2. The increased importance of *d* valence in P, S, and Cl as compared with N, O, and F is a familiar concept introduced by London to explain the differences in chemical properties of these two sets of atoms. Possibly admixture of *3d* in the $4a_1$ and $2b_1$ orbitals may help to explain their rapid descent to the left in Fig. 6, although it is not obvious why *3d* admixture should change much with apex angle. That *3d* valence is of appreciable importance even in CO_2 has already been noted in connection with Eqs. (3).

With 19 outer electrons, the angle in the normal state is probably somewhat smaller than in SO_2 (about 107°, or perhaps 120°, according to preliminary results of an analysis of the visible absorption bands by J. B. Coon in this laboratory[9]). This indicates that the odd nineteenth electron occupies an orbital (here identified as $2b_1$) whose energy curve resembles that of $4a_1$ in descending sharply toward smaller angles. This is qualitatively in agreement with theoretical considerations, although the sharpness of the descent has not been predicted.

With 20 outer electrons, two in the $2b_1$ orbital, we expect a further decrease in angle. While there is no chemically stable molecule AO_2 with 20 electrons, the 20-electron molecule OF_2 is known, with an angle of 100° according to electron diffraction data. The analogous molecule OCl_2 has the larger angle of 115°, but this may be attributed to the large size of the two outer atoms.

INTERPRETATION OF SPECTRA: SO_2, ClO_2, NO_2, O_3, CO_2, CS_2

Sulfur Dioxide

The course of the curves shown in Fig. 6 permits a fairly satisfactory explanation not only

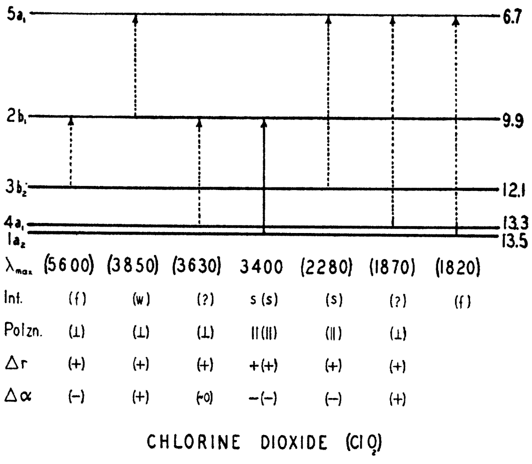

FIG. 7. Predicted and observed electronic spectra of ClO_2; based on Fig. 6.

of the apex angles in the normal states, but also of the known observational facts on the spectra of the molecules mentioned, in particular of their spectral location and their types of polarization, and of the way in which the apex angle changes on going to the excited state. I have already discussed the SO_2 spectrum along these lines with the help of Fig. 5. So far as I know, the available evidence for this and other molecules does not contradict any of the predictions which can be made from Fig. 6, but the evidence is fragmentary, and it will be very interesting to extend it. In this way confirmation of the present scheme, or its contradiction and the discovery of a better one, may be accomplished.

Chlorine Dioxide

Figure 7 shows an interpretation of the ClO_2 absorption spectrum in harmony with the present scheme. It gives correctly the observed polarization and other characteristics of the well-known strong visible-ultraviolet band system as analyzed by Coon,[9] and predicts no other systems of high intensity except at shorter wave-lengths. It does predict two weak systems which may overlie the observed strong bands, and possibly may help to explain the predissociation which is present in the short wave-length parts of the latter. It also predicts a forbidden transition, probably at longer wave-lengths, which might be observable with the use of long absorbing paths.

Nitrogen Peroxide

Figure 8 gives an interpretation of the NO_2 spectrum. Agreement with the observed spectrum can be obtained if it is assumed that the $4a_1$ energy for a 150° angle in NO_2 lies about half way between the energies of the two pairs of orbitals $1a_2$, $3b_2$ and $2b_1$, $5a_1$ which go at 180° into $1\pi_g$ and $2\pi_u$, respectively. This assumption has been used in drawing Fig. 6. The entire spectrum in the near infra-red, visible, and near ultraviolet[1] is here attributed to an overlapping of bands of three electronic transitions of moderate or small intensity, $3b_2 \rightarrow 4a_1$, $4a_1 \rightarrow 2b_1$, and $4a_1 \rightarrow 5a_1$. The long wave-length tail extending into the infra-red is attributed exclusively to $3b_2 \rightarrow 4a_1$, which should give a large (negative) $\Delta\alpha$; the 0,0 band for this transition must then be in the infra-red. The other two transitions probably have smaller $\Delta\alpha$'s and correspondingly less extensive spectra.

The band at λ2491, shown as a typical parallel band in an earlier figure,[3] is here interpreted as belonging to one of the two transitions $3b_2 \rightarrow 5a_1$ and $1a_2 \rightarrow 2b_1$, both of which should give parallel bands. The observed $\Delta\alpha$ is understandable according to the curves of Fig. 6. Other bands of this system extend with increasing intensity toward shorter wave-lengths. After a short distance, bands begin which look as if they belong

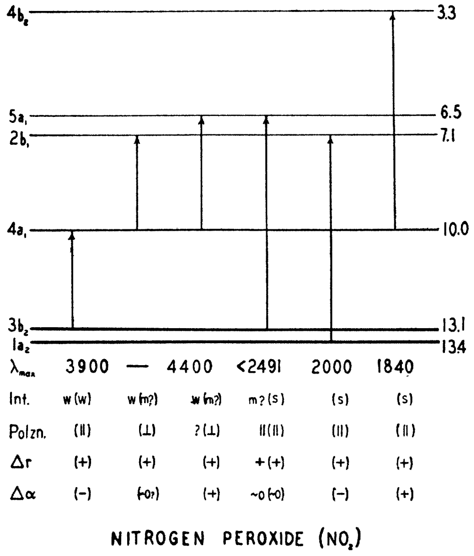

FIG. 8. Predicted and observed electronic spectra of NO_2; based on Fig. 6.

to a different system, which may well be the second of the two mentioned. The strong predissociation observed in this region, merging into strong continuous absorption extending below λ2000, may be connected with a predicted third parallel transition $4a_1 \rightarrow 4b_2$ which is expected to have high intensity.

Ozone

Before seeking to interpret the electronic spectrum of ozone, the evidence for the acute-angled model should be reviewed. This is based largely on the infra-red data and analysis of Hettner, Pohlman, and Schumacher (HPS).[10] HPS show that the only interpretation of the infra-red spectrum which has any high degree of probability is one with an acute apex angle; they obtain 39° from analysis of the vibrational data. Such a model may be interpreted as an O_2 molecule with a third O atom rather loosely attached at one side (see Fig. 1); the third atom is probably at the apex of an isosceles triangle, though it has not been disproved that it may be unsymmetrically located.

The HPS analysis requires that ν_3, ν_2, ν_1 be 710, 1045, and 2110 cm^{-1}, respectively, ν_3 being the antisymmetrical fundamental vibration mode, ν_2 a symmetrical fundamental in which the motion is mainly that of the apex atom toward the two atoms at the base of the triangle, and ν_1 a second symmetrical fundamental in which mainly the two latter vibrate against each other. As Dr. Oliver Wulf has pointed out to me, strong support is given to the conclusion that 1045 cm^{-1} is a symmetrical fundamental by the fact that in the ultraviolet absorption spectrum of ozone the frequency 1047 cm^{-1} belonging to the normal state is found,[11] and that this has the same combining properties with the upper electronic levels as does the vibrationless level of the normal state. Unless the molecule becomes a scalene triangle in the excited state, which seems improbable, this is allowed by the selection rules only if 1045 cm^{-1} is a symmetrical frequency (ν_1 or ν_2).

The high value of ν_1 in the HPS analysis corresponds to a stronger binding of the two basal atoms than in O_2 ($\omega_e = 1580$ cm^{-1}), or even than in O_2^+ ($\omega_e = 1876$ cm^{-1}). This, it is here suggested, might be explained by a structure more or less of the type $O_2^+O^-$, the apex atom being O^-. In Fig. 1, an O−O distance of 1.12A, somewhat less than in O_2^+, has been assumed for the two base atoms; this with an apex angle of 39° gives the other O−O distances as 1.68A.

For an apex angle *either* of about 39° (Fig. 1) or about 120° (Fig. 2), O_3 would be an asymmetric top molecule; but in either case it would approximate a prolate symmetric top fairly closely. While the quasi-symmetry axis of the latter lies along the y axis of Fig. 2 for the obtuse-angled model, it lies along the z axis (geometrical symmetry axis) in the acute-angled model. Therefore in the obtuse-angled model y-polarized bands (e.g., ν_3) are parallel bands, and z-polarized bands (e.g., ν_1 or ν_2) are perpendicular bands; but in the acute-angled model y-polarized bands are perpendicular bands and z-polarized bands parallel bands. In the acute-angled model the bands ν_1 and ν_2 would be parallel bands and ν_3 a perpendicular band, but in the obtuse-angled model these relations would be reversed. Actually, 1045 cm^{-1} and 2110 cm^{-1} showed a central Q branch when examined with high resolution by Gerhard,[12] and so almost certainly are parallel bands,[13] while 710 cm^{-1} has the typical appearance of an infra-red perpendicular band, as does also the combination band 1740 cm^{-1}. This agrees completely with the HPS acute-angled model, but cannot be understood with the obtuse-angled model. An additional point, not utilized by HPS, is the fact that the Q branch is narrow and shaded to long wave-lengths in 1045 cm^{-1}, but broad and unshaded in 2110 cm^{-1}. This can be understood if these are the fundamental frequencies ν_2 and ν_1 with forms as described above, but not very well if, for instance, 2110 cm^{-1} were $2\nu_2$.

Turning to the electronic structure and spectrum, one might begin by extrapolating the curves of Fig. 6 from 60° to 39°. Since, however, the distance from the apex atom to either base atom in the O_3 model of Fig. 1 is materially greater than for the "average molecule" for which Fig. 6 has been drawn, the suggested extrapolation would not be expected to have more than rough qualitative significance here.

The problem can be approached, however, from the viewpoint that the Fig. 1 molecule model corresponds to a tightly bound O_2 or O_2^+

molecule perturbed by a loosely attached O or O^- atom. In this way one arrives at a fairly certain result for the electron configuration of the 39° model, as follows:

$$\begin{array}{cccccccccccccc}
(\sigma_g 2s)^2 & (2s)^2 & (\sigma_u 2s)^2 & (\sigma_g 2p)^2 & (\pi_u 2p)^2 & (\pi_u 2p)^2 & (2p_y)^2 & (2p_x)^2 & (2p_z)^2 & (\pi_g 2p)^0 & (\pi_g 2p)^0 & (\sigma_u 2p)^0 & \\
1a_1^2 & 2a_1^2 & 1b_2^2 & 3a_1^2 & 4a_1^2 & 1b_1^2 & 2b_2^2 & 2b_1^2 & 5a_1^2 & 1a_2^0 & 3b_2^0 & 4b_2^0 & \quad (4) \\
 & & & 18.5 & 17.5 & 16.5 & 13.5 & 13 & 12.5 & 11.5 & 10.8 & 4.5 &
\end{array}$$

The first line in (4) gives the molecular orbitals of O_2 and O_2^+, interspersed with atomic orbitals of O or O^-, in the order of ionization energy which would probably be expected if the O_2 and O perturb each other only slightly. In the second line the symbols appropriate when there is a considerable mutual perturbation are given; here each degenerate π orbital of O_2 has split into two non-degenerate ones; the symbols are now the familiar ones of Fig. 6. The third line in (4) gives estimated ionization energies, in volts, for most of the orbitals. They are based on the known values for O_2 (12 volts for $\pi_g 2p$, 16 volts for $\pi_u 2p$, 18 volts for $\sigma_g 2p$) and for the O atom (about 14.7 volts for an uncoupled $2p$ electron in O, or less in O^-) after allowance for the O_2-O mutual perturbations. The superscript zero is used in (4) for the three unoccupied shells; every other shell given is occupied by two electrons. The subscripts in $2p_x$, $2p_y$, $2p_z$ in (4) correspond to the directions of axes given in Fig. 2.

With the normal electron configuration as in (4), the structure is near $O_2^+O^-$, or between this and $O_2^{++}O^{=}$. There should then be a large permanent dipole moment, whereas a rather small one has been observed,[14] but since this was obtained in oxygen solution, it may not be conclusive. The observed diamagnetism[15] or at most feeble paramagnetism is in agreement with (4).

On the basis of (4), the very weak infra-red ozone absorption system[1] is attributed to the forbidden transition $5a_1 \rightarrow 1a_2$. The weak visible system[1] (oscillator strength $f=0.6\times10^{-4}$) may probably be attributed to $5a_1 \rightarrow 3b_2$, which is predicted to be weak. Three other systems are predicted to occur in the visible: $2b_1 \rightarrow 1a_2$ and $2b_2 \rightarrow 1a_2$ (predicted very weak), and $2b_1 \rightarrow 3b_2$ (forbidden). These may well be represented by faint absorption overlying the visible bands and by the rather weak absorption bands near λ3000.[1] Next, two strong systems are predicted, $1b_1 \rightarrow 1a_2$ and $4a_1 \rightarrow 3b_2$; both are analogous to the well-known intense Schumann-Runge system of O_2 $(\pi_u 2p \rightarrow \pi_g 2p)$ which[16] has $f=0.19$. The strong observed ozone absorption[1] with peak at λ2550 and $f=0.086$ may probably be identified with $1b_1 \rightarrow 1a_2$;[17] the fact that f here is less than in the O_2 Schumann-Runge system may be explained in part by the lower peak frequency[18] and other factors,[16] but probably also indicates that $4a_1 \rightarrow 3b_2$ has a separate peak of similar f value, perhaps in the unexplored range just below λ2000.

A detailed study of existing and new data on the ozone electronic spectrum in relation to Eq. (4) and Fig. 6 would be extremely interesting. The fine structure of the infra-red vibration bands should also be re-examined, with the highest resolution possible.

Carbon Dioxide and Carbon Disulfide

A brief review of existing knowledge of the spectra of CO_2 and CS_2 in relation to Fig. 6 is desirable before concluding. In CS_2, the well-known weak absorption system with λ_{max} near 3200 has been identified[8] as the forbidden transition $1\pi_g \rightarrow 3\sigma_g$, and it has been shown fairly conclusively[8, 19, 7] that the equilibrium form of the molecule in the upper state is bent, with an apex angle perhaps as low as 120°, smaller even than in NO_2. This may be attributed to the combined effect of addition of a $3\sigma_g(\rightarrow 4a_1)$ electron and loss of a $1\pi_g(\rightarrow 1a_2$ or $2b_2)$. The intense CS_2 absorption bands[20] with λ_{max} near 1970A most probably are $1\pi_g \rightarrow 2\pi_u$; whether the molecule becomes bent in the excited state is not yet known, but seems likely.

In CO_2, the $1\pi_g \rightarrow 3\sigma_g$ system is probably to be identified with the weak diffuse absorption bands with λ_{max} near 1600A.[20] At shorter wave-lengths there are several stronger systems,[20] no doubt including $1\pi_g \rightarrow 2\pi_u$ (λ_{max} perhaps 1335A) and $1\pi_g \rightarrow 3\sigma_u$. Finally there are a number of Rydberg series transitions.[1, 8] The important evidence for Fig. 6 obtained from these and the CO_2^+ emission spectrum is reviewed in the following article by Mrozowski.

CONCLUDING REMARKS

In general, the predictions of the present scheme point to the need of further work in the analysis of known bands and band systems and to the desirability of a search for further systems. In particular, more data on absolute absorption intensities of band systems would be valuable. With the help of such additional data, progress in the theoretical understanding of the electronic structures of oxide and other molecules would be aided. It would be of great interest to extend the present scheme to a consideration of the variation of molecular orbital energies and total energy with the A-B distances as well as the apex angle in triatomic molecules AB_2, so that complete potential energy surfaces would be available for these molecules in their normal and low excited states.

The writer is indebted to Mr. J. B. Coon and to WPA, O.P. 265–1–54–132(3) for valuable assistance in drawing the figures.

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(16) Cf. R. S. Mulliken, J. Chem. Phys. **7**, 28 (1939); see this and subsequent articles for methods of predicting intensities.

(17) That the $\lambda 2550$ region is analogous to the Schumann-Runge bands has also frequently been suggested by Dr. O. R. Wulf in conversation.

(18) Cf. R. S. Mulliken, J. Chem. Phys. **7**, 19 (1939), Eq. (9). It may be estimated (taking into consideration that the $\pi_g 2p$ shell is half filled in O_2, but empty here) that f for *each* of the transitions $1b_1 \rightarrow 1a_2$ and $4a_1 \rightarrow 3b_2$ should be as high as for the Schumann-Runge O_2 bands, if it were not for the lower frequency, smaller internuclear distance, etc. These factors could well cut f approximately in half, as observed if $\lambda 2550$ is identified with $1b_1 \rightarrow 1a_2$ alone. If $\lambda 2550$ were a superposition of this and $4a_1 \rightarrow 3b_2$, however, one would probably expect about twice as large an f as the observed, i.e., nearly the same as in the Schumann-Runge bands.

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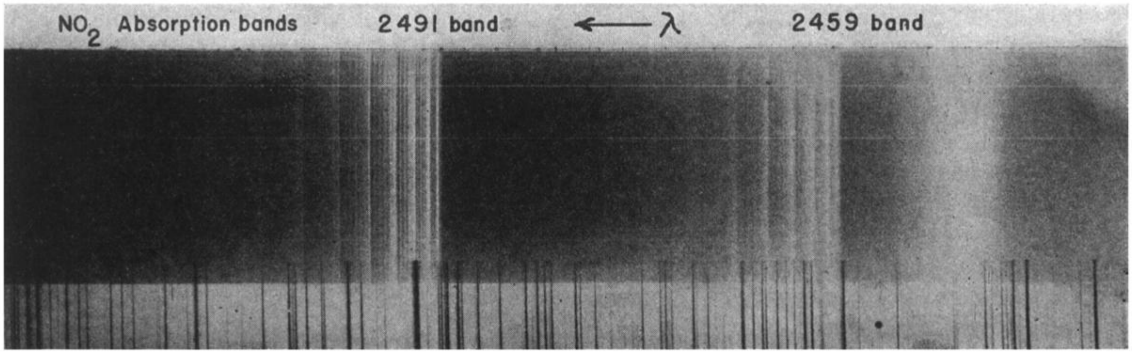

FIG. 3. Reproduced from a photograph by L. Harris with the latter's kind permission. E_1 spectrograph. The print shows two NO_2 absorption bands, λ2491 and λ2459. Both belong to the same electronic transition, but the structure in the former is sharp, while the latter is a very good example of predissociation.

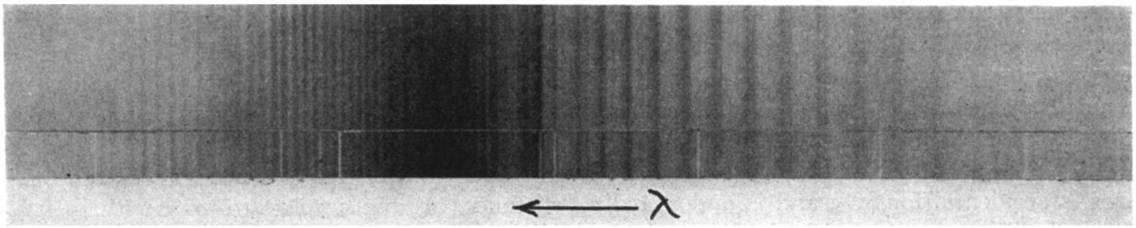

FIG. 4. The 0,0 band (λ3879) of the λ3800 absorption system of SO_2, reproduced from an original photograph by N. C. Metropolis and H. G. Beutler, with the kind permission of the authors.