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VIBRATIONAL AND ROTATIONAL ANALYSIS OF THE EMISSION

SPECTRA OF THE ARC JET FLOW

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Applying atomic and molecular physics to the analysis of the radiation emitted from the arc jet flow provides a means for determining the species and excitation temperature of the constituents of the flow.

The object of this investigation has been a rotational and vibrational analysis of the spectra obtained from the radiation emitted in the shock layer and in the free stream of the arc jet flow, specifically, in the shock layer bands of the First Negative Group of ionized molecular nitrogen $(N_2^+ \; B\,{}^2\Sigma_u^+ \to X\,{}^2\Sigma_g^+)$ and in the free stream bands of the γ-system of nitric oxide $(NO \; A\,{}^2\Sigma_u^+ \to {}^2\Pi_{\frac{1}{2}\frac{3}{2}})$.

INTRODUCTION

The temperature of a gas containing molecules emitting radiation is reflected in the intensity distribution of a vibrational progression and in the intensity distribution of a rotational progression of the electronic transition. Hence, only the identification of the vibrational and rotational levels associated with the observed bands and their relative intensities are necessary to determine the temperature of the gas.

THEORY

The intensity of the radiation of light which accompanies the passage of a molecule from an upper state m to lower state m is determined by the Einstein transition probability for spontaneous emission between the states A_{mm} the number of molecules N_m having the upper state m populated, and the energy of the emitted radiation for the transition $hc\,\nu_{mm}$. The radiation intensity for a gas of molecules is

$$I_{em.}^{m\,m} = N_m\,h\,c\,\nu_{mm}\,A_{mm} \tag{1}$$

The spontaneous emission coefficient can be expressed in terms of the dipole moment for the transition $R^{m\,m}$ by

$$A_{mm} = \frac{64\pi^4\,\nu_{mm}^3}{3h}\,|R^{mm}|^2 \tag{2}$$

It is known that the total dipole moment for an electronic-vibrational-rotational transition in a band system can be expressed in the Born-Oppenheimer approximation by

$$R^{mm} = R_e \, R_{vib}^{v',v''} \, R_{rot}^{J'J''}$$ (3)

where R_e is the dipole moment for the electronic transition, $R_{vib}^{v',v''}$ is the dipole moment for the vibrational transition from an upper vibrational state v' to a lower state v'' and $R_{rot}^{J'J''}$ is the dipole moment for the rotational transition from an upper rotational state J' to a lower state J''.

The expression for the spontaneous emission coefficient in the Born-Oppenheimer approximation for the rotational levels of a molecular system is

$$A_{mm} = 64\pi^4 \nu_{mm}^3 \sum_{M'M''} \frac{|R_{mm}|^2}{2J'+1}$$

$$= 64\pi^4 \nu_{mm}^3 \, |R_e|^2 |R_{vib}^{v',v''}|^2 \sum_{M'M''} \frac{|R_{rot}|^2}{2J'+1}$$ (4)

where the sum over M' and M'' accounts for all the equivalent spacial orientations of J' and J'' and $2J'+1$ is the statistical weight of the rotational level J'. It will also be noted that the square of the dipole moment for a vibrational transition $|R_{rot}^{v',v''}|^2$ is usually designated by $q_{v',v''}$ and referred to as either the Franck-Condon factor or the square of the overlap integral [1,2]. The sum $\sum_{M'M''} |R_{rot}^{J'J''}|^2$ is

generally denoted by $S^{J'J''}$, the line strength, and referred to as the Höln-London factor [1,2][*].

The intensity of the emitted radiation in terms of the dipole moments for the transition is given by

$$I_{em}^{mm} = \frac{64\pi^4}{3} c N_m \nu_{mm}^4 |R_e|^2 |R_{vib}^{mm}|^2 \sum_{M'M''}^{'} |R_{rot}^{J'J''}|^2 / 2J'+1 \qquad (5)$$
$$= \frac{64\pi^4}{3} c N_m \nu_{mm}^4 |R_e|^2 q_{v'v''} \frac{S^{J'J''}}{2J'+1}$$

If the summation is limited to the transition probabilities over , ie a single electronic-vibrational band, one obtains

$$I_{em}^{mm} = \frac{64\pi^4}{3} c N_m \nu_{mm}^4 |R_e|^2 q_{v'v''} \qquad (6)$$

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[*]Summation Rules

The sum of the line strength of all transitions from or to a given rotational level is equal to the statistical weight.

The sum of the squares of the overlap integrals summed over all values of the supper or of the lower state is equal to one.

Calling band strength the emission intensity divided by ν^4, it follows from the vibration sum rule that the sum of the band strengths of all bands with the same upper vibrational state are proportional to the number of molecules in the upper state, ie

$$\sum_{\nu''} \frac{I_{em}^{\nu'\nu''}}{\nu^4} \sim N_{\nu'}$$

(7)

One can readily see that the above derivation is valid only if the electronic transition dipole moment R_e is a constant for all vibrational transitions having band strengths that give an appreciable contribution to the sum. For molecular systems satisfying this condition the sum rule may be used to determine the temperature of the gas emitting the band system. In thermal equilibrium the population $N_{\nu'}$ of the initial state is proportional to $e^{-\frac{G(\nu')hc}{kT}}$. We obtain from (7)

or

$$\sum_{\nu''} \frac{I_{em}^{\nu'\nu''}}{\nu^4} \sim e^{-\frac{G(\nu')hc}{kT}}$$

(8)

$$\ln\left(\sum_{\nu''} \frac{I_{em}^{\nu'\nu''}}{\nu^4}\right) = C - G(\nu')hc/kT$$

Therefore by plotting the logarithms of the sum of the band strengths against the vibrational term values a straight line is obtained whose slope is $\frac{hc}{kT}$. However, if the intensities of sufficient number of bands cannot be measured a determination of the vibrational temperature can be obtained if the Franck-Condon factors have been calculated for the measured bands. Dividing the band strength of each band by its Franck-Condon factor gives again a quantity that is

proportional to the number of molecules in the initial state and may be plotted in the same way as the above.

The intensity of the lines in the rotational branch of an electronic-vibration band is given by

$$I_{em}^{J'J''} = N_{J'} \, \nu^4 \, \frac{S^{J'J''}}{2J'+1} \tag{9}$$

one can readily see from (5) that the above expression is valid only if the electronic-vibration dipole moment is constant for all the rotational transitions that give an appreciable contribution to the branch.

In thermal equilibrium the population $N_{J'}$ of the initial state is proportional to $(2J'+1) \, e^{-F(J') hc/kT}$. We obtain from (9)

$$\frac{I_{em}^{J'J''}}{\nu^4 S^{J'J''}} \sim e^{-F(J') hc/kT} \tag{10}$$

Please note that by assuming ν to be constant over the entire branch an error of less than one percent is introduced and the above expression reduces to

or
$$\frac{I_{em}^{J'J''}}{S^{J'J''}} \sim e^{-F(J') hc/kT}$$

$$\ln\left(\frac{I_{em}^{J'J''}}{S^{J'J''}} \right) = C - F(J') \frac{hc}{kT} \tag{11}$$

In the special case of $^1\Sigma \to {}^1\Sigma$ transitions for which there is only a P and R branch the intensity relations for emission are given by

$$I_{em} \sim (J'+J''+1)\, e^{-B'J'(J'+1)\frac{hc}{kT}}$$

or   (12)

$$\ln\left(\frac{I_{em}}{J'+J''+1}\right) = C - B'J(J'+1)\frac{hc}{kT}$$

(13)

Therefore, by plotting $\ln\left(\frac{I_{em}}{J'+J''+1}\right)$ against $J'(J'+1)$ a straight line is obtained whose slope is $-\frac{B'hc}{kT}$. Thus if the line intensities have been measured and the rotational constant is known the temperature of the gas may be determined.

DISCUSSION AND RESULTS

From the spectra obtained in the shock layer of the arc jet flow, the R branch of the (0,1) band of the First Negative Group of ionized molecular nitrogen N_2^+ $B^2\Sigma_u^+ \to X^2\Sigma_g^+$ has been selected for the determination of an effective rotational temperature. Although both the upper and lower states are doublets, the doublets are not resolved in the R branch of either the (0,0) or (0,1) band, figure 1. Therefore the tempterature can be determined using the special case $^1\Sigma \to {}^1\Sigma$ given by equation (13) using the K values for the rotational band assignments rather than the J values. Please note that if rotational branchs of bands other than (0,0) or (0,1) are selected for the determination of

the temperature the doublet character of the spectra may be resolved and equation 13 is no longer valid for temperature determinations, figure 2.

In figure 1, note the alternation of the intensity between even K, labeled, and odd K. This alternation of intensity is due to the nuclear spin of the nitrogen nuclei which will result in twice as many molecules with even spin as with odd resulting in the observed intensity alternation in the ratio 2:1. For a temperature determination one may either use the even K intensities or the odd K intensities but not a mixture.

For the R branch of the (0,1) band values of Te = 25461.46, We = 2419.84, wexe = 23.189 and weye = -0.537 for the electronic and vibrational terms of the $B^2\Sigma_u^+$

state; and Te = 0, we = 2207.00, wexe = 16.1, and $\omega_e y_e$ = -0.04 for the electronic and vibrational terms of the $X^2\Sigma_g^+$ state were obtained from Huber and Herzberg (4).

The rotational values were obtained from the data reported by K. A. Dick, et al (5) using the combination relations,

and
$$R(J-1) - P(J+1) = (4B_v'' - 6D_v'')(J+\tfrac{1}{2}) - 8D_v''(J+\tfrac{1}{2})^3$$
$$R(J) - P(J) = (4B_v' - 6D_v')(J+\tfrac{1}{2}) - 8D_v'(J+\tfrac{1}{2})^3$$

between the lines of the P and R branch for the evaluation of rotational constants for bands without a Q branch. For the (0,1) band values of

$B_{v'}' = 2.0751$, $D_{v'}' = 6.54 \times 10^{-6}$, $B_{v'}'' = 1.9031$, and $D_{v'}'' = 5.8 \times 10^{-6}$ were obtained. The energy in cm^{-1} for the R branch of the (0,0) and (0,1) bands of the $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ transition of N_2^+ can be fit to the measured values of Dick, etal (5) to within $1\,cm^{-1}$ using

$$\nu_R = 25,570.21 + 4.301\,K + 0.1512\,K^2$$

for the (0,0) band and

$$\nu_R = 23,395.64 + 4.296\,K + 0.1718\,K^2$$

for the (0,1) band.

In table 1 values used for the determrination of the rotational temperature in the shock layer of the arc jet flow are given. The relative intensity of the lines are given in arbitrary units and were obtained from densitometer tracings of plate #14 using the Joyce-Lobel Microdensitometer in the Spectroscopy Laboratory of the Department of Physics at Texas Christian University, Fort Worth, Texas.

Table I

K'	K''	I	$I/(K'+K''+1)$	$\ln\left(\frac{I}{K'+K''+1}\right)$	$K'(K'+1)$
1	0	193	96.5	4.57	2
3	2	224	37.3	3.62	12
5	4	267	26.7	3.28	30
7	6	292	20.9	3.04	56
9	8	309	17.2	2.84	90
11	10	309	14.1	2.65	132
13	12	261	10.0	2.30	182
15	14	295	9.83	2.29	240
19	18	300	7.90	2.07	380
21	20	290	6.90	1.93	462
23	22	296	6.43	1.86	552
2	1	121	30.3	3.41	6
4	3	206	25.8	3.25	20
6	5	192	16.0	2.77	42
8	7	237	14.8	2.69	72
10	9	224	11.2	2.42	110
12	11	245	10.2	2.32	156
14	13	208	7.43	2.01	210
20	19	271	6.78	1.91	420
22	21	255	5.80	1.76	506
24	23	237	4.94	1.60	600

A graph of $\ln\left(\frac{I}{K'+K''+1}\right)$ vs $K'(K'+1)$ from values given in table 1 for even K'' and for odd K'' is shown in figure 3. Note, that for both even and odd K'' the points for the lower values of K'' are found to be above the line obtained for the higher values of K''. From the energy terms of the P and R branches

$$\nu_P = \nu_{01} - (B_{v'}+B_{v''})K + (B_{v'}-B_{v''})K^2$$

and

$$\nu_R = \nu_{01} + 2B_{v'} + (3B_{v'}-B_{v''})K + (B_{v'}-B_{v''})K^2$$

it is seen that at large K the K^2 term is dominant. This will place members of the P branch having high K values in the region of the R

branch of low K values. Thus the observed intensity in the R branch for low K values is both P and R. This will not present any problems in the determination of the temperature since at lower temperature the intensity of the P branch will decrease for high K values and the intensity observed in the R branch at low K values will be due to R only.

The slope of the line was found to be -0.00148 for even K and . -0.00165 for odd K. Using the value B_v' = 2.0751 a temperature of 2020 $^{\circ}$K was obtained for even K and 1810 $^{\circ}$K for odd K.

CONCLUSIONS

The reults presented above indicate that the temperature of the arc jet flow can be determined from the measurements and conditions presented. I regret that the time was not sufficient for the determination of the temperature in the free stream of the arc jet flow from the vibrational analysis of the system of NO. However, the partial analysis has indicated that the intensities of bands having wavelengths less than 2600 are antenuated. Also, bands are observed in the second order that are not observed in the first order. The blaze of the grating is suspect indicating a blaze for wavelengths much greater than the region of interest. Also, results on the system of NO- by N. E. Kuz' menko, etal (6) report a dependence of the electrnoic dipole moment on the vibrations of the molecule. Values for the

electronic dipole moment for each of the bands observed in the free can be obtained from this article and with the Frank-Condon factor for each band the temperature can be obtained.

ACKNOWLEDGEMENTS

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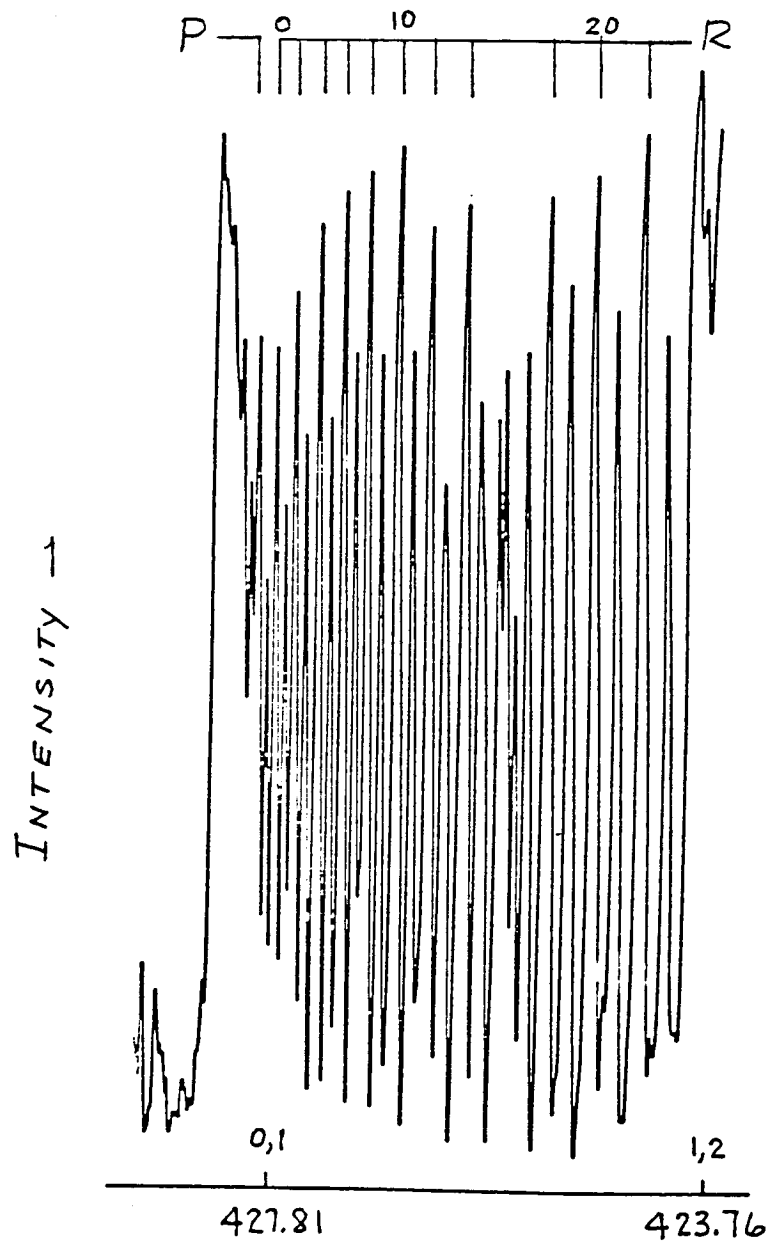
Figure 1.   Densitometer tracing of the (0,1) band in the γ system of NO with even values of K for the R branch indicated.
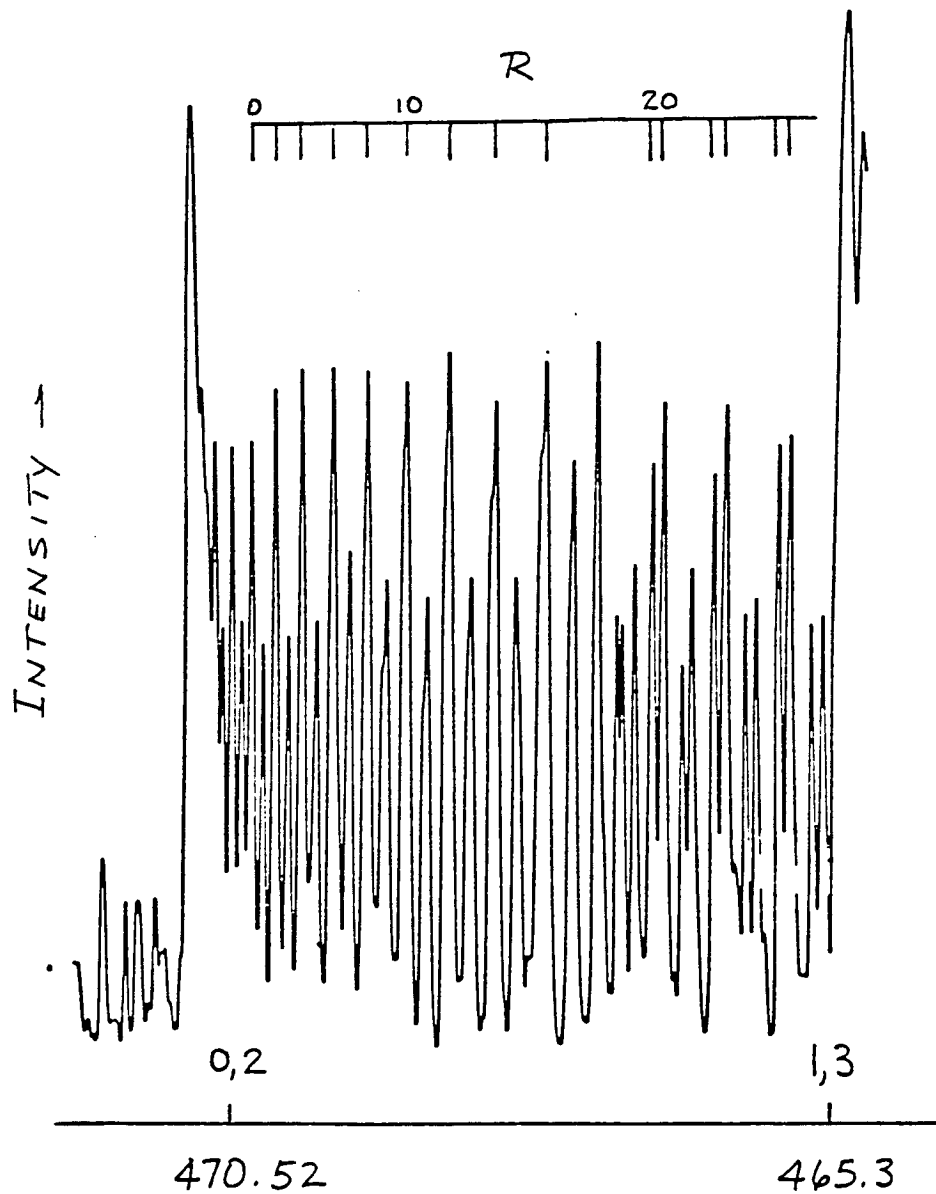
Figure 2. Densitometer tracing of the (0,2) band of
the γ system of NO with even values of
K for the R branch indicated and the
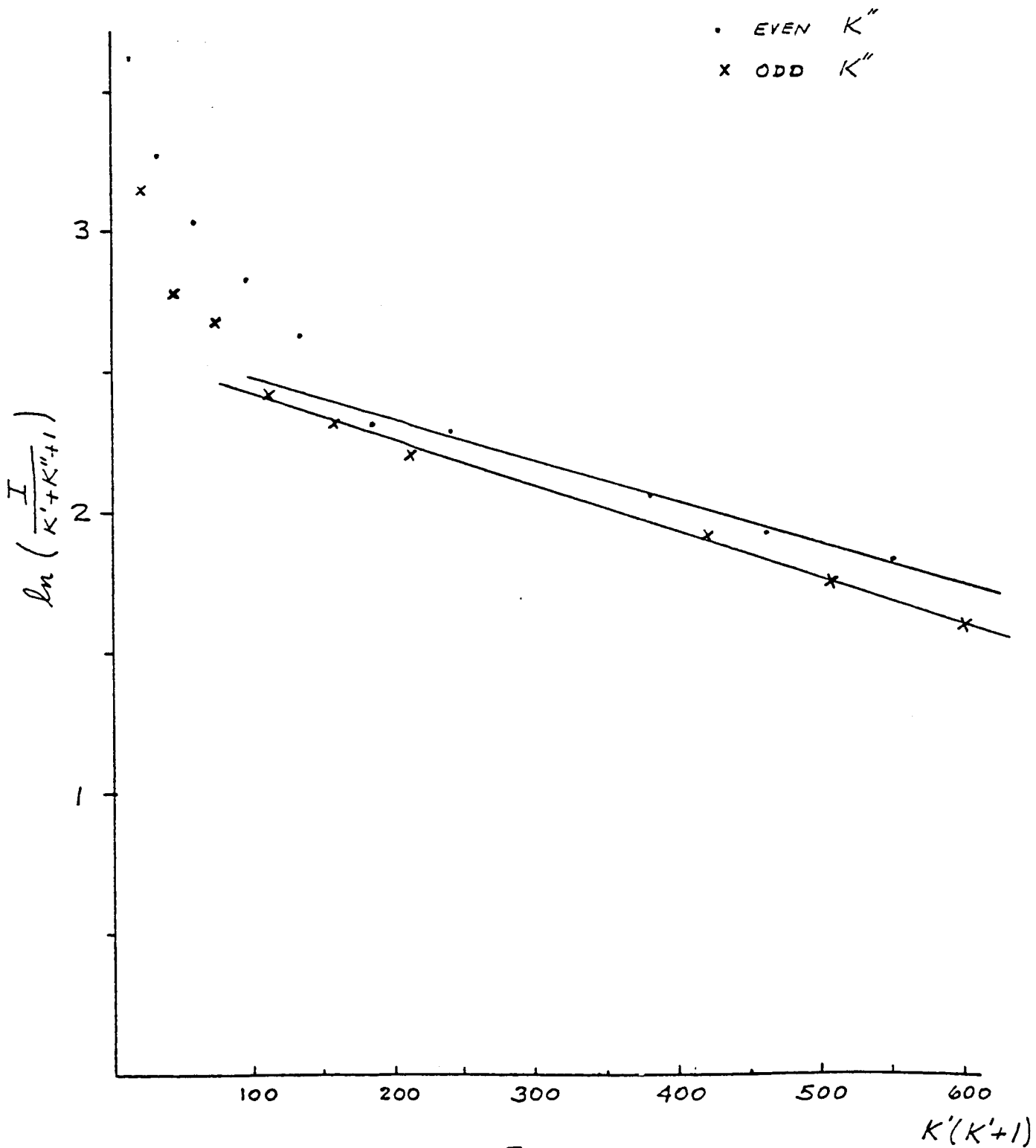doublet structure for large values of K
resolved.

Figure 3. Plot of the $ln\left(\frac{I}{K'+K''+1}\right)$ vs $K'(K'+1)$ for even and odd K of the R branch of the (0,1) band.