



HAL
open science

Rotational collisional line broadening at high temperatures in the N₂ fundamental Q-branch studied with stimulated Raman spectroscopy

B. Lavorel, G. Millot, R. Saint-Loup, C. Wenger, H. Berger, J.P. Sala, J. Bonamy, D. Robert

► **To cite this version:**

B. Lavorel, G. Millot, R. Saint-Loup, C. Wenger, H. Berger, et al.. Rotational collisional line broadening at high temperatures in the N₂ fundamental Q-branch studied with stimulated Raman spectroscopy. *Journal de Physique*, 1986, 47 (3), pp.417-425. 10.1051/jphys:01986004703041700 . jpa-00210221

HAL Id: jpa-00210221

<https://hal.science/jpa-00210221>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

33.20F — 33.70 — 34.20

Rotational collisional line broadening at high temperatures in the N₂ fundamental Q-branch studied with stimulated Raman spectroscopy

B. Lavorel, G. Millot, R. Saint-Loup, C. Wenger, H. Berger

Laboratoire de Spectrométrie Moléculaire (*),
6, Bd Gabriel, Université de Bourgogne, 21100 Dijon, France

J. P. Sala, J. Bonamy and D. Robert

Laboratoire de Physique Moléculaire (+),
Université de Franche-Comté, 25030 Besançon Cedex, France

(Reçu le 22 juillet 1985, accepté le 15 novembre 1985)

Résumé. — Les spectres de la branche Q de N₂ pur sont enregistrés par spectroscopie Raman stimulée à haute résolution dans le domaine de pression 0,25-1,9 atm. et dans le domaine de température 295-1 310 K. La non-additivité des composantes $Q(J)$ due au recouvrement des raies, se produisant pour les plus fortes pressions explorées, est soigneusement prise en compte. Une excellente reproduction du profil enregistré est ainsi obtenue à chaque pression, ce qui conduit bien à une dépendance linéaire en densité des largeurs de raie. Un calcul semi-classique des coefficients d'élargissement des raies conduit à des valeurs en bon accord avec l'ensemble des valeurs mesurées. Ce calcul est étendu à des valeurs de J plus grandes et à des températures plus élevées (jusqu'à 2 500 K). Enfin, un modèle phénoménologique simple basé sur une loi polynomiale, en puissance inverse des écarts d'énergie, pour les taux de transfert d'énergie rotationnelle est utilisé pour déduire les largeurs de raie à haute température. Les largeurs ainsi obtenues sont comparées à celles calculées *a priori*.

Abstract. — Self broadened N₂ Q-branch spectra are measured by high resolution stimulated Raman spectroscopy in the pressure region 0.25-1.9 atm. and in the temperature range 295-1 310 K. Non additivity of the $Q(J)$ components due to line overlap arising in the highest pressure range explored is carefully taken into account. Excellent fit of the whole spectra is thus obtained for each pressure with linearly density-dependent line widths. Semi-classical calculations of the line broadening coefficients lead to consistent values with all the measured ones. These calculations are extended to higher J values and to higher temperatures (up to 2 500 K). At last, a simple phenomenological model based on a polynomial inverse energy gap law for the rotational energy transfer rates is used to predict high temperature line widths. These predicted line widths are compared with those calculated *a priori*.

1. Introduction.

Laser Raman diagnostic techniques (CARS, SRS, RIKES) offer the possibility of carrying out temperature and concentration measurements for non-intrusive study of gases and reactive media (plasma, flames, etc.) [1-3]. The rotational and vibrational Raman spectra of simple molecules such as N₂ are thus often used for temperature and pressure deter-

mination. These studies require the extraction of line intensity and line shape informations from the experimental spectrum. In order to deduce from experimental data information about temperature and pressure, it is necessary to know the dependence of line parameters on these factors. Moreover, for accurate determination, the theoretical profile used in the fit plays an important rôle. Widths of N₂ Q-branch lines at room temperature and methane flame conditions have been explored by different authors [4-7]. In this paper, we report the dependence on the rotational quantum number J and on the

(*) U.A. CNRS n° 777.

(+) U.A. CNRS n° 772.

temperature, of the collisional broadening coefficient for $Q(J)$ branch lines in pure N_2 , in the pressure range 0.25 – 1.9 atm and temperature range 295–1 310 K. Experimental data were collected and compared with the results of theoretical calculations. With regard to the collection of experimental data, stimulated Raman spectroscopy presents a great advantage over other optical methods. In particular, the signal is proportional to the imaginary part of the third order nonlinear susceptibility and therefore proportional to the spontaneous Raman signal. As a consequence the profiles are quite similar, without lineshape distortion [8].

The spectra have been recorded with inverse Raman spectroscopy (Fig. 1), which provides high resolution (about $1 \times 10^{-3} \text{ cm}^{-1}$ HWHM) and good detectivity. The experimental apparatus is described in section 2.1. The analysis of the spectra (Sect. 2.2) is based on least squares fitting procedures of Voigt [9] and Rosenkranz [10] profiles. The latter is used to take line mixing into account.

Experimental conditions in cells do not allow one to explore a sufficient number of lines and to attain highest temperatures for practical applications. Moreover the line broadening coefficients deduced from the measurements in flames are inaccurate due to the presence of various impurities ([6], H_2O , CO_2). So, particular interest lies in calculating the line widths *a priori*. These calculated values may be confronted with cell measurements and extended to higher rotational lines and higher temperatures.

Semi-classical line widths calculations based on a non perturbative approach and using realistic trajectories are presented in section 3. Calculated values are compared with experimental ones and their dependence vs. J number and temperature is discussed.

Since, even at atmospheric pressure, the isotropic Q branch exhibits collisional narrowing, a study of the line coupling effects is needed. A model from a polynomial energy gap law of the line coupling coefficients is proposed (Sect. 4). The resulting line widths for high temperatures are then compared with the values calculated *a priori*.

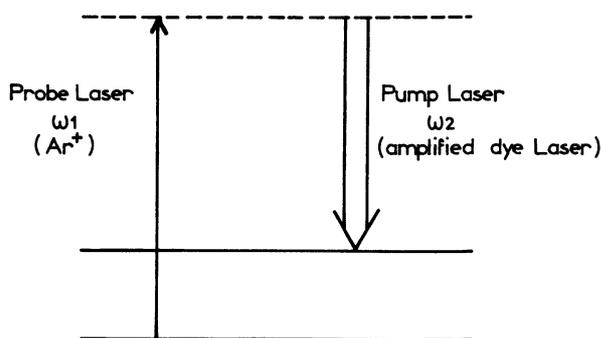


Fig. 1. — Inverse Raman process.

2. Experimental study.

2.1 APPARATUS. — The inverse Raman spectrometer has been described previously [11]. Beams from a pulsed pump laser and a single mode c. w. probe laser (argon ion laser) are overlapped at a common focus in the gas sample (Fig. 2). The pulsed pump laser is obtained by amplifying a tunable single mode dye laser in four dye amplifiers pumped by a frequency-doubled Nd : Yag laser. The Raman loss signal is detected on the probe laser beam by a photodiode, amplified and stored in a data acquisition system. The argon ion laser is actively stabilized with a Fabry-Perot interferometer and therefore has a narrow line width (about 1 MHz). The Raman spectra are recorded by scanning the dye laser over a range of about 1 cm^{-1} . For temperature dependence measurements the gas cell is introduced in an electric oven.

2.2 SPECTRA ANALYSIS. — The analysis is based on an iterative least squares fitting procedure of line profiles in which some of the line parameters are fixed in order to reduce their correlation. The frequencies and intensities of $Q(J)$ lines are calculated with the following expressions :

$$\nu(J) = \nu_0 + (B_1 - B_0) J(J + 1) \quad (1)$$

$$I(J) \propto g_{NS}(2J + 1) \exp\left(-\frac{hc}{kT} B_0 J(J + 1)\right). \quad (2)$$

In equation (2), the J -dependence of the isotropic polarizability $\bar{\alpha}$ has been disregarded (cf. Ref. [12]); k is Boltzmann's constant and g_{NS} the statistical nuclear weight which is equal to 6 for even J and 3 for odd J . ν_0 and $(B_1 - B_0)$ are taken equal to the values of reference [13] : $\nu_0 = 2 329.917 \text{ cm}^{-1}$, $B_1 - B_0 = -0.017384 \text{ cm}^{-1}$, T is the measured temperature. Since it is important to accurately know the baseline, the latter is measured for each experimental condition by evacuating the gas cell.

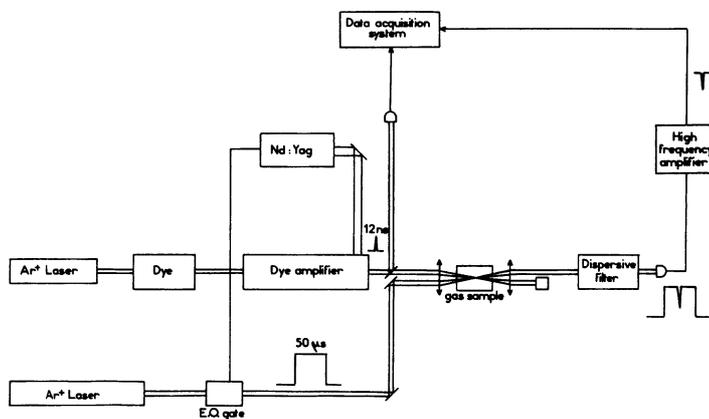


Fig. 2. — Inverse Raman experimental apparatus.

The adjusted parameters are the overall scale intensity factor, the collisional line widths for each J value and, if necessary, the line mixing coefficients defined below in the Rosenkranz profile [10].

2.2.1. *Profile for isolated lines.* — We have to use a profile which takes into account the three main broadening sources : experimental apparatus function, Doppler effect and collisions. In fact, the experimental function width estimated to be about $1 \times 10^{-3} \text{ cm}^{-1}$ (HWHM) [11], can be neglected. The lineshape including the Doppler effect and the collisions is the well known Voigt profile [9], convolution product of both line shapes, respectively Gaussian and Lorentzian for Doppler and collisional broadening. The Lorentzian shape arises from the impact approximation [14].

The Voigt profile is correct at low pressure, but when the pressure increases, the Doppler width is reduced through the Dicke narrowing [15]. In order to account for this phenomenon, a Galatry profile can be used [16], as recently shown in N₂ backward scattering [17]. However, in our forward scattering experiment, the Doppler width is small compared to the collisional width. Furthermore, the Dicke narrowing and the signal-to-noise ratio become smaller at high temperature [17]. Consequently, it is not useful to introduce a Galatry profile.

2.2.2. *Profile for overlapped lines.* — A problem appears when the pressure leads to significant line overlap (from $P = 0.5 \text{ atm}$ at room temperature for N₂). It then becomes very difficult to fit a superposition of Voigt line shapes to the experimental spectra (Fig. 3b). This non additivity results from line mixing and is responsible for collisional narrowing observed in some molecules (HD [18], CO₂ [19], N₂O [20], N₂ [21, 22]).

The intensity observed for isotropic Raman scattering is proportional to the following expression [14, 23] :

$$I(\omega) = \frac{N}{\pi} \left| \langle v_i = 0 | \bar{\alpha} | v_f = 1 \rangle \right|^2 \text{Im} \sum_J \rho_J \times \sum_{J'} \langle J J | (\omega - L_a - PA)^{-1} | J' J' \rangle \quad (3)$$

where N is the density of molecules and P the pressure (in atm), L_a the Liouville operator and A the relaxation matrix. The diagonal elements A_{JJ} are related to the halfwidth γ_J by :

$$\gamma_J \text{ (in } \text{cm}^{-1} \cdot \text{atm}^{-1}) = (2\pi c)^{-1} \text{Im } A_{JJ} \quad (4)$$

The off-diagonal elements $A_{J'J}$ express line mixing. The line shift proportional to $\text{Re } A_{JJ}$ is small and will be neglected (as well as $\text{Re } A_{J'J}$). For a given model for the off-diagonal elements $A_{J'J}$, one could calculate the profile by inversion of the matrix $(\omega - L_a - PA)$.

From a perturbation expansion in powers of the pressure, Rosenkranz has derived an expression for

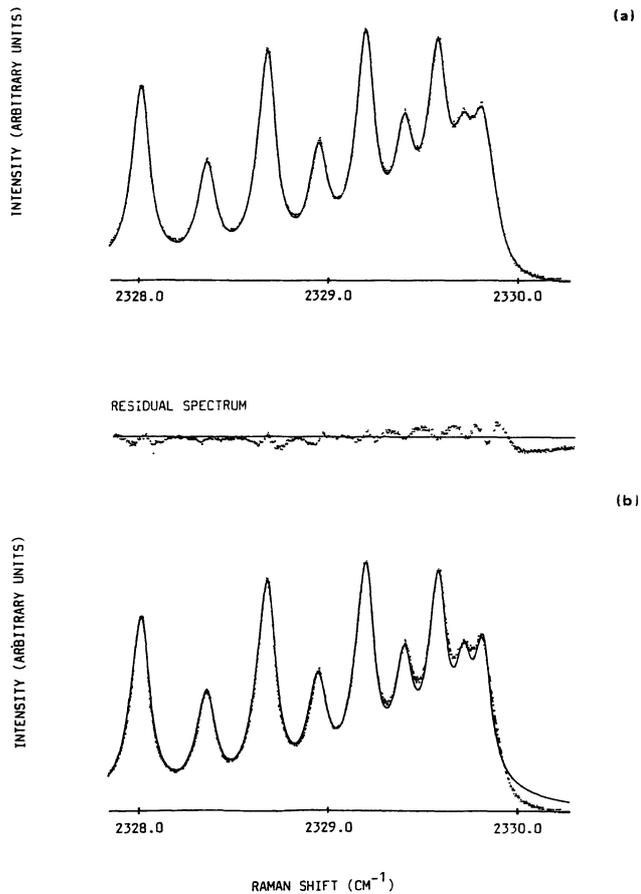


Fig. 3. — Least-squares Rosenkranz (a) and Voigt (b) profile fit (solid line) to the experimental spectrum (points) for the band head of self perturbed N₂ molecule at $T = 295 \text{ K}$ and $P = 965 \text{ torr}$. The residual spectrum is the difference between experimental and fitted profiles.

$I(\omega)$ in the case of small overlap [10], and Rosasco has applied this expression to the Raman scattering [7]

$$I(\omega) = \frac{N}{\pi} \left| \langle v_i = 0 | \bar{\alpha} | v_f = 1 \rangle \right|^2 \sum_J \rho_J \times \left\{ \frac{\gamma_J P - (\omega - \omega_J) Y_J P}{(\omega - \omega_J)^2 + (\gamma_J P)^2} \right\} \quad (5)$$

where

$$Y_J = 2 \times \sum_{J' \neq J} \frac{A_{J'J}}{\omega_{J'} - \omega_J} \quad (6)$$

and ω_J is the line frequency. The line mixing is expressed through the coefficient Y_J , which is a new adjustable parameter. Figure 3a shows a good agreement between the fitted Rosenkranz-like profile and the experimental one, in contrast to the Voigt profile case (Fig. 3b). The Y_J components deduced from such a fit have been listed in table I and compared, at room temperature, to those determined previously by Rosasco *et al.* [7].

Table I. — Y_J (in atm⁻¹) line mixing coefficient at various temperatures.

J	$T_1 = 298$ K From Ref[7]	$T_1 = 295$ K	$T_2 = 600$ K	$T_3 = 940$ K
0	0.46	0.16	0.09	-
1	0.60	0.43	0.35	0.25
2	0.21	0.14	0.09	0.07
3	0.05	0.07	0.05	0.07
4	0.04	0.02	0.02	-
5	-0.04	-0.02	0.02	-
6 à 18	-0.03	-0.02	0.02	-

2.3 RESULTS. — From the above considerations, we have selected the following profile for the fitting procedure depending on the temperature and pressure range :

$T = 295$ K	Rosenkranz
$T = 600 - 940$ K	$P \geq 1$ atm Rosenkranz
$T = 600 - 940$ K	$P < 1$ atm Voigt
$T = 1310$ K	Voigt .

Results are shown in figure 4. For each $Q(J)$ line and each temperature, the broadening is measured by applying a linear regression. Figure 5 shows the so obtained excellent linear dependence of the line broadening coefficient at room temperature.

3. The calculated J and T dependence of line widths.

Anderson-like theories [24, 25] of infrared and Raman line broadening based on a perturbative approach and using a long range multipolar potential are inadequate for high temperatures. Indeed, close collisions play an increasing rôle as temperature increases and these close collisions are roughly taken into account through a cut-off procedure. This is physically reasonable only if the cut-off parameter is significantly larger than the kinetic diameter, which is not precisely the case for high temperature.

Non-perturbative semi-classical theories have been proposed as well for atomic perturbers [26] as for molecular ones [27]. In the latter case the resummation of the infinite order series of the S matrix elements is less accurate than for atomic perturbers but resonant rotational energy transfers are well taken into account. Applications of this theory to the calculation of the infrared line broadening coefficients for various molecular systems such as CO [27, 28], CO₂ [29], N₂O [30, 31] selfperturbed and perturbed by N₂ and O₂ have been recently performed. For all rotational lines for which semi-classical theories apply, fairly good agreement was obtained with experimental data for a large range of temperatures.

The main features of this theory [27] are the non-perturbative treatment of the S matrix elements through the use of the linked cluster theorem and a convenient description of the classical trajectories as

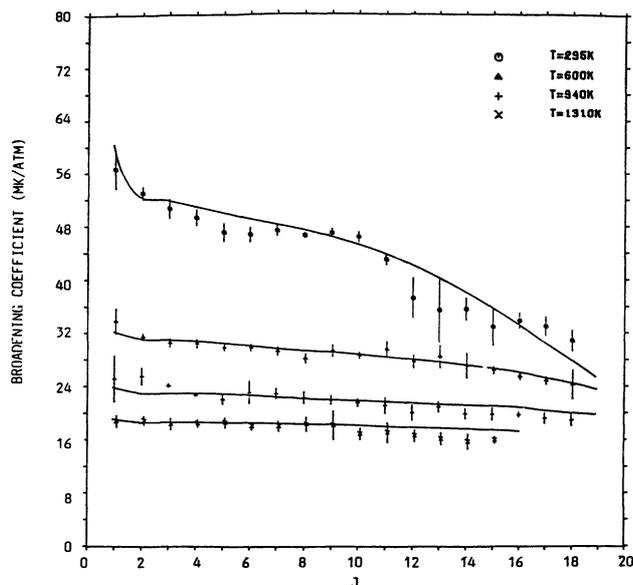


Fig. 4. — Measured (points) and calculated (solid line) collisional broadening coefficient as a function of J for each explored temperature.

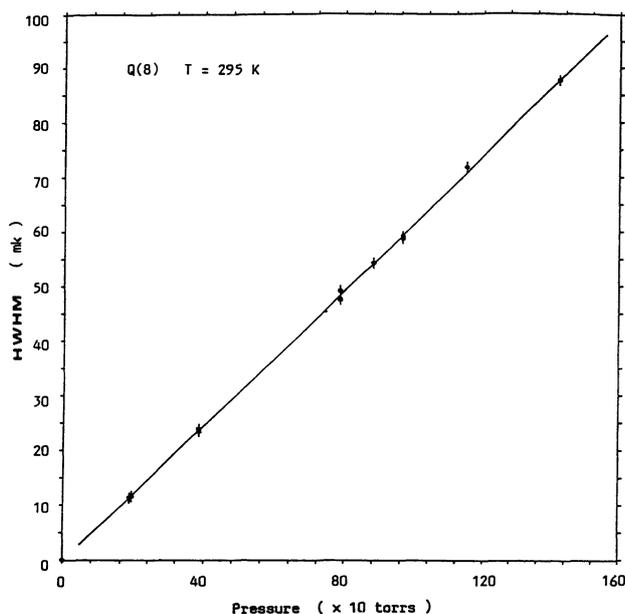


Fig. 5. — Collisional half-width of N₂ Q(8) line versus pressure at $T = 295$ K. The slope of the least-squares straight line is the collisional broadening coefficient ($\gamma(8) = 46.9$ mk/atm.).

well for large impact parameters as for the closest approach. Moreover the angular anisotropic part of the intermolecular potential is described by an atom-atom pairwise additive Lennard-Jones potential supplemented with the electrostatic interaction. Consequently the parameters characterizing the N₂-N₂ interaction potential energy in this empirical model

are the quadrupole moment ($Q = -1.4 \times 10^{-26}$ e.s.u.; cf. Ref. [32]), the equilibrium interatomic distance $r_{\text{NN}} = 1.097685 \text{ \AA}$ [35] and the energy parameters for the attractive and repulsive atom-atom contributions ($e_{\text{NN}} = 0.25 \times 10^{-10} \text{ erg \AA}^6$ and $d_{\text{NN}} = 0.29 \times 10^{-7} \text{ erg. \AA}^{12}$).

These values for e_{NN} and d_{NN} are derived from an experimental study of the temperature dependence of the second virial coefficients [36]. Starting from an analysis of the uncertainties, the authors of this study have proposed three sets of such parameters for the N-N interaction. The above set of atom-atom parameters has been retained because they give better overall agreement of the calculated line widths with the experimental data of section 2.3. Let us mention that the other two sets lead calculated line width values which are close but systematically higher by around ten per cent.

The parameter set (Q , r_{NN} , e_{NN} and d_{NN}) completely determine the used potential surface. The calculation of trajectories necessitates the knowledge of the N₂-N₂ isotropic potential. It has been determined by fitting the spherically averaged atom-atom potential by a molecular Lennard-Jones form (cf. Ref. [27]). The deduced constants ($\sigma = 0.373 \text{ nm}$ and $\varepsilon = 0.807 \text{ kJ mol}^{-1}$) are consistent with accurate theoretical and experimental data [37].

The calculated line width values (HWHM) are compared with those measured in figure 4. Let us note that the experimental curve $\gamma_J(T)$ vs. J exhibits a marked hump around $J \sim 9$ for $T = 295 \text{ K}$. This hump is less pronounced at 600 K and shifted towards higher J values ($J \sim 11 - 13$). It disappears for higher temperatures. The presence of these humps is easily understood from the consideration of resonance effects [38] in the population rotational transfers. Indeed this resonance takes place for N₂-N₂ near the most populated rotational levels J_{mp} . These levels are $J_{\text{mp}} \sim 6 - 8$ at 295 K and $J_{\text{mp}} \sim 8 - 12$ at 600 K. For increasing temperatures the spread of population makes this resonance process less and less localized with respect to J .

The good agreement obtained between calculated and measured line widths is verified over a great number of rotational lines and a large temperature range (Fig. 4). This allows us to extend the explored domain (J , T) by means of a calculation. The corresponding results are presented in table II.

The upper J value (J_{max}) retained for the calculation has been chosen, for each considered temperature, such that the population of this level J_{max} is higher than 5×10^{-3} of the total population. Let us note that such a criterion is consistent with the limit of validity of a semi-classical calculation. Indeed, for the lowest considered temperature (295 K), the energy defect in the rotational transfer by collisions $J_{\text{max}} = 22 \rightarrow J' = 20$ and $J_2 = J_{\text{mp}} \sim 6 - 8 \rightarrow J'_2 \sim 8 - 10$ (where J_{mp} is the most populated level) is lower than the kinetic energy. This ratio is

nevertheless of the order of 0.5. This explains the fact that for the highest calculated $Q(J)$ line widths at $T = 295 \text{ K}$ the limit of validity is reached and the calculated values are underestimated for $18 \gtrsim J \gtrsim 22$. Let us note that for higher temperatures, the criterion becomes less stringent and the semi-classical calculations are more accurate, even for $J \sim J_{\text{max}}$. So, for $T = 600 \text{ K}$, $J_{\text{max}} = 30$, $J_{\text{mp}} = 8 - 12$ and the above mentioned ratio is about 1/4.

The calculated temperature dependence $\gamma_J^{\text{calc}}(T)$ for some lines is shown in figure 6. It is useful for practical reasons [39-41] to fit these curves $\gamma_J^{\text{calc}}(T)$ by the simple analytical law :

$$\gamma_J^{\text{calc}}(T) = \gamma_J^{\text{calc}}(T_{\text{ref}}) (T/T_{\text{ref}})^{-N(J)} \quad (7)$$

where, in the general case, the J dependence of the exponent N is neglected. The calculated $N(J)$ values from equation (4) have been gathered in table III. It clearly shows that the variations of N vs. J is too large to reasonably deduce a single exponent law. In addition this table shows, as previously discussed in reference [28], that simple models based on purely resonant rotational transfers and only considering a single anisotropic potential contribution are too crude to predict the temperature dependence of line widths in a large (J , T) domain.

In section 2.3 and 3, a large set of experimental and theoretical line widths for all the $Q(J)$ components has been obtained in a very large range of temperatures (up to 2500 K). It allows us to investigate the line mixing effects by using a rotational relaxation model.

4. Line coupling model from line broadening coefficients.

As mentioned in section 2.2, significant overlap of $Q(J)$ lines arises in the band head (low J levels) for $p \gtrsim 0.5 \text{ atm}$. These overlapping effects and concomitant cross-correlations [14, 42] result in non-additivity of these $Q(J)$ lines which is well-known as the motional narrowing for densities such that the

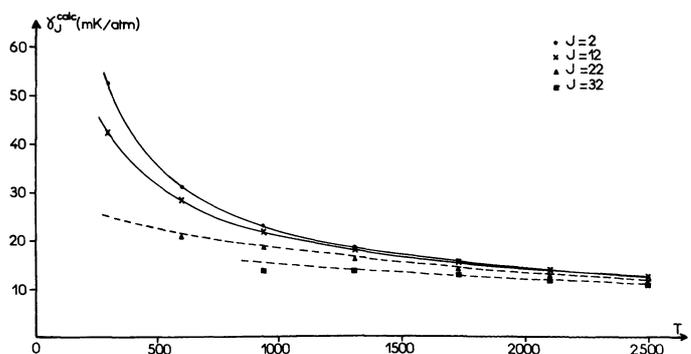


Fig. 6. — Calculated temperature dependence for some $Q(J)$ lines.

Table III. — *Temperature exponent $N(J)$ for some $Q(J)$ lines. (Let us recall that for high J values ($J=22$ and 32) the calculated line widths are underestimated at low temperatures and a higher reference temperature is required).*

T(K)	$J = 2$	$J = 12$	$J = 22$	$J = 32$
	$T_{\text{ref}} = 295$ K	$T_{\text{ref}} = 295$ K	$T_{\text{ref}} = 940$ K	$T_{\text{ref}} = 1730$ K
600	0.73	0.57	—	—
940	0.71	0.58	—	—
1310	0.70	0.58	0.41	—
1730	0.68	0.57	0.44	—
2100	0.67	0.57	0.45	0.38
2500	0.67	0.57	0.46	0.39

Q band becomes unresolved [18, 43]. Particular interest lies in a modelling of the $Q(J)$ lines coupling in a large temperature range. Such a model would allow one to calculate the stimulated or spontaneous isotropic Raman band profile whatever the density, in the range of validity of binary interactions (i.e. lower than one hundred Amagat units for N₂). The *a priori* calculation of all the inelastic rotational matrix elements, on the same basis as the diagonal ones (cf. Sect. 3) is unrealistic due to the very large number of levels populated at high temperatures. In the experimental study of section 2, only low pressures were investigated ($p \leq 1.9$ atm). So, the simplified Rosenkranz model [10] used with the assumption that line broadening is lower than line spacing is approximately justified. For higher pressures, such an approximation becomes unsuitable and the matrix inversion involved in equation (3) is needed [44]. An alternate approach to describe the resultant collapse due to the line coupling is to use the rotational diffusion model [45-47]. Nevertheless, the range of applicability of this model over density and temperature remains limited. The limits depend on the required degree of accuracy. Recently, several simple phenomenological models for predicting off-diagonal matrix elements $A_{J',J}$ from the fitting laws for rotationally inelastic collisions [48] have been proposed. These models give more or less satisfactory agreements with experiment. Reasonable results have been obtained from exponential gap laws [22, 49], statistical power gap laws [7, 50] or hybrid exponential-power gap laws [44] in the range 300-2 000 K, 1-100 atm. An improved version of the polynomial inverse energy gap law has been recently proposed by Greenhalgh and coworkers [51]. We have adopted their model :

$$(2 \pi c)^{-1} A_{J',J}(T) = \left(\frac{T}{T_{\text{ref}}} \right)^{-A} \rho_{J'}(T) \sum_{l=0}^{l_{\text{max}}} c_l \left| \frac{E_{J'} - E_J}{hc} \right|^{-1} \quad (8)$$

In equation (8) $A, c_0, \dots, c_{l_{\text{max}}}$ are coefficients to be determined and T_{ref} is the reference temperature.

Such an expression satisfies the detailed balance principle ($\rho_J A_{J',J} = \rho_{J'} A_{J,J'}$). The unitarity of the S matrix leads to an exact relation for the isotropic Q band between diagonal and off-diagonal matrix elements [52] :

$$\gamma_J(T) = (2 \pi c)^{-1} A_{JJ}(T) = - (2 \pi c)^{-1} \sum_{J' \neq J} A_{J',J}(T) \quad (9)$$

This equation together with equation (8) allows the determination of the A and $\{c_l\}$ coefficients if sufficient information is available on the J and T dependence of the line widths.

The previous study [51] following this procedure was based only on N₂ line widths measurements at room temperature in cell [7] and in the post flame gases of a methane-air flat flame at $T = 1 730$ K [6]. This flame contained a significant amount of foreign perturbers ($\sim 20\%$ of H₂O and $\sim 10\%$ of CO₂). Such perturbers are particularly efficient at inducing rotational transfers by collisions [53, 29]. So, even minor H₂O and CO₂ components add important contributions to the broadening.

This fact may be verified by comparing the experimental data in flame with the present calculated self broadening coefficients γ_J ($T = 1 730$ K). Indeed, the measured values [6] vary from 18.4 mK for $J = 2$ to 11 mK for $J = 45$. These values are to be compared respectively to 15.7 and 9.8 mK (cf. Table II).

The present measured and calculated line widths constitute a new set of coherent and reliable data in a large (J, T) domain. Thus, we have reestimated the A and $\{c_l\}$ coefficients of equation (8) starting from all the measured values of table II supplemented by calculated values for higher J levels (up to J_{max}). The optimization procedure is similar to that proposed in reference [51], our least squares criterion is to minimize the following quantity :

$$S = \sum_{i=1}^4 \sum_{J=0}^{J_{\text{max}}(T_i)} p_J(T_i) [\gamma_J^{\text{mod}}(T_i) - \gamma_J^{\text{exp}}(T_i)]^2 \quad (10)$$

In equation (10), the temperatures considered are : $T_1 = 295$ K, $T_2 = 600$ K, $T_3 = 940$ K, $T_4 = 1 310$ K with the corresponding J_{max} values : $J_{\text{max}}(T_1) = 22$, $J_{\text{max}}(T_2) = 30$, $J_{\text{max}}(T_3) = 38$, $J_{\text{max}}(T_4) = 44$. Moreover $p_J(T_i)$ ($i = 1, \dots, 4$) is the weighting coefficient chosen as $[\Delta \gamma_J(T_i)]^{-2}$ where $\Delta \gamma_J(T_i)$ is the experimental uncertainty (cf. caption Table II) for each measured $\gamma_J(T_i)$ value and $\text{Max} \{ \Delta \gamma_J \}_{T_i}$ for the calculated ones, at each temperature T_i . This choice reduces the relative importance of the calculated values in the determination of the set of coefficients A and $\{c_l\}$. Let us note that for N₂, the J' summation in equation (9) is over either even or odd values, and the fractional populations must also be calculated using parity-separated rotational partition function. On increasing the degree of the polynomial in

equation (8) above to $l_{\max} = 5$ we do not improve the convergence of the fitted values to the experimental ones.

We have obtained the following set of coefficients (for $T_{\text{ref}} = 295 \text{ K}$):

$$\begin{aligned} A &= 0.446, & c_0 &= -0.0177 \text{ cm}^{-1} \text{ atm}^{-1}, \\ c_1 &= -7.227 \text{ cm}^{-2} \text{ atm}^{-1}, & c_2 &= 379.2 \text{ cm}^{-3} \text{ atm}^{-1}, \\ c_3 &= -9.815 \times 10^3 \text{ cm}^{-4} \text{ atm}^{-1}, \\ c_4 &= 9.672 \times 10^4 \text{ cm}^{-5} \text{ atm}^{-1} \\ \text{and} \\ c_5 &= -2.944 \times 10^5 \text{ cm}^{-6} \text{ atm}^{-1}. \end{aligned} \quad (11)$$

This set is different from that found previously [51]. This is easily understood from the above discussion concerning the nature of the input data and the fact that significant correlation exists between the various coefficients of this set. The quality of the fit is shown in figure 7.

A possible test of the consistency of the above phenomenological model (Eqs. (8) and (9)) with the parameters given in equation (11) is to deduce line width values $\gamma_J^{\text{mod}}(T_i)$ for higher temperatures and to compare them to those calculated *a priori* calculated. Such a comparison is made in table II.

5. Conclusion.

The present experimental and theoretical study has allowed us to obtain a precise set of individual line widths for the isotropic Q branch of pure nitrogen. The dependence of these line widths on rotational states and temperature covers a very large domain never attained until now. This set of line width values contains much information on the J and T dependence of the inelastic rotational cross-sections.

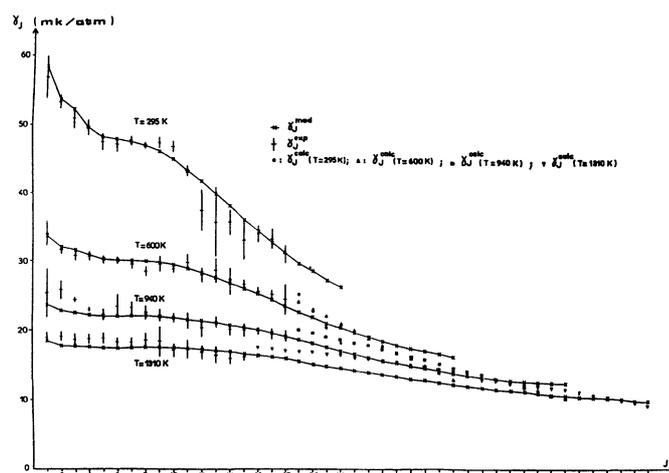


Fig. 7. — Comparison between the resulting values from the phenomenological model (Eqs. (8), (9) and (11)) and the input (measured and calculated) line broadening coefficients.

So, a reliable model for rotational relaxation has been deduced. This model allows the predictive synthesis of the whole band profile for pressures higher than atmospheric pressure when the line mixing becomes crucial. Such a study will be presented in a further publication.

Acknowledgments.

The authors greatly acknowledge Pr H. W. Schrötter and Dr J. P. Taran for stimulating discussions and for helpful comments on the manuscript. This work was supported by a DRET grant (Contract DRET n° 83-1045).

References

- [1] KIEFFER, W. and LONG, D. A., *NATO* (D. Reidel) 1982.
- [2] PÉALAT, M., TARAN, J. P. and MOYA, F., *Optics Laser tech.* (1980) 21.
- [3] HALL, R. J. and BOEDEKER, L. R., *Appl. Optics* **23** (1984) 1340.
- [4] JAMMU, K. S., JOHN, G. E. St. and WELSH, H. L., *Can. J. Phys.* **44** (1966) 797.
- [5] BÉRARD, M., Thèse d'état, Paris VI (1983).
- [6] RAHN, L. A., OWYOUNG, A., COLTRIN, M. E. and KOSZYKOWSKI, M. L., Proc. 7th Int. Conf. on Raman Spectrosc. (W. F. Murphy) p. 694, North Holland Amsterdam (1980).
- [7] ROSASCO, G. J., LEMPERT, W., HURST, W. S., Proc. 6 Int. Conf. on Spectral line shape, 2 Boulder, CD, USA (1982); ROSASCO, G. J., LEMPERT W., HURST, W. S. and FEIN, A., *Chem. Phys. Lett.* **97** (1983) 435.
- [8] BLOEMBERGEN, N., *Am. J. Phys.* **35** (1967) 989.
- [9] HUMLICEK, J., *J. Quant. Spectrosc. Radiat. Transfer* **23** (1975) 498.
- [10] ROSENKRANZ, P. W., *IEEE Trans. Antennas Propag.* **23** (1975) 498.
- [11] LAVOREL, B., Thèse Dijon (1984); LAVOREL, B., SAINT-LOUP, R., PIERRE, G. et BERGER, H., *J. Physique Lett.* **45** (1984) L-295.
- [12] LAANE, J. and KIEFFER, W., *J. Raman Spectros.* **9** (1980) 353.
- [13] BENDTSEN, J., *J. Raman Spectros.* **2** (1974) 133.
- [14] FANO, U., *Phys. Rev.* **141** (1966) 34.
- [15] DICKE, R. H., *Phys. Rev.* **89** (1953) 472.
- [16] GALATRY, L., *Phys. Rev.* **122** (1961) 1218.
- [17] MILLOT, G., LAVOREL, B., SAINT-LOUP, R. and BERGER, H., *J. Physique* **46** (1985) 1925.
- [18] DION, P. and MAY, A. D., *Can. J. Phys.* **51** (1973) 36; WITKOWICZ, T. and MAY, A. D., *Can. J. Phys.* **54** (1976) 575.
- [19] BARAN, J., GROFCSIK, A. and JONES, W. J., *Mol. Phys.* **45** (1982) 1291.
- [20] NEWMANN, M. N. and TABISZ, G. C., *Mol. Phys.* **47** (1982) 86.

- [21] MAY, A. D., STRYLAND, J. C. and VARGHESE, G., *Can. J. Phys.* **48** (1970) 2331.
- [22] HALL, R. J., VERDIEK, J. F. and ECKBRETH, A. C., *Opt. Commun.* **35** (1980) 69.
- [23] BEN REUVEN, A., *Adv. Chem. Phys.* **33** (1975) 235.
- [24] ANDERSON, P. W., *Phys. Rev.* **76** (1949) 647;
TSAO, C. J. and CURNUTTE, B., *J. Quant. Spectrosc. Radiat. Transfer* **2** (1962) 41;
FIUTAK, J. and VAN KRANENDONK, J., *Can. J. Phys.* **40** (1962) 1085; *Can. J. Phys.* **41** (1963) 21.
- [25] DAVIES, R. W. and OLI, B. A., *J. Quant. Spectrosc. Radiat. Transfer* **20** (1978) 95.
- [26] SMITH, E. W., GIRAUD, M. and COOPER, J., *J. Chem. Phys.* **65** (1976) 1256.
- [27] ROBERT, D. and BONAMY, J., *J. Physique* **40** (1979) 923.
- [28] BONAMY, J., ROBERT, D. and BOULET, C., *J. Quant. Spectrosc. Radiat. Transfer* **31** (1984) 23.
- [29] LE DOUCEN, R., COUSIN, C., BOULET, C. and HENRY, A., *Appl. Opt.* (in press).
- [30] LACOME, N., LEVY, A. and GUELACHVILI, G., *Appl. Opt.* **23** (1984) 425.
- [31] MARGOTTIN-MACLOU, M., DAHOO, P. and HENRY, A., *J. Mol. Spectrosc.* (in press).
- [32] This value has been recently obtained from accurate *ab initio* calculations by A. Van der Avoird and Coworkers [33]. It is close to the value $Q = -1.52 \times 10^{-26}$ e.s.u. previously recommended by Stogryn and Stogryn [34].
- [33] MULDER, F., VAN DIJK, G. and VAN DER AVOIRD, A., *Ad. Mol. Phys.* **39** (1980) 407.
- [34] STOGRYN, D. E. and STOGRYN, A. P., *Mol. Phys.* **11** (1966) 371.
- [35] HUBER, K. P. and HERZBERG, G., M. Sp.a.M.St. IV, v. Nostr.; Reinh. New York, 1979.
- [36] OOBATAKE, M. and OOI, T., *Prog. Theor. Phys.* **48** (1972) 2132.
- [37] BERNS, R. M. and VAN DER AVOIRD, A., *J. Chem. Phys.* **72** (1980) 6107.
- [38] GIRAUD, M., ROBERT, D. and GALATRY, L., *C.R. Hebd. Séan. Acad. Sci.* **272** (1971) 1252.
- [39] VARANASI, P. and SARANGI, S., *J. Quant. Spectrosc. Radiat. Transfer* **14** (1974) 845.
- [40] SELL, J. A., *J. Quant. Spectrosc. Radiat. Transfer* **23** (1980) 595.
- [41] HANSON, R. K., *Shock Tube and Shock Wave Research* (University of Washington Press) 1978, p. 432.
- [42] BARANGER, M., *Phys. Rev.* **112** (1958) 855.
- [43] BONAMY, J., BONAMY, L. and ROBERT, D., *J. Chem. Phys.* **67** (1977) 4441.
- [44] LEMPERT, W., ROSASCO, G. J. and HURST, W. S., *J. Chem. Phys.* **81** (1984) 4241.
- [45] GORDON, R. G., *J. Chem. Phys.* **44** (1966) 1830.
- [46] MCCLUNG, R. E. D., *Adv. Mol. Relax. Inter. Proc.* **10** (1972) 83.
- [47] HALL, R. J. and GREENHALGH D. A., *Opt. Commun.* **40** (1982) 417.
- [48] BRUNNER, T. A. and PRITCHARD, P., *Adv. Chem. Phys.* **50** (1982) 589.
- [49] KATAOKA, H., MAIDA, S., HIROGE, C. and KAJIYAMA, K., *Appl. Spectrosc.* **37** (1983) 508.
- [50] HALL, R. J., *Opt. Eng.* **22** (1983) 322.
- [51] GREENHALGH, D. A., PORTER, F. M. and BARTON, S. A., *J. Quant. Spectrosc. Radiat. Transfer* **34** (1985) 95.
- [52] SHAFER, R. and GORDON, R. G., *J. Chem. Phys.* **58** (1973) 5422.
- [53] MANDIN, J. Y., FLAUD, J. M. and CAMY-PERET, C., *J. Quant. Spectrosc. Radiat. Transfer* **26** (1981) 483.
-