field, (2) whether a loose-bound scalar type theory or a tight-bound pseudoscalar-type theory is preferable, and (3) how much faith can be placed in the "quantum electrodynamical radiative corrections" to scattering and in the far more dubious second-order meson corrections to scattering.

I would like to thank Professor L. I. Schiff for many helpful discussions and suggestions. I would like to express my gratitude also to Dr. Ross Thompson of Cornell University who has performed most of these calculations independently, and who very kindly checked, and improved upon one of, my results.

PHYSICAL REVIEW VOLUME 79, NUMBER 4 AUGUST 15, 1950

Anomalous Molecular Rotation and the Temperature of the Upper Atmosphere*

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(Received May 12, 1950)

This experiment verifies the prediction of Oldenberg that the spectroscopically measured rotational temperature of a diatomic gas will be lower than the translational temperature when (1) the pressure is low, (2) the gas is excited by electron impact, and (3) the excited electronic state from which the measured bands are radiated has an equilibrium nuclear separation greater than the internuclear distance in the ground state. For gas temperatures from 400 to 670°K rotational temperatures from the second negative bands of O_2^+ were found in qualitative agreement with the predicted relation $T_{\mathrm{rot}}=T_{\mathrm{trans}}\,B'/B''$. Upper atmosphere temperatures derived from band profiles in night sky spectra are consistently lower than temperatures estimated from other data. The possible occurrence of anomalous rotation of the night sky molecules casts some doubt on the meaningfulness of the night sky temperature measurements. A partial rotational analysis in the course of this experiment suggests revisions of the B_0 and α-values for the O_2^+ molecule in the $^2\Pi_u$- and $^2\Pi_g$-states.

I. INTRODUCTION

A KNOWLEDGE of the molecular density and temperature at high altitudes is fundamental to an understanding of the processes occurring in the earth's upper atmosphere. For the region above 80 km the atmospheric temperature is deduced from indirect evidence from various sources. Unfortunately most of the data is only qualitative and, to make matters worse, much of it is contradictory. Evidence for a steadily increasing temperature above 80 km (a gradient of perhaps 4°/km) is found in the relative widths of the ionosphere layers, the apparent scarcity of helium at high altitudes, and the slow decrease in density at very great heights (as is indicated by high altitude auroral rays).[1] On the other hand, the more direct spectroscopic measurements on bands in the spectra of the aurora and the night sky luminescence are interpreted by some authors as conclusive evidence for a constant temperature of about 250°K above 90 km, a result which seems quite incompatible with the other temperature estimates.

These spectroscopic temperature measurements are based on the relationship between the equilibrium temperature of a radiating diatomic gas and the relative intensities of the lines in the rotational fine structure of an emission spectrum. The relative intensities of the rotational lines depend on two quantities: the relative transition probabilities of the lines, and the population of the initial rotational levels. If the temperature dependence of the populations of the initial rotational states is known, one can calculate the transition probabilities from quantum theory and can then calculate the gas temperature from the experimental relative intensities of the lines in a band.

In the measurements on upper atmospheric spectra it was assumed that the excited molecules in the aurora and night sky are in a Boltzmann distribution with respect to rotational energy, at an equilibrium temperature T. The significance of the spectroscopic temperature measurements depends on the validity of this assumption. Laboratory investigations of bands excited by electron impact in a glow discharge have afforded many examples of cases in which the excited radiating molecules are indeed in a Boltzmann rotational energy distribution, for the spectroscopically determined temperatures were quite close to the directly measured gas temperatures.

In 1934 Oldenberg[2] pointed out that although the molecules in a low pressure glow discharge are initially in thermal equilibrium, the assumption of thermal equilibrium in the *excited* rotational states is justified only for molecules whose nuclear separation is the same in the excited and ground states. Although this is usually the case, there are certain molecules in which the excited state has a much larger nuclear separation

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* This work is described in detail in the author's Ph.D. thesis, Harvard University (1949).

** Now a member of the Society of Fellows, Harvard University.

[1] S. K. Mitra, *The Upper Atmosphere* (the Royal Society of Bengal, Calcutta, 1947); G. P. Kuiper, *The Atmosphere of the Earth and Planets* (University of Chicago Press, Chicago, 1947). See especially chapters by P. Swings and L. Spitzer, Jr.

[2] O. Oldenberg, Phys. Rev. 46, 210 (1934).

than in the ground state. By coincidence all of the night sky bands used for temperature measurements arise from just such states. Taking into account this change in internuclear distance in the upper atmosphere spectra yields values of the temperature almost twice as high as those found by assuming an equilibrium distribution in the excited states (as was done in the original experiments). Although it is not at all clear that the correct excitation conditions prevail in the upper atmosphere for the production of this abnormal rotation effect, any type of excitation other than electron impact renders the assumption of thermal equilibrium in the excited states equally doubtful. The purpose of this research was to demonstrate this anomalously low rotation in the laboratory, using one of the atmospheric gases, and then to discuss the spectroscopic temperature measurements in the upper atmosphere in light of the results.

II. LOW ROTATION AFTER ELECTRONIC EXCITATION AND INCREASED INERTIA

Consider a diatomic gas in thermal equilibrium at a low pressure and excited by a weak electric current in a glow discharge. The relative population of the rotational states of the unexcited molecules is given by

$$N''(j) \propto j(j+1)\exp(-E''/kT) \propto j(j+1)\exp(-E_r''/kT) \quad (1)$$

where the double prime refers to the ground state, E is the total energy, and E_r is the rotational energy. The vibrational and electronic components of the energy may be neglected since they lead to exponential factors independent of j. The rotational energy of a diatomic molecule is, to a good approximation,

$$E_r = (h/4\pi c I_v)j(j+1) = B_v j(j+1)\ \mathrm{cm}^{-1}, \quad (2)$$

so that[3]

$$N''(j) \propto j(j+1)\exp[-B_v''j''(j''+1)/kT]. \quad (3)$$

Owing to the large disparity between the masses of the molecule and of the exciting electron, the electron does not impart an appreciable angular momentum to the molecule. Since the total angular momentum of the molecule is $[j(j+1)]^{\frac{1}{2}}\hbar$, such an excitation process requires that the rotational quantum number j remain constant. If the value of B_v' (in the upper electronic state) is smaller than B_v'', the rotational energy levels of the excited state are more closely spaced than in the ground state, and the rotational *energy* of the molecules in the state j is decreased after excitation by the ratio of B_v' to B_v''. Thus the population of the jth rotational state remains constant during excitation, and the compression of the energy levels yields a new energy distribution which no longer corresponds to equilibrium at the original temperature. Quantitatively,

$$N'(j) = N''(j) \propto j(j+1)\exp[-B''j(j+1)/kT] \propto j(j+1)\exp[-B'j(j+1)/kT_{\mathrm{eff}}]$$

where

$$T_{\mathrm{eff}} \equiv TB_v'/B_v''. \quad (4)$$

The new population distribution is indeed of the Boltzmann form, but corresponds to equilibrium at a smaller value of the temperature, T_{eff}. In order for the band spectrum to indicate this low temperature distribution, the pressure must be sufficiently low that collisions during the life of the excited molecule do not partially restore thermal equilibrium before radiation can occur. This condition is fulfilled in the upper atmosphere for allowed transitions and may also be achieved in low pressure laboratory discharges. Under such conditions it should be possible to measure the gas temperature fairly accurately by multiplying the result obtained assuming thermal equilibrium in the excited state (T_{eff}) by the ratio B''/B'.

Although there are many well-known experimental examples of excessively high rotational temperatures in band spectra (resulting from other mechanisms), abnormally low rotation is relatively rare because of the very special conditions which must be met. We have found only two reports of observation of this effect. The first case is the discovery by Schüler and others[4] of remarkably deficient rotation in the spectrum of CuH in a very low pressure hollow cathode discharge. At 0.03 mm pressure of helium with a trace of hydrogen, they found the P_1 line to be the only rotational line with appreciable strength, indicating that only the zeroth rotational level was populated before radiation. The molecular free path was of the order of the cathode diameter, making gas collisions quite rare, so that Schüler was doubtless observing CuH molecules in the rotational state in which they left the cathode. This absence of rotation is probably due to the mechanism of formation and ejection of the CuH from the cathode surface. Plans are underway to investigate this phenomenon further in this laboratory. It is quite certain that the small increase in the inertia of the CuH molecule which does occur upon electronic excitation is quite inadequate to account for the extraordinary absence of rotation observed by Schüler.

The second observation of deficient rotation is probably explained by Oldenberg's prediction. In 1941 Ginsburg and Dieke[5] found an effective temperature of only 237° in the Fulcher bands of hydrogen excited in an a.c. discharge at 0.06 mm pressure. In this case $B''/B' \sim 2$. No direct temperature measurements of the discharge were made; one can only say that the molecular

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[3] This is strictly true only for $^1\Sigma$-states, with additional terms appearing in the energy formula for states of higher multiplicity and orbital angular momentum. The terms which are constant for a particular sub-band may be factored out with the vibrational energy. Other terms involve B_v as a factor and do not affect the following argument.

[4] H. Schüler and H. Gollnow, Zeits. f. Physik **108**, 714 (1938); **109**, 432 (1938); **111**, 484 (1939). H. Schüler and H. Haber, Zeits. f. Physik **112**, 614 (1939).

[5] N. Ginsburg and G. H. Dieke, Phys. Rev. **59**, 632 (1941).

kinetic temperature must have been above room temperature. It was our purpose to demonstrate the existence of this low rotation effect conclusively using one of the atmospheric gases with more carefully controlled temperature conditions, so that the results might be less ambiguously applicable to the upper atmosphere.

III. SELECTION OF BAND SYSTEM

A. Schumann-Runge Bands of O_2

We would like to have studied in this experiment the same bands which are observed to give very low effective temperatures in night sky spectra. Unfortunately these bands (the Herzberg system of O_2 and the Vegard-Kaplan bands of N_2) are forbidden transitions which cannot be excited with sufficient intensity by electron impact in the laboratory. The Schumann-Runge bands of O_2 would have been ideal, for they involve states for which B_0''/B_0' is 1.76 and have a conveniently simple rotational structure. Although usually excited in an arc through oxygen at atmospheric pressure, intense production of these bands in the r-f electrodeless discharge has been reported by Lal in India.[6] We made a thorough search for the Schumann bands in glow discharges at pressures below 1 mm from 1800 to 7000A using electrodeless, condensed and uncondensed a.c. and d.c. discharges through spectroscopically pure oxygen. No trace of the Schumann bands was found, even when the gas was heated to 1000°K in an electric furnace. The failure to excite these bands (which arise from a completely allowed transition) is easily understood on the basis of the Frank-Condon principle. The desirable property of large inertial change after excitation is the very factor which causes the molecules to dissociate, so great is the vibrational potential energy produced. This result was also found by Feast[7] and must be kept in mind when discussing the identification of the Schumann bands in emission in night sky spectra. These experiments and theoretical considerations throw grave doubt on the results of Lal.

B. Second Negative Bands of O_2^+

The beta-bands of NO were considered but rejected to avoid possible excitation by chemical reaction or polyatomic dissociation. The O_2^+ second negative system was finally used, in spite of the difficulties resulting from the complex structure. The transition is from a $^2\Pi_u$-state intermediate between Hund's case (a) and case (b) to a $^2\Pi_g$-state in case (a). The ground states of both the ion and the neutral molecule have roughly equal internuclear distances. Hence, the anticipated temperature effect would be almost the same, whether the oxygen molecule is first ionized and later excited, or is ionized and excited in a single step.

IV. APPARATUS

The discharge tube was a cylindrical Vycor tube, 1 in. O.D. and 24 in. long, with a fused quartz window melted directly to one end of the tube. An electric furnace was constructed about the tube so that the walls of the discharge tube could be maintained at any temperature from room temperature up to 1000°K.

The electrodeless discharge was excited by a self-excited oscillator which could deliver up to 50 watts at 23.9 Mc to the discharge. The oscillator was capacitively coupled to the discharge tube by connecting the tank circuit in parallel with strips of copper wrapped around the discharge tube just outside each end of the furnace.

The oxygen was prepared electrolytically from distilled water. Hydrogen was removed by passing the gas through heated platinized asbestos and over phosphorus pentoxide. Carbon dioxide was removed in a liquid air trap, which also served to condense any traces of water vapor and the mercury vapor from the diffusion pump.

Because of the complexity of the rotational structure of the bands, high resolving power was required. A discharge sufficiently intense to allow use of a large grating would have prevented controlled temperature conditions in the gas. As a compromise the Hilger *E*-1 Littrow-type quartz spectrograph was used. It was found that the ultimate resolving power of the instrument could only be achieved if the room temperature was held constant to about 0.1°C because of the thermal coefficient of the prism refractive index and the very large *f* ratio of the instrument. A change in room temperature of two degrees between two exposures to an iron arc produced doubled spectrum lines.

V. PROCEDURE

To measure the relative intensities of the rotational lines in the O_2^+ bands we calibrated our plates by a method described by Barbier.[8] There are two great advantages in this method of plate calibration. First, each spectrum is its own calibration, eliminating errors due to non-uniform emulsion or development. Second, a fairly non-uniform slit illumination can be tolerated since only two adjacent parts of each line require photometry.

For comparison with the effective temperatures calculated from rotational profiles, it was necessary to measure the molecular translational temperatures by some direct and independent method. Metal thermocouples cannot be trusted in an oxygen discharge because of the reassociation of oxygen atoms which occurs very readily at metal surfaces. By operating the discharge at 10 microns pressure, the mean free path is slightly larger than the tube radius, and collisions with the walls are more numerous than collisions with excited molecules. Then if the discharge current is kept

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[6] Lalji Lal, Nature **161**, 477 (1948).

[7] M. W. Feast, Nature **162**, 215 (1948); Proc. Phys. Soc. (A) **62**, part 2, 114 (1949).

[8] D. Barbier, Ann. d'Astrophys. **10**, No. 2 (1947).

weak, the temperature of the walls should determine the molecular translational temperature.[9] In any event, the average wall temperature is a lower bound to the average gas temperature, after the small cooling effect of diffusion into the cooler part of the system is taken into account. The effect of any radial temperature inhomogeneity was minimized by restricting the power drawn by the discharge to about 10 watts and then heating the discharge tube with the furnace to several hundred degrees C.

So many vibrational transitions are allowed with appreciable intensity in the first negative bands of O_2^+ (a direct result of the desired large difference in the internuclear distance of the two electronic states involved) that many of the bands are confused by the overlapping of weaker bands of the same system. If all of the rotational lines are not resolved, this precludes accurate intensity measurements in the overlapped bands. The (8, 1) band at 2343.3A and the (1, 6) band at 3494.2A were found to be most free from overlapping and of sufficient intensity. The complete rotational analysis of the (0, 6), (0, 7), (1, 6), and (1, 7) bands near 3500A has been carried out by Stevens[10] so that the line identifications and molecular constants are known for these bands. However, the rotational lines in the (1, 6) band could not be completely resolved, while those in the (8, 1) band could, since the dispersion increases fourfold from 3500 to 2350A. The advantage gained by the greater dispersion at 2350A is partially offset by the necessity for making a rotational analysis of the (8, 1) band, for an extrapolation of the empirical constants describing the vibration-rotation interaction from $v'=0$ and 1 to $v'=8$ proved to be in serious error. As a mutual check and as an investigation of method, effective temperatures were measured from both the (1, 6) and the (8, 1) bands, using quite different techniques.

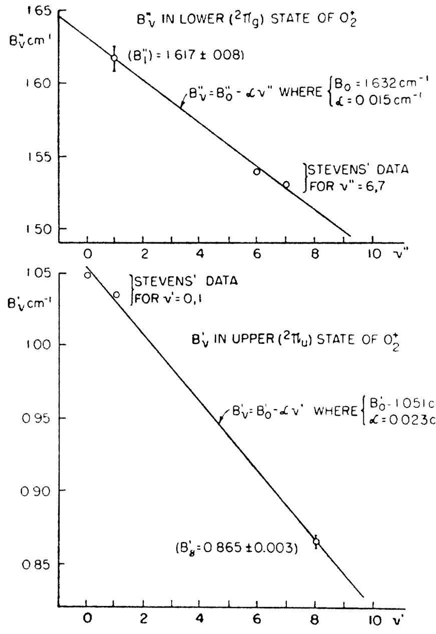

FIG. 1. This plot of B_v against vibrational quantum number for the upper and lower $^2\pi$-states of O_2^+ shows the data of Stevens and the two new points from our partial rotational analysis. New values of B_0 and α are found.

VI. ROTATIONAL TEMPERATURES FROM THE RESOLVED (8, 1) BAND

In addition to intensity measurements, calculation of the rotational temperature from a band requires accurate knowledge of both line identifications and the molecular constants from which the transition probabilities are calculated. The bands are double headed, and we confine our measurements to the first sub-band, in which the lines are not so closely spaced. B_8' and $B_1^{*\prime\prime}$, as well as the assignment of rotational quantum numbers to the branches, were determined graphically, principally from the frequency difference relations

$$\Delta\nu_R=\nu_{R(k)}-\nu_{R(k+1)}=2(B^{*\prime\prime}-B')k+B^{*\prime\prime}-2B'+(-1)^{k+1}(2k+1)(0.018)$$

$$\Delta\nu_P=\nu_{P(k)}-\nu_{P(k+1)}=2(B^{*\prime\prime}-B')k+5B^{*\prime\prime}-2B'+(-1)^{k+1}(2k+1)(0.018)$$

from which

$$d(\Delta\nu_R)/dk=d(\Delta\nu_P)/dk\simeq 2(B^{*\prime\prime}-B')$$
$$\Delta\nu_P-\Delta\nu_R=4B^{*\prime\prime}+0.076\text{ cm}^{-1}.$$

The last term in the first two equations gives the Λ-type doubling. By standard spectroscopic notation, $B_v^*=B_v(1-B_v/A)$, and the rotational quantum number k is used instead of j for convenience. These equations can be derived from the selection rules, the Λ-doubling results of Stevens,[10] and the Hill-Van Vleck[11] formula for the rotational terms of a $^2\Pi$-molecule. In the graphical method used, one need only know at the outset which lines belong to main branches, as can be determined from inspection. Identification of the main branches as P and R comes out of the analysis. The method actually yields several possible values of B^* (0.8, 1.6, and 2.5 cm^{-1}), from which we must pick the only reasonable one (1.6), since the extrapolation of Stevens' data is certainly *roughly* correct and yields[12] 1.56 cm^{-1} for B_1^*. Using the line and branch identifications so obtained, the accuracy of B' and $B^{*\prime\prime}$ was improved by plotting 11 other combination difference

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[9] The extent of dissociation in the discharge is unknown. Oxygen atoms produced with considerable kinetic energy may be sufficiently numerous to exert an appreciable heating effect in the volume of the discharge.

[10] D. S. Stevens, Phys. Rev. **38**, 1292 (1931). Note that Stevens assigns v'' values which are two units larger than those used in this paper. The smaller v'' values are now generally accepted. Stevens' values of α must also be corrected in light of this change in Stevens' vibrational numbering. See R. S. Mulliken and D. S. Stevens, Phys. Rev. **44**, 720 (1933).

[11] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

[12] For a detailed description of this method of line identification the reader is referred to the author's thesis.

relations between lines in the P, R, and ${}^SR$ branches. (The ${}^QP$ branch was badly masked by the P branch.) The final results obtained are

$$B_8'=0.865\pm0.003\ \text{cm}^{-1},\qquad B_1^{*\prime\prime}=1.604\pm0.008\ \text{cm}^{-1}.$$

From the definition of B^* and using $A=195$ cm^{-1},

$$B_1''=1.617\pm0.008\ \text{cm}^{-1}.$$

To obtain B_0 and α for the upper and lower electronic states we combine these results graphically with Stevens' measurements in Fig. 1. These results suggest revision of the constants of the O_2^+ molecule as given below, although a complete rotational analysis with a large grating should be carried out before final adoption of these values, for more accurate values could be obtained.

Upper $^2\Pi$-state: $B_0'=1.051$ cm^{-1}; $\alpha'=0.023$ cm^{-1}.
Lower $^2\Pi$-state: $B_0''=1.623$ cm^{-1}; $\alpha''=0.015$ cm^{-1}; $r_e''=1.132$A.

The rotational transition probabilities were calculated for $v'=8$ and 1, applying the theory of Hill and Van Vleck[11] to the lines in the first sub-band. Their general theory was applied to this special case of a $^2\Pi-{}^2\Pi$-transition from a state of intermediate coupling to a case (a) state. Algebraic manipulation yields the following simple formulas for the relative transition probabilities, $i(j)$, of the lines in the first sub-band of such a transition:

$$\begin{aligned} i_P(j)&=A(j+1)(1+B) & i_R(j)&=A(j)(1+B)\\ iQ_P(j)&=A(j+1)(1-B) & iS_R(j)&=A(j)(1-B) \end{aligned}\tag{5}$$

where

$$\begin{aligned} A(j)&=(4j^2-1)/8j & C&=A/B'(A/4B'-1)\\ B(j)&=\tfrac{1}{2}(\lambda-2)[(j-\tfrac{1}{2})^2+C]^{-\frac{1}{2}} & \lambda&=A/B'. \end{aligned}$$

Figure 2 shows a microphotometer trace of the (8, 1) band at 2343A, showing the two-headed structure and the prominence of the main P and R branches.

The intensity of the jth line in a branch is

$$I(j)\propto i(j)\ \exp[-(B'/kT_{\text{eff}})\{j(j+1)\pm[(j+\tfrac{1}{2})^2+C]^{\frac{1}{2}}\}].$$

The terms in the braces are the parts of the rotational energy dependent on j from the Hill-Van Vleck formula.[3] If one plots

$$\ln I(j)/i(j)=\text{const.}-(B'/kT_{\text{eff}})\times\{j(j+1)\pm[(j+\tfrac{1}{2})^2-C]^{\frac{1}{2}}\},\tag{7}$$

T_{eff} is found from the slope of the resulting straight line. (In these formulas the plus sign is used with the satellite branches, the minus with the main branches.) Figure 3 shows a typical result; for an average gas temperature of about 512°K the effective temperature is 285±70°K, yielding $T/T_{\text{eff}}=1.80\pm0.45$. The points on the plot are very badly scattered. The vertical lines drawn through the points indicate only the uncertainty in the position of the points due to grain in the plate. This is a considerably smaller effect than the scatter in the points due to the overlapping of weak bands in the background. The intensity available did not permit the increased dispersion which might have eliminated this scatter.

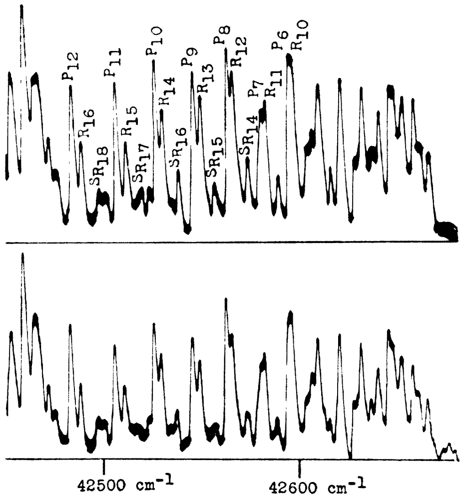

FIG. 2. Microphotometer traces of the first sub-band of the (8, 1) band at 2343.3A showing strong main branches, weak satellite branches, and the beginning of the second band on the left. The lower trace is of that part of the spectral lines which were attentated by an aluminized disk to provide an intensity calibration.

These results show conclusively that the effective temperature lies well below the lower bound of the gas temperature, as was anticipated. The experimental error in the determination of the slope of the straight line in Fig. 3 makes it impossible to determine whether there is accurate experimental agreement with Eq. (4). The ratio of the B values of the vibrationless ground states of the *neutral* O_2 and the excited *ionized* molecule with $v'=8$ is $1.422/0.865=1.644$. If the $v'=0$ level of the ground state of the *ionized* molecule is the initial state of the excitation, the ratio is $1.583/0.865=1.829$. Since the molecules are originally close to thermal equilibrium and the pressure is sufficiently low, T/T_{eff} should lie between 1.64 and 1.83, probably closer to the first value. The mean of results from three spectra of the (8, 1) band yields $T/T_{\text{eff}}=2.1\pm0.5$, which does not contradict the prediction of Eq. (4).

VII. ROTATIONAL TEMPERATURES FROM THE UNRESOLVED (1,6) BAND

In the case of the (1, 6) band at 3494.2A it was necessary to open the spectrograph slit and intentionally smear out the rotational structure because the maximum resolution was not sufficient. Since this is the method which must perforce be applied to night sky bands, it is instructive to investigate its limitations. Spectra were obtained with the slit widened so that the lines were rectangular and of width 30 cm^{-1}. A typical

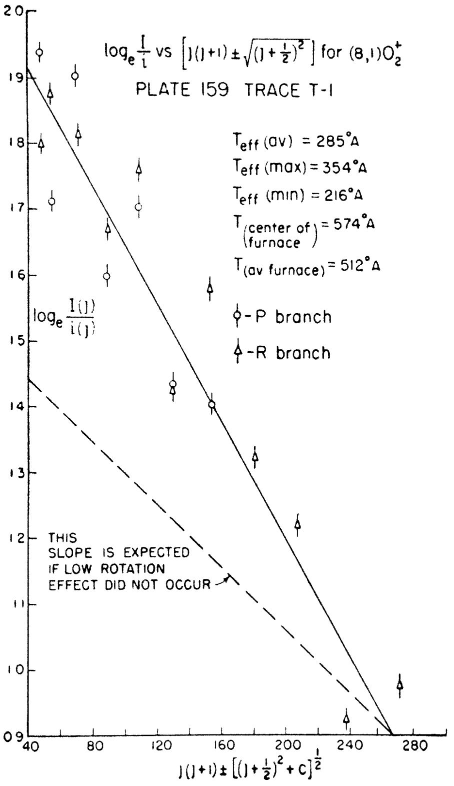

FIG. 3. Typical measurement of effective rotational temperatures from the (8, 1) band of O_2^+. Vertical lines through points indicate grain errors only and not the large scatter produced by overlapping weak lines.

trace is shown in Fig. 4. Virtually all of the rotational structure has been removed, the first sub-band having a smooth shape (except for an annoying faint overlapping near the tail). Using Stevens' analysis of this band, artificial band shapes were computed for six effective temperatures ranging from 200 to 600°K. The experimental band shapes were compared graphically with the family of theoretical shapes predicted for various temperatures. The results for three plates are shown in Fig. 5.

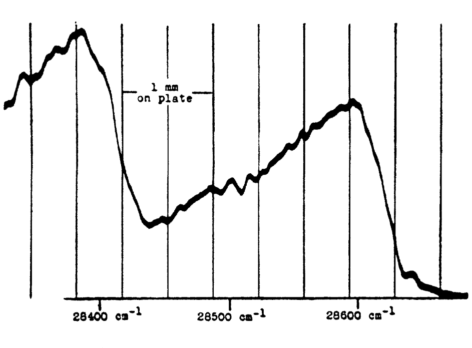

FIG. 4. Microphotometer trace of the (1, 6) band of O_2^+ at 3494A. The slit was opened to produce a line width of 30 cm^{-1}. Both first and second band heads are shown. After intensity calibration this band shape is related to rotational temperature in Fig. 5.

Again the increase in moment of inertia after excitation acts indirectly to reduce the sensitivity of the band profile to changes in temperature. The band branches are so strongly degraded that the line spacing changes rapidly from head to tail. As a result, the crowding of the lines near the head is more effective in determining the position of the intensity maximum than are the relative intensities of the individual lines. The slope of the tail of such an unresolved band is the only useful temperature indication, and it is rather insensitive to temperature changes.

Table I shows a summary of seven runs on the (1, 6) band for furnace temperatures ranging from about 400 to 670°K. The mean value of T/T_{eff} is 1.50 ± 0.25, where the assigned error is a necessarily subjective estimate. In this case we expect T/T_{eff} to lie between 1.37 and 1.59, depending on whether the initial state of the excitation process is the neutral molecule or the ion. Again the experimental result is in qualitative agreement with the theory.

Since experimental difficulties prohibited precise quantitative results, no detailed discussion of sources of error will be included here. Suffice it to say that we have observed an effect characteristic of abnormally low rotation in the excited state of the O_2^+ molecule, and the magnitude of the abnormality is in general agreement with the prediction of Oldenberg.

VIII. THE UPPER ATMOSPHERE

A. Schumann-Runge Bands of O_2

As regards the Schumann-Runge bands of O_2, tentatively identified in night sky spectra,[1] we conclude that their presence requires an excitation mechanism producing a molecule with low vibration or removing the excess vibrational energy after the O_2 molecule is excited. Three-body reassociation of oxygen atoms in the presence of an oxygen or nitrogen molecule has been postulated as the mechanism for producing the Schumann bands in the upper atmosphere. Such a process has a density cubed dependance and becomes most improbable at auroral densities. Whether the low specific probability of three-body collisions at auroral densities

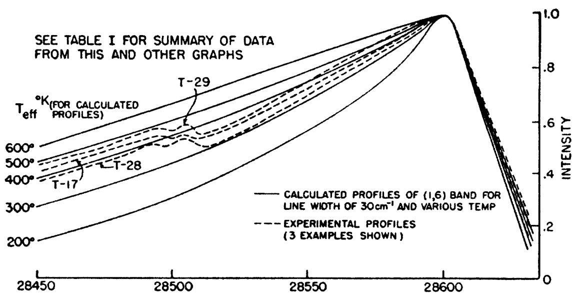

FIG. 5. Graphical method of deducing rotational temperatures from the (1, 6) band of O_2^+. This method is much less sensitive than that of Fig. 3, but must be used in the unresolved night sky bands.

is compensated for by the large volume without walls which the upper atmosphere represents remains to be seen. Consideration of the oxygen potential curves and the Frank-Condon principle shows that any excitation of the Schumann bands which does result from electron impact at low pressure will lead to radiation in the vacuum ultraviolet and perhaps in the infra-red, but not in the near ultraviolet. For if the oxygen molecule is excited by electron impact, the Frank-Condon rule tells us that the excited state will be strongly vibrating. Radiation is most probable at the turning points of the vibrational motion; the quantum jumps to the ground state are quite large when the nuclei are closest and small when swinging farthest apart. The well-known near ultraviolet bands of the Schumann-Runge system result from the population of the lowest vibrational levels of the upper state. Hence the positive identification of the near ultraviolet Schumann-Runge bands in the night sky would require the existence of an excitation process other than electron impact.

B. Upper Atmosphere Temperature

For discussions of the diverse evidence regarding the kinetic temperature of the atmosphere above 80 km the reader is referred to the detailed reviews on the subject.[1] In general most of the evidence, except that derived from spectroscopic band profiles, suggests an increasing temperature above 80 km. At 100 km the N.A.C.A. "most probable" temperature[13] is about 310°K. In night sky spectra, Cabannes and Dufay[14] found $T_{\text{eff}}=230°\text{K}$ for the Vegard-Kaplan bands of N_2. Barbier[15] found values ranging from 170 to 220°K for the Herzberg bands of O_2. Swings[16] roughly estimated the rotational temperature in the Herzberg bands to be about 150°K. The altitude of emission of these bands is not established, although the most recent evidence[17] favors a layer at 100 km. If the altitude of emission of the night sky bands is equal to or greater than 100 km, the disparity between the spectroscopic temperature data and the N.A.C.A. value is 70° or greater for the N_2 bands, and over 100° for the O_2 data. If the night sky radiation originates as low as 80 km, there is no obvious discrepancy between the spectroscopic temperature measurements and the N.A.C.A. curve. Also, as D. R. Bates has pointed out, there is a possibility that the rotational temperature measurements in the particular case of the Vegard-Kaplan bands are reliable. For if the lifetime of the excited state is sufficiently long, collisions may restore equilibrium even at auroral densities. The evidence for the existence of these collisions is the small intensity of the Vegard-Kaplan bands compared to the first positive bands, suggesting strong collisional depopulation of the metastable level[18] in N_2.

TABLE I. Comparison of measured gas temperatures and effective rotation temperatures in the (1, 6) O_2^+ (2nd neg.) band.

Trace No.	T_f[a]	T_{eff}	T_f/T_{eff}
16	447±20°K	330°K	1.35
17	573±30	350	1.64
19	462±20	340	1.36
24	400±20	320	1.25
25	432±20	330	1.31
28	542±20	310	1.75
29	667±40	370	1.80
		Average	1.50

[a] T_f is the average temperature of the walls of the discharge and is approximately the translational gas temperature.

The most widely favored night sky excitation theories are based on: (a) three-body recombination processes (which are well known to produce abnormally high, not low rotation[19]) and (b) two-body charge transfer processes involving positive and negative ions (whose effect on rotation is unknown). With such types of excitation, spectroscopic temperatures are quite unreliable, providing collisions do not restore equilibrium in the excited state.

On the other hand, if the excitation is by electron impact (as seems improbable) and the pressure is sufficiently low, we must correct the spectroscopic data for the effect of the changes in inertia during excitation of the Vegard-Kaplan and Herzberg bands. If we multiply these spectroscopic effective temperatures by the respective values of B''/B' (1.5 and 1.4) we get temperatures of 260 to 340°K for the Herzberg bands and 320°K for the Vegard-Kaplan bands. This brings the O_2 and the N_2 data into harmony with each other and with the N.A.C.A. conclusions (at an emission altitude of 100 km).

In any case, we may conclude that the rotational temperatures found from night sky bands should not be relied on as an indication of the kinetic molecular temperature in the emitting layer until we know the lifetimes of the excited states. For if the excitation is by electron impact (or any other method conserving molecular angular momentum) the temperatures must be revised upward by a factor B''/B', and if the excitation is by any other method we can only conclude that this method is totally unreliable, inasmuch as there is no experimental or theoretical basis for predicting the amount of angular momentum gained or lost by the excited molecule.

This discussion cannot be complete without reference

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[17] Lecture by C. T. Elvey concerning the unpublished results of Elvey, Swings, and Barbier.

[18] This statement may require revision if Elvey is proved correct in suggesting that the strong radiation at about 10,400A may be OH and not the (O, O) band of the N_2 first positive system.

[19] Feast (reference 7) found rotational temperatures of 2000 to 3000°K in an investigation of the Schumann-Runge bands of O_2, apparently excited by three-body reassociation.

to the rotational temperatures measured by Vegard[20] and his collaborators[21] from the intensity distribution in the *R* branch of the 4278A (0, 1) band of N_2^+ in the *aurora* at Trömso, Norway. Vegard and Tönsberg found $T_{\mathrm{eff}}=219\pm25$°K for the auroral region from 90 to 140 km. Although most of their spectra are of auroras at this altitude, studies of rays extending to 600 to 800 km show no increase in rotational temperature. In this band system the moments of inertia of the molecule are almost identical in the excited N_2^+ state and in the ground states of both N_2^+ and N_2, so that B''/B' is unity. In addition, the intensities of the auroras permit the use of a much greater resolving power than in the case of night sky spectra. A third factor increasing the reliability of these measurements is that the N_2^+ band involves no inertial change upon radiation, so that the shape of the unresolved band profile is much more sensitive to the temperature than are the shapes of the Herzberg and Vegard-Kaplan bands. Penndorf[22] calls attention to the fact that Vegard's measurements are all made in the arctic winter, while the night sky experiments and radio sounding data have been primarily low latitude experiments. However, Penndorf's criticism does not explain the extension of auroral rays to 1000 km which is occasionally observed in the arctic winter and is one of the best evidences of a high mean temperature at high altitudes. Comparison of measurements made in widely different latitudes using different techniques should perhaps be interpreted with caution.

It would be very desirable to obtain independent confirmation of Vegard's results, particularly in low latitudes. In addition, a systematic investigation of the latitude dependence of the temperature at 100 km is called for using the same experimental method at all latitudes.

I am greatly indebted to Professor Otto Oldenberg who suggested this problem and assisted with many stimulating discussions. I also wish to acknowledge the generous support of a Predoctoral Research Fellowship from the National Institute of Health.

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PHYSICAL REVIEW VOLUME 79, NUMBER 4 AUGUST 15, 1950

The Liquid-Solid Transformation in Helium near Absolute Zero

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(Received March 13, 1950)

Although helium is normally a liquid to absolute zero, it can be solidified by the application of moderately high pressures. This transformation is of particular interest, since by the third law of thermodynamics the entropy difference between the liquid and the solid must disappear as the absolute zero is approached. This can most easily be shown by the disappearance of the heat of melting. Measurements from 1.0° to 1.8° of the slope of the melting pressure curve and the change in the molar volume of helium on melting are described, from which the heat of melting and the change in internal energy on melting were calculated. These results verify the predictions made by the third law. The measurements are also combined with those due to earlier workers to show the discontinuities in the various thermodynamic functions at the intersection of the λ-point-pressure curve with the melting pressure curve.

I. INTRODUCTION

SOLID helium, in contrast with liquid helium, is a relatively normal substance, although it exists only under relatively high pressures (Fig. 1). W. H. Keesom and his collaborators were the first investigators to observe solid helium,[1] and they have performed many fundamental experiments with it, all of which point to the fact that a transformation of the λ-type does not take place.

The fact that helium can be solidified by the application of pressure, although under its saturated vapor pressure it remains a liquid to absolute zero, makes the liquid-solid transformation very interesting from the thermodynamic point of view. This has been pointed out in another paper,[2] and it is worth noting that, by the third law of thermodynamics, the entropies of liquid and solid helium must become the same at very low temperatures. This means that both the heat of melting and dP/dT must approach zero as a limit. The fact that the melting pressure curve as first determined by Keesom (Fig. 1)[3] did seem to approach a positive pressure with $dP/dT=0$ at absolute zero was taken as a direct confirmation of the validity of the third law.

Probably the most interesting point on the melting pressure curve, with the exception of the point at the absolute zero, is the intersection of the melting pressure and λ-point pressure curves[3,4] at 1.8°. This is a form of

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