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The Question of the Possibility of Measuring the Temperature of the Column of a Jet Discharge Using the 3064 Å Hydroxyl Band

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It is shown that measurements of the temperature of the column of a jet discharge at pressures greater than 100 mm Hg using the 3064 Å hydroxyl band yield the temperature of the neutral gas. This is connected with the predominant role of thermal dissociation of water at the pressures indicated as compared with dissociation due to the action of fast electrons with simultaneous excitation of the hydroxyl which is formed.

ONE of the difficulties in using molecular bands to determine the temperature of a neutral gas in an electric discharge lies in the fact that the distribution of molecules by rotational states corresponding to the temperature of the neutral gas can be stated a priori only for stable molecules. In this case, because of the "duplicating" property of the collisions between an electron and the molecules[1], the distribution over rotational levels for the upper electronic state is similar to the distribution for the ground state where it is determined by the temperature of the neutral gas. Hence, using molecular spectra it is possible to determine the temperature of the neutral gas in non-isothermal states; under the same conditions the relative intensity of the atomic lines yields only the excitation temperature. In the case of the nitrogen molecule, which is of interest in what follows, this method has been verified experimentally by comparison with independent temperature measurements performed with thermocouples[2,3].

Once the applicability of the method is established, the temperature, as is well known, can be determined by starting with the relation:

$$\ln \frac{I}{i\nu^4} = C + \frac{B}{kT} J(J+1), \tag{1}$$

where I is the intensity of the spectral line at a frequency ν corresponding to a transition characterized by a rotational quantum number J (the upper electronic state) and transition probability i, B is the rotational constant, T is the absolute temperature and C is a constant.

In the case of the unstable molecules which are formed in the same discharge, there is at hand experimental evidence giving examples both of a deviation from the distribution given in Eq. (1) as well as the maintenance of a particular type of distribution for which the obtained temperature values cannot possibly coincide with the temperature of the neutral gas under these conditions. Thus, for example, Hori[4] has observed a case (for a discharge between carbon electrodes at 4 mm Hg, using the molecules CO and CN) in which there was observed a Boltzmann distribution over the rotational levels but with sharply differentiated temperatures (1600 °K and 5200 °K respectively). What has been stated applies also in the hydroxyl case. Moreover there has been observed for this molecule a case of two intensity maxima in the Q_1-branch of the 3064 Å band[5]. One of these can be interpreted as the temperature, but the other arises as a result of the dissociation of water under the action of electronic collisions with simultaneous excitation of the hydroxyl which is formed under these conditions[6]. In this reaction part of the activation energy can be converted to rotational energy and thus can disturb the temperature distribution of the molecules over rotational states.

Cristesku and Grigorovici[7] have employed the hydroxyl method using the 3064 Å band in a study of a jet discharge at atmospheric pressure (62.5 and 84.5 mc). At various points of the column of the discharge a Boltzmann distribution of the molecules over rotational states was observed with temperatures ranging from 3600 °K to 4180 °K which the authors interpreted as the temperature of the neutral gas. However, substantial doubts as to

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[1] A. D. Sakharov, Izv. Akad. Nauk SSSR, Ser. Fiz. 12, 229 (1948).

[2] W. Wijk, Z. Physik 59, 313 (1930).

[3] O. S. Duffendack and Kuang Tseng Chao, Phys. Rev. 56, 176 (1939)

[4] T. Hori, Proc. Phys. Math. Soc. Japan 25, 595 (1943).

[5] E. Lyman, Phys. Rev. 53, 379 (1938).

[6] V. H. Kondrat'ev, *Free Hydroxyl*, State Inst. Tech. (1939).

[7] G. Critesku and R. Grigorovici, Bul. Soc. Roum. Phys. 42, 78 (1941).

the validity of these results have been raised in the work of Mochalov, Nikiforov and Bogonostsev[8], and up to the present time the temperature of the column of a jet discharge has remained an open question. An attempt to verify the hydroxyl method by a comparison with the spectral-line reversal method undertaken in reference 7 is not conclusive, since the reversal method is valid only under isothermal conditions, and these cannot possibly be assumed to apply in the column of a jet discharge (Saha calculations for a discharge in air are too crude because of the arbitrary choice of the effective ionization potential).

Attempts to verify the applicability of the hydroxyl method in other types of discharges have also been unsuccessful. In an investigation of the arc between copper electrodes at atmospheric pressure in air, Mikhalevskii and Prokof' eva[9] compared the temperature obtained by the hydroxyl method with the temperature determined from the intensity of iron lines. As stated above, however, in non-isothermal situations one can only discuss the excitation temperature of the iron lines in question.

Considerable interest attaches to the spectroscopic investigation of a jet discharge at reduced pressures because in this case conditions are realized which make feasible the verification of thehydroxyl method; namely, the appearance of bands due to stable molecules which are suitable for temperature measurements.

EXPERIMENT AND DISCUSSION

The experimental arrangement is essentially the same as that in reference 10. The operating frequency of the oscillator was 32-33 mc. The discharge tube and the electrodes were oil-cooled; this provided the possibility of prolonged photography under stable temperature conditions of the spectrum of the jet discharge. With the exception of the last two copper lines at rather high discharge powers, lines due to the metals in the electrode were not present in the discharge spectrum.

An ISP-22 spectroscope having a three-lens system for slit illumination was used. The slit width was 0.015 mm and the height of the intermediate-image diaphragm was 2 mm. With this choice of diaphragm the exposure was never greater than 2-3 hours. The mercury lines at 3132 Å and 3342 Å, which lie close to the portion of the discharge spectrum being studied, were used as intensity reference marks.

At atmospheric pressure the most intense band in the spectrum of the jet discharge in air is the 3064 Å band. With a reduction in pressure, starting at approximately 400 mm Hg the 2nd positive nitrogen system becomes quite strong (Fig. 2). The most suitable for the temperature determination is the (0,0) band at 3371 Å. The 3064 Å hydroxyl band partly overlaps the 2nd positive system (2,0) but the lines which are not overlapped remain sufficiently clear to permit a simultaneous temperature determination with the hydroxyl.

Assuming that at temperatures ranging from 2000 °K to 3500 °K the intensity of the lines of the Q_1-branch falls off rapidly with an increase in K, the most suitable branch for the temperature measurements is the P_1-branch, and this was used for the principal measurements. Lines for K equal to 4, 5, 8, 14, 16, 17, 18, and 19 were used. Separate measurements using the Q_1-branch yielded values which did not differ from the values measured using the P_1-branch by more than 1-2% which is within the limits of accuracy of this method. In those cases for which the intensity of the bands was not great enough, certain other lines of the 3064 Å band were used. The value of the intensity factor for the 3064 Å band was taken from references 6, 9. Missing values were calculated according to Earls[11]*.

In making the measurements with the 3371 Å nitrogen band, following Cristesku and Grigorovici, we used the value of i associated with the $^1\Pi - {}^1\Pi$ transition because in working with the ISP – 22 with $j > 28$ the branches $P_{1,2,3}$ of the $^3\Pi - {}^3\Pi$ transition run together and practically form one branch of the $^1\Pi - {}^1\Pi$ transition.

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* We may note that the use of the Hill-Van Vleck limit formulas, particularly by Cristesku and Grigorovici, leads to a temperature which is somewhat high (200 ° for a measured temperature of 4000°K and 50° for 2000 °K). In the work of Cristesku and Grigorovici this error was accidentally compensated by another: That due to the neglect of the ν^4 factor, which in the case of the P_1-branch leads a value which is too low by 250° for a measured temperature of 4000 °K and 65 ° for 2000 °K.

[8] K. N. Mochalov, A. Ia. Nikiforov and A. S. Bogonostsev, J. Exper. Theoret. Phys. USSR **20**, 474 (1950).

[9] V. D. Mikhalevskii and V. V. Prokof'eva, J. Exper. Theoret. Phys. USSR **20**, 7 (1950).

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[11] L. T. Earls, Phys. Rev. **48**, 423 (1935).

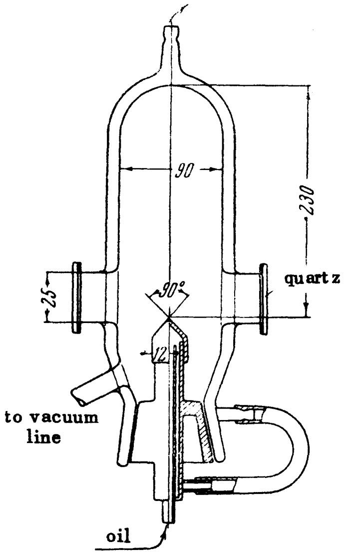

FIG. 1. Diagram of the apparatus (dimensions in mm)

After substitution of the calculated values of the constants, Eq. (1) assumes the form:
for the 3064 Å band

$$0.00945 \lg \frac{I}{i\nu^4} = C - \frac{K(K+1)}{T} \tag{2}$$

for the 3371 Å band

$$0.89 \cdot \lg \frac{i}{i\nu^4} = C - \frac{J(J+1)}{T} \tag{3}$$

(J is the value of the total angular momentum including the electron spins, and K is the value exclusive of the electronic spin).

In Fig. 3 are shown plots of Eqs. (2) and (3) for the column of the jet discharge. Also shown are cases in which lines of the four branches ($P_{1,2}Q_{1,2}$) of the 3064 Å band were used.

We now consider the effect of self-absorption. Self-absorption, as is well known, is most important for the strongest lines of the band and this leads to a characteristic departure of the points from the line $\frac{I}{i\nu^4} = C + \frac{B}{kT} J(J+1)$ for the central portion[12]. In the present case this departure was not observed. Because of the freedom from self-absorption it is possible to reduce the estimate of the optical thickness $\tau = k_0 l$ for the strongest lines of the bands in question. The estimate was made on the basis of a pressure of 200 mm Hg and a temperature of 3000 °K. At this temperature the most intense lines are those of the P_1 - branch of the 3064 Å band with $K = 7$ and the P - branch of the 3371 Å band with $J = 25$. Under these conditions the concentration of water molecules is $\sim 10^{16}\text{cm}^{-3}$ and the degree of thermal dissociation of the water is $\sim 10^{-1} - 10^{-2}$. Then the population of the level characterized by $K = 7$, $N_7 = 0.8 \times 10^{-2}$ is $N_{OH} \sim 8 \times 10^{13}\text{cm}^{-3}$. According to Kondrat'ev, k_0/N may be taken as $6.85 \times 10^{-16}\text{cm}^{-1}$ (for 300 °K). Coverting to $T = 3000\,°\text{K}$ ($k_0/N \sim 1/\sqrt{T}$) gives $k_0/N \sim 2 \times 10^{-16}\text{cm}^{-1}$. From these data we find in any case that τ is less than 1.6×10^{-2} since l is less than 1 cm.

In nitrogen it is necessary to take account of the fact that the lower level of the $C^3\Pi_u - C^3\Pi_g$ has an excitation potential of 7.5 ev, whence it follows that the equilibrium concentration of nitrogen molecules in the $C^3\Pi_g$ state is approximately $5 \times 10^5\text{cm}^{-3}, N_{25} = 27 \times 10^{-2} N_{C^3\Pi_g}$. The lifetime of the upper state is $\sim 10^{-8}$ sec and the Doppler width of the line is ~ 0.015 Å, thus $k_0/N \sim 10^{-12}\text{cm}^{-1}$ and $\tau < 10^{-8}$ so that for $\tau \sim 1$ concentrations of nitrogen in the $C^3\Pi_g$ state exceeding equilibrium by a factor of 10^8 would be required and this is not very probable.

In the table are shown the results of measurements of the temperature at various pressures for those cases in which it was possible to carry out simultaneous measurements with nitrogen (T_{N_2}) and the hydroxyl (T_{OH}).

In view of the fact that the shape of the jet discharge varies markedly with changes in the power and the pressure, for definiteness all measurements were made in the part of the column close to the electrodes (point A, Fig. 4). The height of the flame h_1 (Fig. 4) was taken as a parameter with p = const.

From the present data it is apparent that for pressures above 100 mm Hg the temperatures as measured with the hydroxyl and with nitrogen are in agreement within the limits of the accuracy of the method (5%) and consequently that the temperature as measured with the hydroxyl yields the temperature of the neutral gas. At lower pressures the temperature measured by the hydroxyl method exceeds significantly the temperature of the neutral gas as determined with nitrogen. We may note that in certain pressure cases the temperature determination is not unique (Fig. 5).

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[12] W. Lochte-Holtgreven and H. Maecker, Z. Physik 105, 1 (1937).

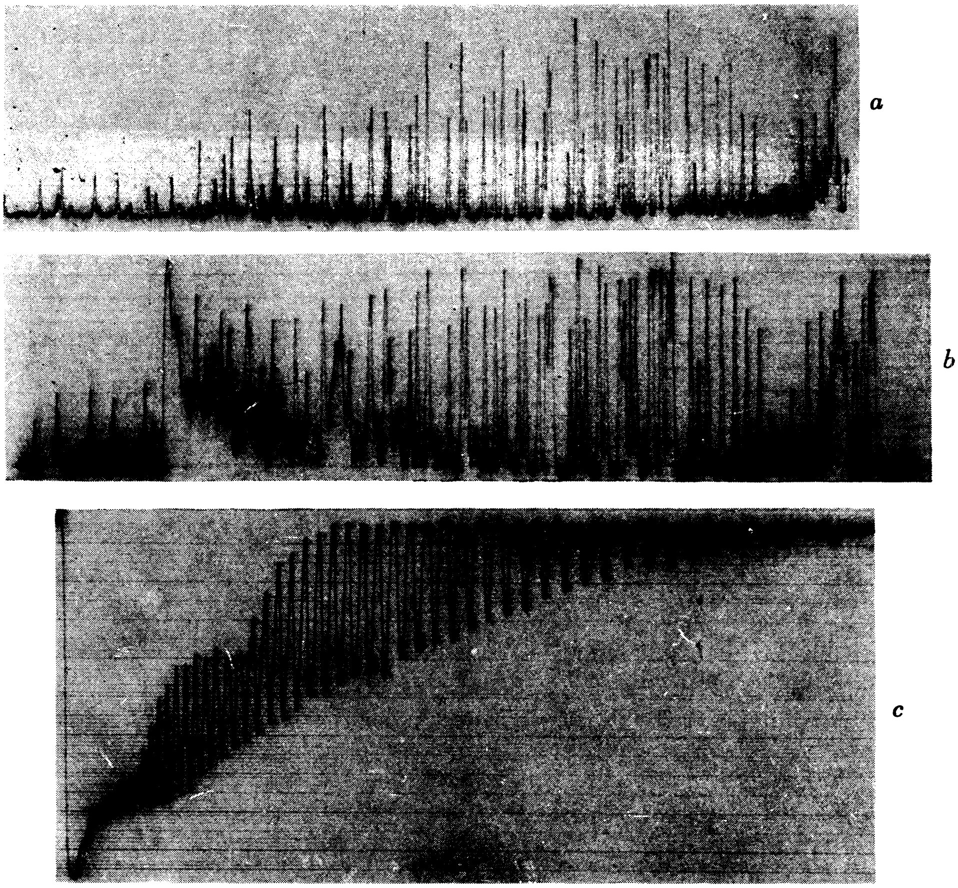

FIG. 2. Microphotograms** of the spectrum of the column of the jet discharge: *a*) 3064Å band at atmospheric pressure; *b*) 3064 Å band at 100 mm Hg overlapped by the (2,0) band of the 2nd positive system of nitrogen; *c*) 3371 Å band of the 2nd positive system of nitrogen at 150 mm Hg.

From the given data it is also apparent that for pressures less than 150 mm Hg there occurs a rapid reduction in the temperature of the discharge.

It would seem that the disagreement between the rotational temperature for the hydroxyl and for nitrogen for $p < 100$ mm Hg is a direct indication of the nonisothermal conditions in the plasma of the column of the jet discharge at these pressures. However, the agreement of these temperatures at higher pressures is still not a sufficient basis for the converse conclusion. The fact that the hydroxyl method gives the correct values of the temperature of the neutral gas in the discharge can be explained by the fact that for $p > 100$ mm Hg the temperature in the jet discharge is sufficiently high for strong thermal dissociation of water. The molecules obtained under these conditions do not have surplus rotational energy. On going over to pressures < 100 mm Hg, however, along with the reduction of the temperature of the discharge there is an increase in the strength of the hydroxyl formation process which takes place by virtue of collisions between water molecules and fast electrons with simultaneous excitation of anomalously high rotational levels.

Thus the possibility of applying the hydroxyl method under the conditions which obtain in the column of a jet discharge depends on the existence of a sufficiently high temperature, not lower than approximately 2500 °K. Experimentally this has

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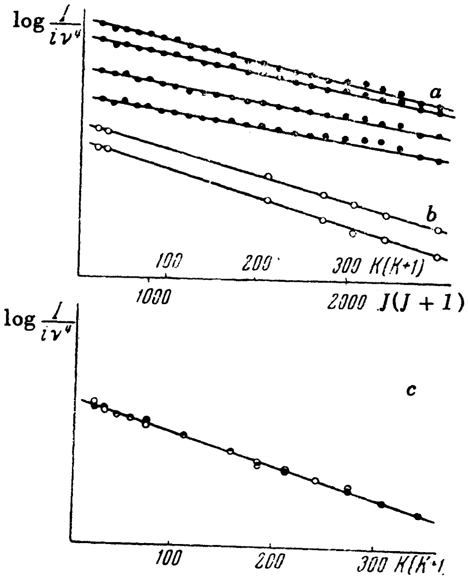

FIG. 3. *a*) *P*-branch of the 3371 Å band (100 mm); P_1 - branch of the 3064 Å band (210 mm); *c*) 3064 Å band (210 mm); ● P_1 - branch; O Q_1 - branch; ◒ Q_2-branch; ⊗ P_2 - branch.

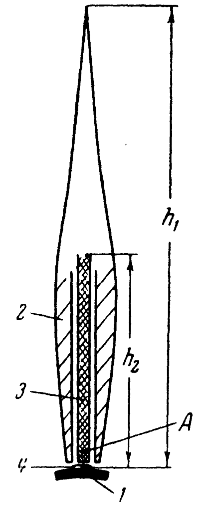

FIG. 4. Structure of the jet discharge: *1* - electrode; *2*- outer shell of the discharge; *3*- column of the discharge; *4* - electrode layer.

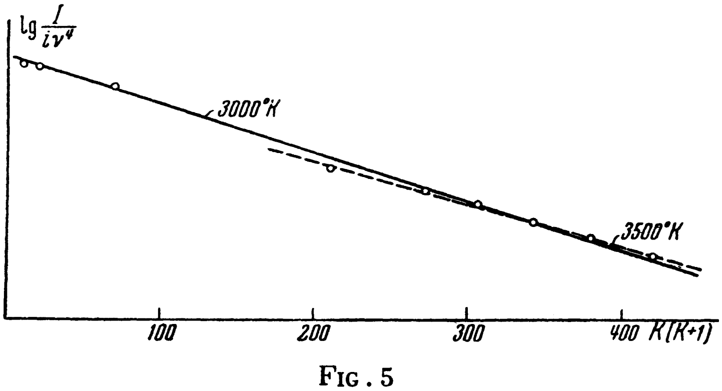

FIG. 5

been shown to hold up to a pressure of 316 mm Hg; but since there is no reason to expect that the temperature of the discharge is reduced to any significant degree upon a further increase of the pressure, these results should apply up to atmospheric pressure and beyond. Hence, the results of a temperature measurement in a jet discharge by the hydroxyl method and, in particular, those obtained by Cristesku and Grigorovici should be valid. The effect of a reduction of the temperature because of the concentration of the hydroxyl in the cooler peripheral parts of the discharge as noted by Mikhalevskii and Prokof'eva is considerably smaller in the present case presumably because of the lower source temperature; this makes it reasonable to suppose that the maximum hydroxyl concentration will be along the axis of the column of the discharge. Another basis for this conclusion is the agreement of the temperatures obtained with nitrogen and with the hydroxyl at pressures below 316 mm Hg. At

TABLE

p, mm Hg	h_1, mm	T_{OH} °K	T_{N_2} °K	$\|T_{OH} - T_{N_2}\|$
316	50	3610	3510	100
	70	3580	3620	40
	100	3640	3700	60
	150	3640	3570	70
210	50	3480	3410	70
	65	3690	3630	30
	70	3700	3520	180
	85	3570	3520	50
	180	3690	3630	60
	220	3670	3750	80
150	35	3140	3070	70
	50	3260	3250	10
	60	3220	3340	120
	80	3510	3400	110
	90	3480	3510	30
100	45	2370	2310	60
	55	2360	2670	190
	70	2820	2880	60
	85	3020	3100	20
66	40	2160	1970	190
	45	2530	1880	650
	60	2720	2100	620
	70	2980	2200	780
30	50	2300	2080	220
	70	2620	2290	330
	100	3010	2250	760

atmospheric pressure, where according to Cristesku and Grigorovici the temperature of the discharge reaches 4000 °K, this question apparently requires further study.

In conclusion we wish to take this opportunity to express our gratitude to Prof. N. A. Kaptsov for continued interest in the present work.

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