Application of Smith's Model to Rotational Temperature Measurements in Nitrogen

JEAN-CLAUDE LENGRAND* AND MICHEL CLOUPEAU†
Laboratoire d'Aérothermique du Centre National de la Recherche Scientifique, Meudon, France

Improvements are brought to Smith's method for determining rotational temperature in low density nitrogen using the electron beam technique. All constants to be taken into account in the model are calculated numerically. The parameter which characterizes the relative contribution of secondary electrons to luminescence is deduced from an empirical expression based on previous experimental work. All information is given for a practical use of the method. Its precision is estimated to 5% in the density and temperature range investigated.

Nomenclature

H = probability of a quadrupole interaction to occur
$I_{K'}$ = intensity of the K' line of the R-branch
K = rotational quantum number
L = ratio of respective contributions of secondary and primary electrons to luminescence
m = mass of electrons
n = gas number density
N_K = population of K level
N_s, N_p = number density of secondary and primary electrons, respectively
P = probability of transition
Q = cross section
R = ratio of respective intensities of (0–2)2P band and (0–0)1N band
T = temperature
$\langle K|X^{\Delta K}|K'\rangle$ = matrix element
$Y_{K'K}$ = normalized matrix element
ε = energy of electrons

Subscripts and Superscripts

n = electronic state
v = vibrational level
K = rotational level
m = measured
r = rotational
s = secondary electrons
p = primary electrons
1 = (0–0)1N band
2 = (0–2)2P band
$'$ = excited state
$''$ = final state

Introduction

THE electron beam probe has been used by numerous experimenters for measuring local rotational temperature T_r in low density nitrogen flows. The early method proposed by Muntz[1] allows T_r to be calculated from the relative intensities of rotational lines of the emitted light, assuming that electron beam excitation obeys the dipole selection rule. Using Muntz' model, Ashkenas[2] clearly showed that the ratio T_m/T_r of the measured to the real rotational temperatures essentially depends on number density n, on temperature T, and on the number of lines used in the calculation. Other experiments[3-5] lead to the same conclusion. Different authors, then, improved Muntz' theory with either empirical corrections to measured temperature[2-5] or generalizations of the initial model.[6,7]

The model proposed by Smith[7] appears to be one of the most complete. It tries to correct errors due to the influence of secondary electrons; however, it has rarely been used because of some practical difficulties. The present paper attempts to solve those difficulties.

Smith's Model

Smith assumes that secondary electrons may cause transitions which do not obey the dipole selection rule. During a collision, the rotational quantum number may vary by $\Delta K = |K'-K| = 1, 3, 5\ldots$, instead of varying exclusively by 1 as in Muntz' model. Intuitive considerations lead to express the probability of a $K \rightarrow K'$ transition as

$$^{K}P^{K'} \sim H^{(\Delta K-1)/2}\langle K|X^{\Delta K}|K'\rangle \tag{1}$$

where H is the probability of a quadrupole interaction to occur during a collision. The following equation is derived from Eqs. (10–12, 19) of Ref. 7:

$$I_{K'} = [K'/(2K'+1)] \sum_{K=0}^{\infty} {}^{K}\bar{P}^{K'} N_K \tag{2}$$

where

$$^{K}\bar{P}^{K'} = \frac{\langle K|X^{\Delta K}|K'\rangle \displaystyle\int_{18.7}^{\infty} {}^{nv}Q^{n'v'}(\varepsilon)\left(\frac{2\varepsilon}{m}\right)^{1/2}\left[N_s\left(\frac{1}{\varepsilon}\right)^n + N_p\,\delta(\varepsilon-\varepsilon_p)\right]\frac{\exp[-(\Delta K-1)(\varepsilon-18.7)/100]}{\sum_{\Delta K}\exp[-(\Delta K-1)(\varepsilon-18.7)/100]}\,d\varepsilon}{\displaystyle\int_{18.7}^{\infty} {}^{nv}Q^{n'v'}(\varepsilon)\left(\frac{2\varepsilon}{m}\right)^{1/2}\left[N_s\left(\frac{1}{\varepsilon}\right)^n + N_p\,\delta(\varepsilon-\varepsilon_p)\right]d\varepsilon} \tag{3}$$

where δ is the Dirac-function; N_K is the population of rotational level K; $I_K{}'$ is the intensity of line $K' \rightarrow K'-1$; $^{nv}Q^{n'v'}(\varepsilon)$ is the absolute cross section for excitation from electronic state n and vibrational level v to n' and v', respectively [all molecules are assumed to be initially in the state (n, v)]; ε is the energy of electrons; and N_s and N_p, respectively are the number density of secondary and primary electrons.

Now, our application of preceding equations will be somewhat different to Smith's original one.

A question arises about the factor $\langle K|X^{\Delta K}|K'\rangle$. In Ref. 7, the normalization introduced by Eq. (16) does not appear in Eq. (19). It seems that $^{K}P^{K'}$ must be normalized using following equations:

$$^{K}P^{K+\Delta K} + {}^{K}P^{K-\Delta K} \left| \begin{array}{ll} = H^{(\Delta K-1)/2} & \text{if } \Delta K \text{ odd} \\ = 0 & \text{if } \Delta K \text{ even} \end{array} \right.$$

and

$$\sum_{K'=0}^{\infty} {}^{K}P^{K'} = 1$$

Received April 2, 1973; revision received September 11, 1973.
Index category: Rarefied Flows.

* Attaché de Recherche.

† Directeur de Recherche.

Hence

$$ {}^{K}p^{K'} = Y_{K'K} \cdot H^{(\Delta K-1)/2} \Big/ \left(\sum_{\Delta K} H^{(\Delta K-1)/2} \right) \tag{4} $$

where

$$ \begin{aligned} Y_{KK'} &= \langle K|X^{\Delta K}|K'\rangle / [\langle K|X^{\Delta K}|K+\Delta K\rangle + \\ &\qquad \langle K|X^{\Delta K}|K-\Delta K\rangle] \quad \text{if } \Delta K \text{ odd} \\ &= 0 \quad \text{if } \Delta K \text{ even} \end{aligned} $$

Equation (3) becomes valid when $\langle K|X^{\Delta K}|K'\rangle$ is replaced by $Y_{K'K}$.

The following equations are easily deduced from Eq. (14) of Ref. 7 after correction of a typographical error in that equation:

$$ \left. \begin{aligned} \langle K|X^{\Delta K}|K+\Delta K\rangle &= \prod_{i=0}^{\Delta K-1} (K+1+i)/[2(K+i)+1] \\ \langle K|X^{\Delta K}|K-\Delta K\rangle &= \prod_{i=0}^{\Delta K-1} (K-i)/[2(K-i)+1] \end{aligned} \right\} \tag{5} $$

$$ H(\varepsilon) = \exp[-2(\varepsilon-18.7)/100] \tag{6} $$

Notice that for primary electrons, ε is large and $H(\varepsilon_p)$ is practically equal to zero. Numerical values of $Y_{K'K}$ are given in Ref. 8.

Let $Q_1(\varepsilon)$ be the cross section for excitation of the $(n'v'-n''v'')$ band, from the state (n, v). Then

$$ Q_1(\varepsilon) = {}^{nv}Q^{n'v'}(\varepsilon)^{n'v'}p^{n''v''} \tag{7} $$

where the probability of de-excitation ${}^{n'v'}p^{n''v''}$ is constant for a given band. Therefore ${}^{nv}Q^{n'v'}(\varepsilon)$ may be replaced by $Q_1(\varepsilon)$ in Eq. (3). The vibrational band generally used for rotational temperature measurements in Nitrogen is the first negative (0–0) band. Its cross section may serve as Q_1. We only need relative cross sections for Eq. (3). However, in the next section, we shall have to compare the intensities of the preceding band [(0–0)1N] with that of the second positive (0–2) band [(0–2)2P], the cross section of which is denoted as Q_2. This requires absolute cross sections Q_1 and Q_2. Smith[7] determines Q_1 from a straight line fit to the results of Ref. 9. That approximation is only valid near the threshold and is thought to be in error in the present case because the integrals in Eq. (3) do not converge rapidly (especially for $\Delta K = 1$). For low energy electrons, the results of McConkey, Woolsey, and Burns[10] for Q_1 and the results of Burns, Simpson, and McConkey[11] for Q_2 were used. For high energy electrons, the following asymptotic expressions were used (see Ref. 8 for justification):

$$ \left. \begin{aligned} Q_1(\varepsilon) &= 1585\,\varepsilon^{-1} \log(\varepsilon/22) \\ Q_2(\varepsilon) &= 25\,\varepsilon^{-1} \end{aligned} \right\} \tag{8} $$

the units of ε and Q are respectively 1 ev and 10^{-18} cm^2.

In Eq. (3) the factor $N_s(1/\varepsilon)^n + N_p\delta(\varepsilon-\varepsilon_p)$ is the energy distribution function $f(\varepsilon)$ of electrons; the terms concern, respectively, secondary and primary electrons. We used a slightly different expression, consistent with the experimental data of Ishino quoted by Muntz[12]

$$ f(\varepsilon) = 0.937\,N_s\varepsilon^{-1.75} + N_p\delta(\varepsilon-\varepsilon_p) \tag{9} $$

Equation (2) can now be rewritten

$$ I_{K'} = \sum_{K=0}^{\infty} P_{K'K} N_K $$

where

$$ P_{K'K} = [K'/(2K'+1)] \cdot Y_{K'K} \cdot [LC_{\Delta K}+M]/[L+1] $$

$$ M = 0 \quad \text{if} \quad \Delta K \neq 1 \quad \text{and} \quad M = 1 \quad \text{if} \quad \Delta K = 1 $$

$$ L = N_s A_1/N_p A_{1p}, \quad \text{with} \quad A_1 = 0.937 \int_{18.7}^{\infty} Q_1(\varepsilon) \cdot \varepsilon^{-1.25}\, d\varepsilon $$

$$ \text{and} \quad A_{1p} = Q_1(\varepsilon_p)(\varepsilon_p)^{1/2} $$

$$ C_{\Delta K} = \frac{\displaystyle\int_{18.7}^{\infty} Q_1(\varepsilon)\varepsilon^{-1.25} \exp[(18.7-\varepsilon)(\Delta K-1)/100] \times [1-\exp[\![(18.7-\varepsilon)/50]\!]]\, d\varepsilon}{\displaystyle\int_{18.7}^{\infty} Q_1(\varepsilon)\varepsilon^{-1.25}\, d\varepsilon} \tag{10} $$

Table 1 Numerical values of $C_{\Delta K}$ and A_1

A_1	C_1	C_3	C_5	C_7	C_9	C_{11}	C_{13}
12.63	0.7595	0.1086	0.0453	0.0242	0.0146	0.0096	0.0067
C_{15}	C_{17}	C_{19}	C_{21}	C_{23}	C_{25}	C_{27}	C_{29}
0.0048	0.0036	0.0028	0.0022	0.0018	0.0014	0.0012	0.0010

L is recognized as the ratio of respective contributions of secondary and primary electrons to luminescence. If $L = 0$, $P_{K'K} = 0$, except for $\Delta K = 1$, and Smith's model reduces to Muntz'. Numerical values of $C_{\Delta K}$ and A_1 are given in Table 1. $C_{\Delta K}$ is dimensionless and the dimension of A_1 is determined by the same units of ε and Q_1, as above mentioned.

The method first proposed by Smith consists in solving the set of Eqs. (10) and determining T_r from the values of N_K assuming a Boltzmann repartition. The number of lines available is necessarily limited and the intensity of unknown lines is set equal to zero. In most cases, the number of lines is not large enough, and a non-negligible error is introduced into the values of N_K and T_r. Our procedure was different. As suggested by Lewy,[13] whatever the theoretical model for excitation may be, the repartition of molecules among the rotational levels of the excited state is not far from the initial one and the rate of excitation for a given K' level may be written, just as in Muntz' theory

$$ R^{K'} \sim (2K'+1)\exp[-K'(K'+1)\theta/T_r]G(K', T_r) \tag{11} $$

where G is a "correction factor" not very different from unity. Hence

$$ I_{K'} \sim K'G(K', T_r)\exp[-K'(K'+1)\theta/T_r] \tag{12} $$

Applying this to Smith's model gives an expression for G deduced from Eqs. (10) and (12)

$$ G(K', T_r) = \sum_{K=0}^{\infty} Y_{K'K} \cdot \frac{L \cdot C_{\Delta K} + \big|_0^1}{L+1} \cdot \frac{2K+1}{2K'+1} \cdot \frac{\exp[-K(K+1)\theta/T_r]}{\exp[-K'(K'+1)\theta/T_r]} \tag{13} $$

Then, the determination of T_r exactly follows Muntz' iterative procedure: guessing a first value of T_r and plotting $\log(I_{K'}/K'G)$ against $[-K'(K'+1)\theta]$, after correction of the 2:1 alternance for odd and even lines, gives approximately a straight line, the slope of which is $1/T_r$. The calculation is repeated with the new value of T_r. A few iterations are generally sufficient to give the definitive result.

Now, the remaining parameter is L. If we can estimate it, T_r can be obtained from Eqs. (12) and (13).

Determination of L

Smith[7] estimates a parameter D, which plays a role similar to our L, from the intensity ratio R of the second positive system (0–2) band to the first negative system (0–0) band. Instead of measuring R in each point, as Smith does, one can use a result of Maguire[14] giving R as a function of the gas number density n. We propose a relation between R and L. The second positive system is due to transitions from the $N_2C^3\Pi_u$ state. Assuming direct excitation from the ground state and absence of non-radiative de-excitations, we get

$$ R = \left[\int_0^{\infty} Q_2(\varepsilon)f(\varepsilon)\left(\frac{2\varepsilon}{m}\right)^{1/2} d\varepsilon\right] \Big/ \left[\int_0^{\infty} Q_1(\varepsilon)f(\varepsilon)\left(\frac{2\varepsilon}{m}\right)^{1/2} d\varepsilon\right] = (N_sA_2+N_pA_{2p})/(N_sA_1+N_pA_{1p}) \tag{14} $$

Hence

$$ L = N_sA_1/N_pA_{1p} = (A_{2p}/A_{1p}-R)/(R-A_2/A_1) \tag{15} $$

where A_2 and A_{2p} are defined in the same way as A_1 and A_{1p} ($A_2 = 0.7787$, with the same units as previously shown).

However, owing to uncertainties as to the population-depopulation processes of $N_2C^3\Pi_u$, every attempt to relate R

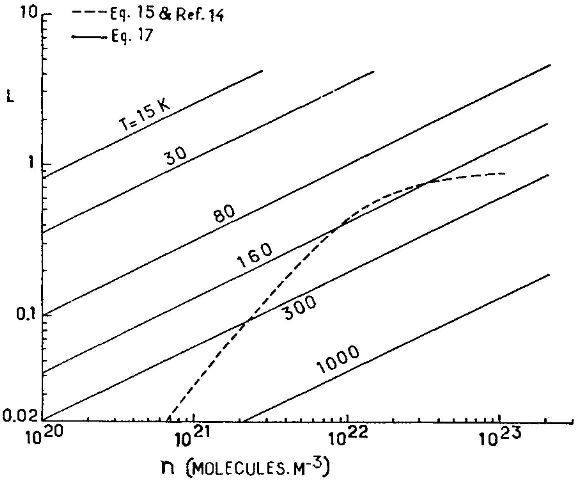

Fig. 1 Relative contribution of secondary and primary electrons to luminescence vs density.

and L (or R and D) must be very careful and ought to be controlled by experiment. As L was the last parameter to be determined, we preferred to get a purely empirical expression by selecting values which made Smith's model fit with experimental results of Ref. 2–4, 8, 14, and we did not need to relate L to R.

A first procedure[8] consisted in calculating theoretical spectra for different temperatures and different values of L, assuming the preceding model was correct. Then an apparent rotational temperature was deduced from Muntz' method, as if those spectra were experimental ones. The difference between the calculated temperature and the temperature assumed for calculating the spectra was compared with the experimentally observed errors.[2–4,8,14] This comparison led to the following expression:

$$L = (n/n^*)^{1/2}, \quad \text{with} \quad n^* = 10^{22}\ \text{molecules.m}^{-3} \tag{16}$$

Equation (16) is relatively simple and gives correct values of T_m to $\pm 10\%$, if T_r is greater than 30K. However, at lower temperatures, the agreement between measured and real temperatures is still poor, although better than using Muntz' model.

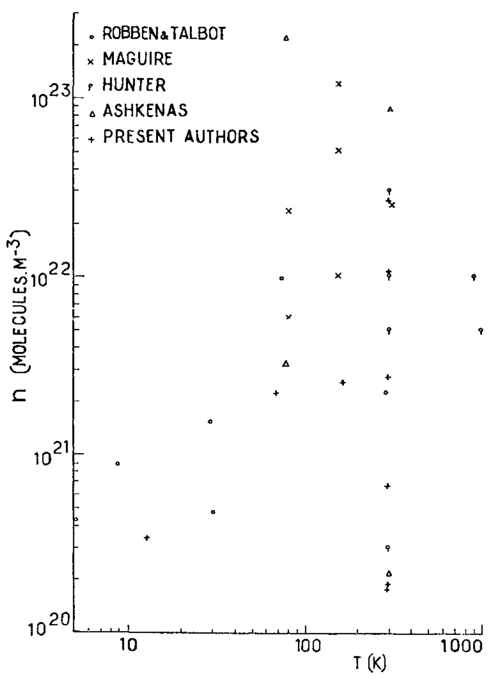

Fig. 2 Experimental conditions of available data.

A second procedure allows a better estimation of L. It consists in calculating T_r directly from experimental spectra. Different values of L are tried until T_m is equal to T_r. The optimal values of L found are approximated by a new equation

$$L = (n/n^*)^{1/2}(T_r/T^*)^{-5/4} \tag{17}$$

with $T^* = 80\text{K}$ and $n^* = 10^{22}$ molecules/m^{-3}. Figure 1 illustrates Eq. (17).

As the experimental spectra of Ashkenas[2] and Hunter[4] were not available, this procedure was not possible and we still used the first one for the data of those authors. Some data of Robben and Talbot concerning freejets were corrected for rotational relaxation, according to Ref. 15. For all spectra considered, correct values of T_r were obtained to 5% except for 1) a spectrum[3] recorded at 5K where a precision of 5% (0.25K) is thought to be unrealistic, both for the method and for the knowledge of the real temperature, and 2) a spectrum[8] recorded at 160K where the error (10%) has not been clearly explained and may be due to accidental fluctuation of electron beam intensity during recording.

Values of L given by Eqs. (16) and (17) may be very different from each other, but we must keep in mind that large variations of L mostly involve small variations in calculated temperatures. Figure 2 shows the range of temperature and density for which Eq. (17) has been tested. Table 2 shows the extremal values of T_m/T_r for all spectra and clearly shows the successive improvements brought by Smith's model and Eqs. (16) and (17).

The variation of L with T_r is not a drawback, as G is already a function of T_r, and an iterative procedure must necessarily be employed for solving Eq. (12). However, we do not see any theoretical explanation to the variation. But, owing to our procedure, it is possible that the values obtained for L would be affected by inadequacies either in the estimation of some quantities [such as $H(\varepsilon)$] or in Smith's model itself. Equation (17) would then "correct" those inadequacies. Nevertheless, it should be noticed that the empirical values of L given by Eq. (17) at 300K are of the same order of magnitude as the values of L deduced independently from experimental measurements [Eq. (15) and Ref. 14], which confirms the physical meaning of this fitting parameter and consequently the validity of Smith's model. Furthermore, this model is able to explain variations of measured rotational temperature with density, temperature and number of lines, that have been previously observed. Therefore, it is thought to be a better description of the physical phenomena than the previous models.

The precedent estimations of errors were all made with a number of lines determined by the following rule: when the intensity of a line with K' odd was smaller than the tenth of the greatest line intensity, this line and the following ones were dropped. This rule made the number of lines vary from 4($T_r \simeq 10$K) to 20($T_r \simeq 300$K). However, it is worth pointing out that temperatures obtained by Smith's model are much less depending on the number of lines involved, than temperatures obtained by Muntz' model.

Table 2 Extremal values of T_m/T_r for different expressions of L

Temperature range (K)	$L = 0$ (Muntz)	$L = (n/n^*)^{1/2}$ Eq. (16)	$L = (n/n^*)^{1/2}(T/T^*)^{-5/4}$ Eq. (17)
1 000	0.96–1.01	0.94–0.99	0.95–1.01
750	0.98–1.02	0.96–0.99	0.98–1.02
300	0.96–1.08	0.93–1.02	0.96–1.05
160	1.02–1.14	0.92–1.07	0.96–1.10
75	1.06–1.17	0.95–1.05	0.95–1.04
30	1.16–1.17	1.08–1.10	0.98–1.02
13	1.69	1.56	0.96
9	1.93	1.73	1.04
5	2.03	1.87	0.87

Conclusion

Based on the theoretical excitation/de-excitation model proposed by Smith,[7] a method has been proposed for calculating rotational temperatures from an analysis of the light emitted by nitrogen when it is excited by an electron beam. The original model has been improved in the following way in order to increase its accuracy and to make it easier to use: 1) a normalization coefficient that had been omitted by Smith has been added to Eq. (3); 2) an incorrect approximation for Q_1 has been removed; 3) instead of using an approximate expression ${}^{K}\bar{p}^{K'} \sim D/(\Delta K - 1)^2$, all constants appearing in ${}^{K}\bar{p}^{K'}$ have been calculated numerically; 4) the influence of secondary electrons, which is characterized by L, has been estimated by fitting Smith's model to available experimental data and an empirical expression has been proposed. Such a procedure avoids Smith's additional measurement of R; and 5) the iterative procedure suggested by Lewy[13] has been applied to Smith's model. Difficulties related to solving Eqs. (10) using the inversion of a matrix which should have an infinite dimension thus disappear.

All information has been given for a practical use of the method in the future. Its precision is estimated to 5% in the temperature and density range investigated.

References

[1] Muntz, E. P., "Static Temperature Measurements in a Flowing Gas," *The Physics of Fluids*, Vol. 5, No. 1, Jan. 1962, pp. 80–90.

[2] Ashkenas, H., "Rotational Temperature Measurements in Electron Beam Excited Nitrogen," *The Physics of Fluids*, Vol. 10, No. 12, Dec. 1967, pp. 2509–2520.

[3] Robben, F. and Talbot, L., "Some Measurements of Rotational Temperatures in a Low Density Wind Tunnel Using Electron Beam Fluorescence," AS-65-5, May 1965, Univ. of California, Berkeley, Calif.

[4] Hunter, W. W., "Rotational Temperature Measurements from 300 to 1000K with Electron Beam Probe," Paper 16.2-4-66, 21st Annual Conference, Instrument Society of America, New York, 1966.

[5] Lillicrap, D. C., "Experimental Determination of Density and Rotational Temperature by an Improved Electron Beam Technique," AIAA Paper 71-605, Palo Alto, Calif., 1971.

[6] Hickman, R. S., "Rotational Temperature Measurements in Nitrogen using an Electron Beam," USCAE 103, Sept. 1966, Univ. of Southern California, Los Angeles, Calif.

[7] Smith, R. B., "N_2 First Negative Band Broadening due to Electron Beam Excitation," *Rarefied Gas Dynamics 6th Symposium*, Vol. 2, Academic Press, New York, 1969, pp. 1749–1760.

[8] Lengrand, J. C. and Cloupeau, M., "Mesures de température de rotation dans l'azote excité par faisceau électronique. Utilisation pratique du modèle de Smith," Rapport 72-2, Avril 1972, Lab. d'Aérothermique du C.N.R.S., Meudon, France.

[9] Steward, D. T., "Electron Excitation Functions of the First Negative Bands of N_2^+," *Proceedings of the Physical Society*, Vol. 69, Pt. 6, No. 438 A, June 1956, pp. 437–440.

[10] McConkey, J. W., Woolsey, J. M., and Burns, D. J., "Absolute Cross Section for Electron Impact Excitation of 3914 Å N_2^+," *Planetary and Space Science*, Vol. 15, No. 8, Aug. 1967, pp. 1332–1334.

[11] Burns, D. J., Simpson, F. R., and McConkey, J. W., "Absolute Cross Sections for Electron Excitation of the 2nd Positive Bands of N_2," *Journal of Physics B*, Ser. 2, Vol. 2, Jan. 1969, pp. 52–64.

[12] Muntz, E. P., "The Electron Beam Fluorescence Technique," AGARDograph 132, Dec. 1968.

[13] Lewy, S., "Mesure de la température de rotation de l'azote en écoulement hypersonique par une sonde à faisceau d'électrons," *Journal de Physique*, Vol. 33, No. 11–12, Nov.–Déc. 1972, pp. 955–969.

[14] Maguire, B. L., "Density Effects on Rotational Temperature Measurements in Nitrogen using the Electron Beam Excitation Technique," *Rarefied Gas Dynamics 6th Symposium*, Vol. 2, Academic Press, New York, 1969, pp. 1761–1782.

[15] Lengrand, J. C., "La relaxation de rotation dans quelques types d'écoulements," Rapport 72-5, Déc. 1972, Lab. d'Aérothermique du C.N.R.S., Meudon, France.