

**Air broadened NO linewidths in a temperature range of atmospheric interest**

J. P. Houdeau, C. Boulet, Jeanine Bonamy, A. Khayar, and G. Guelachvili

Citation: *The Journal of Chemical Physics* **79**, 1634 (1983); doi: 10.1063/1.446007

View online: <http://dx.doi.org/10.1063/1.446007>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/79/4?ver=pdfcov>

Published by the [AIP Publishing](#)

---

**Articles you may be interested in**

[Calculation of the linewidth broadening in vertical-cavity surface-emitting lasers due to temperature fluctuations](#)  
Appl. Phys. Lett. **86**, 191108 (2005); 10.1063/1.1924868

[Pressurebroadened linewidths of formaldehyde](#)  
J. Chem. Phys. **66**, 4915 (1977); 10.1063/1.433830

[Temperature dependence of pressure broadened linewidths in the microwave region](#)  
J. Chem. Phys. **66**, 20 (1977); 10.1063/1.433666

[Pressurebroadened linewidths of ozone](#)  
J. Chem. Phys. **63**, 1513 (1975); 10.1063/1.431516

[A Plan for Broadening Active Interest in Physics](#)  
Rev. Sci. Instrum. **6**, 181 (1935); 10.1063/1.1751969

---



# Air broadened NO linewidths in a temperature range of atmospheric interest

J. P. Houdeau and C. Boulet

*Département de Physique Atomique et Moléculaire, Université de Rennes, Campus de Beaulieu, 35042-Rennes Cedex, France*

J. Bonamy and A. Khayar

*Laboratoire de Physique Moléculaire, ERA 834, Université de Besançon, 25030-Besançon Cedex, France*

G. Guelachvili

*Laboratoire d'Infrarouge, Associé au CNRS, Université de Paris sud, Bâtiment 350, Campus d'Orsay, 91405-Orsay Cedex, France*

(Received 25 October 1982; accepted 14 December 1982)

Self- and  $N_2$ -broadened linewidths of NO in the  $5.4 \mu\text{m}$  band have been measured at 163 and 295 K using high resolution Fourier transform spectroscopy. These linewidths have been calculated using the formalism of Robert and Bonamy. The calculated values are in good agreement with the experimental one. Therefore, the same formalism can be reasonably used in order to calculate  $O_2$ -broadened widths which cannot be easily measured. Air-broadened linewidths calculations have been performed in the temperature range [163–295 K]. From the results the  $J$  dependence of the exponent  $m(J)$  which gives the temperature dependence of the widths, according to the power law  $\gamma(T) = \gamma(T_0) (T/T_0)^{-m(J)}$  has been established.

## I. INTRODUCTION

The strengths  $S_{fi}$ , widths  $\gamma_{fi}$ , and frequencies  $\omega_{fi}$  of individual spectral lines in the fundamental band of NO are important in a variety of applications such as measurements of NO concentrations in the stratosphere<sup>1</sup> or in automotive exhaust.<sup>2</sup> Many modern methods, using for instance IR diode laser spectroscopy, are developed in order to determine NO abundance or vertical concentration profiles. It is now evident that the three molecular parameters  $S_{fi}$ ,  $\gamma_{fi}$ , and  $\omega_{fi}$  have to be known to a fairly high accuracy to get reliable information from these experiments.

Extensive data on the line positions and intensities in the 0–1 band of NO are available in the literature.<sup>3–5</sup> Concerning the linewidths, we have examined the most recent laboratory measurements.<sup>6–11</sup> In our opinion, the conclusion of Tejwani *et al.*<sup>8</sup> on the scatter of the data still holds, especially for  $N_2$  broadening. Moreover it seems that no measurements of  $N_2$ -broadened widths at low temperature, of atmospheric interest, have been previously published. We present such measurements here together with a theoretical analysis. A simple power-law dependence of air broadened widths of NO upon temperature has been deduced from this comprehensive study. In Sec. II we present the experimental conditions and a brief review of the procedure of data reduction. Section III gives the experimental results and a comparison with some previous studies. In Sec. V the data for self- and  $N_2$ -broadened widths are compared with the results of calculations using the formalism due to Robert and Bonamy which is reviewed in Sec. IV.<sup>12</sup> The aim was to establish the reliability of the theoretical model. Then, confident widths can be calculated for  $O_2$  broadening. Indeed, the chemical instability of the NO– $O_2$  system does not allow a direct measurement of  $\gamma_{NO-O_2}$ . Air-broadened widths of NO at

different temperatures between 163 and 295 K have been computed so that the temperature dependence of the widths can be established.

## II. EXPERIMENTAL PROCEDURE

### A. Experimental conditions

The spectra have been recorded with the Fourier–Connes type interferometer of the Laboratoire d'Infrarouge.<sup>13</sup> The capability of Fourier transform spectroscopy to furnish simultaneously a great number of line intensities and widths is now clearly established.<sup>11</sup> For the purpose of width and intensity measurements, it is of the utmost importance to use an apodized apparatus function, in order to eliminate the oscillating feet of the nonapodized function.<sup>14</sup> Among the apodization functions described by Delouis,<sup>15</sup> we have used the so-called "APØ1" function (for details see Refs. 14 and 16).

The half-width of the apodized apparatus function was generally equal to  $2.9 \times 10^{-3} \text{ cm}^{-1}$  in our spectra (cf. Table I). With such a high resolution, the use of relatively low pressures of perturber does not lead to important distortions of the profiles. Therefore, only small corrections are necessary to obtain the "true" parameters from "apparent" measured ones. Moreover, we will see later that low pressures of perturber have to be used for NO, in order to minimize a possible interference effect between the two components of each  $\Lambda$  doublet (see later Sec. III).

The experimental conditions are gathered in Table I. The variable path length cell used in the present study has been described previously.<sup>17</sup> It is a stainless steel double body cell cooled by a refrigerant (methylcyclohexane). In order to obtain better thermal insulation and to reduce the water vapor absorption, the cell has been set in a vacuum chamber. During the recording

TABLE I. Experimental conditions.

Spectrum number	Resolution <sup>a</sup> (10 <sup>-3</sup> cm <sup>-1</sup> )	Temperature (K)	NO pressure (Torr)	N <sub>2</sub> pressure (Torr)
1453	2.9	295	150	...
1454	2.9	163	83.2	...
1457	4.3	163	1.1	82
1458	2.9	295	2	148

<sup>a</sup>The resolution is defined here as the half-width of the apodized apparatus function AP $\beta$ 1.

of the interferograms, the gas temperature remained stable within  $\pm 1$  K.

## B. Data reduction

A detailed description of the procedure of data reduction has already been given previously.<sup>14</sup> Briefly for each doublet two apparent parameters are measured, the observed peak transmission [ $T_{\text{obs}}(\sigma_0)$ ] and the half-width at half-height of the *observed absorption* ( $w$ ). From these parameters, the true value of the half-width  $\gamma_{fi}$  is retrieved from a correspondence table, previously built, which gives  $\gamma_{fi}$  as a function of  $T_{\text{obs}}(\sigma_0)$ ,  $w$  and  $d$ , distance between the two components of each  $\Lambda$  doublet. Indeed, for the pressures used here,  $\gamma_{fi}$  and  $d$  are often of similar magnitude (particularly in the  ${}^2\Pi_{1/2}$ - ${}^2\Pi_{1/2}$  subband), and the two components, although not

resolved, cannot be considered as completely merged. It has been shown previously that  $\gamma_{fi}$  can be retrieved without any loss of precision, provided  $d$  is known with sufficient accuracy.<sup>14</sup> Recent publications on  $\Lambda$  doubling parameters<sup>18-20</sup> allow the present compilation of very precise values of  $d$  as a function of  $J$  in each subband.

Finally, it must be pointed out that two assumptions underlie the data analysis:

(1) We neglect a possible influence of collision-induced transitions between the  $\Lambda$  doublet levels. As outlined by Gordon<sup>21</sup> the possibility of this mechanism exists, leading to an interference effect between the two components and a narrowing of the resulting profile, this narrowing being more pronounced as the pressure increases. However, it seems reasonable to ignore

TABLE II. Observed HWHM (in 10<sup>-3</sup> cm<sup>-1</sup> atm<sup>-1</sup>) for the R branch (0-1 band) of NO perturbed by N<sub>2</sub>; T = 295 K.

J	$\Pi_{3/2} - \Pi_{3/2}$ Subband		$\Pi_{1/2} - \Pi_{1/2}$ Subband		Previous measurements			
	Obs.	Smoothed <sup>e</sup> values	Obs.	Smoothed <sup>e</sup> values	$\Pi_{3/2} - \Pi_{3/2}$		$\Pi_{1/2} - \Pi_{1/2}$	
0.5			62 $\pm$ 7				65 $\pm$ 3 <sup>c</sup>	72 <sup>d</sup>
2.5	72 $\pm$ 7	69.7	72 $\pm$ 7					
3.5	68.4 $\pm$ 7	68.8	61.1 $\pm$ 7	62.3	55 <sup>a</sup>		50 <sup>a</sup>	
4.5	68.2 $\pm$ 7	68	62.9 $\pm$ 7	62.2		60 $\pm$ 2.5 <sup>c</sup>		58 $\pm$ 3.5 <sup>c</sup>
5.5	67.3 $\pm$ 7	67.1	62.1 $\pm$ 6	62.1	55 <sup>a</sup>		51 <sup>a</sup>	
6.5	63 $\pm$ 6	66.3	63.3 $\pm$ 6	62				
7.5	62.3 $\pm$ 6	65.4	60.8 $\pm$ 6	61.8	54 <sup>a</sup>		51 <sup>a</sup>	
8.5	66.6 $\pm$ 6	64.6	60.2 $\pm$ 6	61.5			57 <sup>b</sup>	
9.5	63.8 $\pm$ 6	63.7	65 $\pm$ 6	61.2		60 <sup>b</sup>	55 <sup>b</sup>	
10.5	62.3 $\pm$ 6	62.9	59.3 $\pm$ 6	60.8	52 <sup>a</sup>		50 <sup>a</sup>	50 $\pm$ 4 <sup>c</sup>
11.5	64.2 $\pm$ 6	62	58.9 $\pm$ 6	60.4				
12.5	60.7 $\pm$ 6	61.2	61.1 $\pm$ 6	59.9				
13.5	61.8 $\pm$ 6	60.3	61.9 $\pm$ 6	59.4				
14.5	60.3 $\pm$ 6	59.4	57.5 $\pm$ 6	58.8		58 <sup>d</sup>		58 <sup>d</sup>
15.5	55.4 $\pm$ 6	58.6	55.6 $\pm$ 6	58.1	53 <sup>a</sup>	54 <sup>d</sup>	50 <sup>a</sup>	54 <sup>d</sup>
16.5	57.8 $\pm$ 6	57.7	57.2 $\pm$ 6	57.4		53 <sup>d</sup>		53 <sup>d</sup>
17.5	60.8 $\pm$ 6	56.9	57 $\pm$ 6	56.6		50 <sup>d</sup>		50 <sup>d</sup>
18.5	55.7 $\pm$ 6	56.3	54.8 $\pm$ 6	55.8		48 <sup>d</sup>		48 <sup>d</sup>
19.5	53.2 $\pm$ 6	55.2	55.4 $\pm$ 6	54.9		48 <sup>d</sup>		48 <sup>d</sup>
20.5	54.2 $\pm$ 6	54.3	56.5 $\pm$ 6	53.9	48 <sup>a</sup>		47 <sup>a</sup>	
21.5			51.4 $\pm$ 6	52.9				
22.5			52 $\pm$ 6	51.9				

<sup>a</sup>From Ref. 7.

<sup>b</sup>From Ref. 6.

<sup>c</sup>From Ref. 9.

<sup>d</sup>Reference 8; The  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  components having the same  $J$  have been assumed to have identical widths.

<sup>e</sup>Smoothed values have been obtained through a least squares Chebyshev polynomial fit.

TABLE III. Observed HWHM (in  $10^{-3}$   $\text{cm}^{-1} \text{atm}^{-1}$ ) for the *R* branch (0–1 band) of NO perturbed by  $\text{N}_2$ ;  $T=163$  K.

<i>J</i>	$\Pi_{3/2}-\Pi_{3/2}$ subband	$\Pi_{1/2}-\Pi_{1/2}$ subband
10.5	87.7 ± 9	
11.5	89.6 ± 9	
12.5	90.4 ± 9	
13.5	82.3 ± 9	82 ± 8
14.5	84 ± 8	82.7 ± 8
15.5	82.3 ± 8	81.3 ± 8
16.5	86.8 ± 8	77.3 ± 8
17.5	83.2 ± 9	79.7 ± 8
18.5	82.5 ± 9	77.1 ± 8

this mechanism at pressures below or around 150 Torr, which is the upper limit of the present study. In other words, the components of each  $\Lambda$  doublet are supposed to be additive.

(2) Moreover, we assume that these components have equal widths and intensities. Here, too, experimental and theoretical evidence support this assumption. For instance, there appears to be no significant difference between the widths and intensities of the  $\Lambda$  components for well resolved doublets recorded at lower pressures and high resolution (see Refs. 18 and 22).

### III. EXPERIMENTAL RESULTS

Our experimental results are presented in Tables II–IV and Fig. 1. Measurements have been restricted to the *R* branches of the allowed  ${}^2\Pi_{3/2}-{}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}-{}^2\Pi_{1/2}$  subbands.

#### A. NO– $\text{N}_2$ system

The  $\gamma_{fi}$  values at room temperature reported here are in reasonable agreement with the most recent published results. Let us note however that our data are about 15% higher than those of Henry *et al.*<sup>7</sup> also obtained from high resolution measurement, but using a higher range of pressure (250 to 700 mm Hg). The same conclusion holds when considering the data of Tejwani *et al.*<sup>8</sup> ( $P_{\text{N}_2} \approx 4.8$  atm). A possible explanation of this slight discrepancy is in direct relation with the different conditions of pressure of these experiments. There seems to be no doubt that if the  $\Lambda$  components interfere in a significant manner, the resulting narrowing will be more pronounced as the pressure is more elevated.

To our knowledge, at low temperature, no data are presently available for comparison.

#### B. NO–NO system

The study has been restricted to only a few lines, this system being of minor importance for atmospheric applications. Let us note that our results obtained with  $P_{\text{NO}} = 150$  Torr, lie between those of Abels and Shaw<sup>10</sup> ( $200 < P_{\text{NO}} < 760$  Torr) and those of Mandin *et al.* ( $P_{\text{NO}} \approx 21$  Torr).<sup>11</sup> Here too the question may be raised of the possibility of an interference mechanism. However, it is difficult to go further in that analysis. Let us note, for instance, that the results of Abels and Shaw for self-broadening appear to be questionable when compared to the  $\text{N}_2$  broadening (cf. Tables II and IV). From this comparison, it seems that NO would be less effective than  $\text{N}_2$  in broadening. This is not very plausible, considering the fact that the quadrupolar interactions are higher in NO–NO than in NO– $\text{N}_2$  and that weak dipolar

TABLE IV. Observed HWHM (in  $10^{-3}$   $\text{cm}^{-1} \text{atm}^{-1}$ ) for the fundamental band of self-broadened NO (*R* branch).

<i>J</i>	$T = 295$ K				$T = 163$ K	
	Present work		Previous measurements		Present work	
	$\Pi_{3/2}-\Pi_{3/2}$	$\Pi_{1/2}-\Pi_{1/2}$	From Ref. 10	From Ref. 11 <sup>a</sup>	$\Pi_{3/2}-\Pi_{3/2}$	$\Pi_{1/2}-\Pi_{1/2}$
		$\Pi_{3/2}-\Pi_{3/2}$	$\Pi_{1/2}-\Pi_{1/2}$			
12.5	74 ± 7		56	58	87, 97	100.5 ± 9
13.5	70 ± 7		55	55	87, 97	96 ± 9
14.5	68 ± 7		55	57	88, 98	93 ± 9
15.5	68 ± 7		55	56	85, 97	91 ± 9
16.5	67 ± 7		49	47	82, 98	92 ± 9
17.5	66 ± 7	63.7 ± 7	49	42	83, 102	86 ± 9
18.5	66 ± 7	61.8 ± 6	50	45	81, 94	92 ± 9
19.5	66 ± 7	62.2 ± 6	55	46	79, 95	88 ± 9
20.5	62 ± 7	59.8 ± 6		45		
21.5	65 ± 7	61.1 ± 6		45		
22.5	65 ± 7	60.4 ± 6				
23.5		60.7 ± 7				

<sup>a</sup>*R* branch of the  ${}^2\Pi_{3/2}-{}^2\Pi_{1/2}$  (0–1) band of  ${}^{15}\text{N}{}^{16}\text{O}$ ; the results correspond, respectively, to *e–e* and *f–f* transitions. The average uncertainty is 25%.

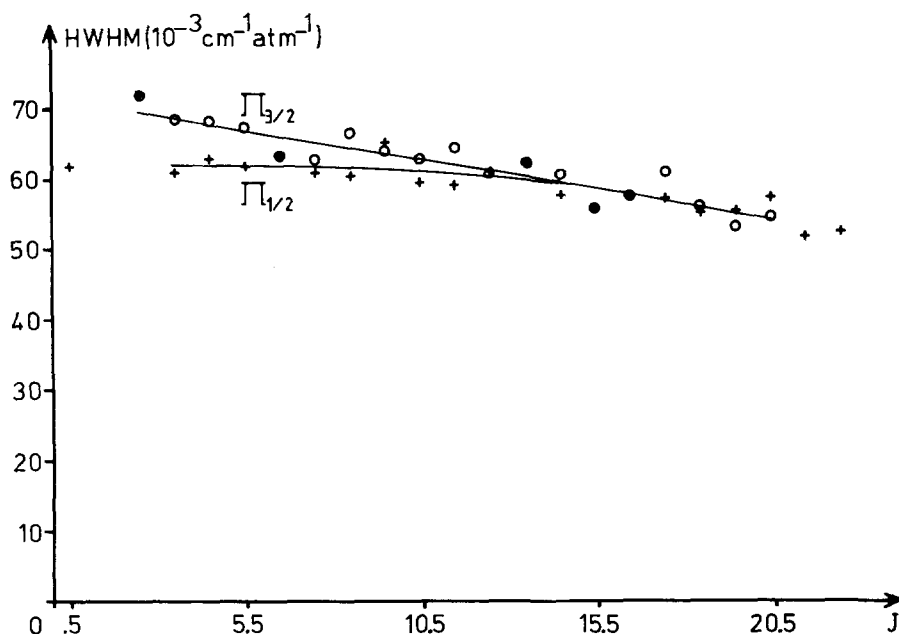


FIG. 1.  $N_2$ -broadening coefficients vs  $J$  at  $T = 295$  K. Observed values  $\circ$ :  ${}^2\Pi_{3/2}-{}^2\Pi_{3/2}$  subband;  $+$ :  ${}^2\Pi_{1/2}-{}^2\Pi_{1/2}$  subband. The straight lines are Chebyshev polynomial fits to the measurements.

interactions also contribute in pure NO broadening. Note for instance that the CO-NO linewidths have been found 10% to 15% higher than the CO- $N_2$  ones as expected.<sup>23</sup> In contrast with the results of Abels and Shaw,<sup>10</sup> our results exhibit the expected behavior, either at room or low temperature (cf. Tables II-IV, III-IV).

#### IV. THEORY

The purpose of this section is to compute the half-width at half-maximum (HWHM)  $\gamma_{fi}$  for self- and foreign-gas ( $N_2$  and  $O_2$ ) broadened NO linewidths by using the semiclassical formalism developed by Robert and Bonamy.<sup>12</sup> This theory has been successfully applied to many diatom-diatom systems in the ground  $\Sigma$  state and has been recently extended to systems in the  $\Pi$  state.<sup>24,25</sup>

The expression for the HWHM of some  $f-i$  transition is

$$\gamma_{fi} = \frac{n_b}{2\pi c} \sum_{J_2} \rho_{J_2} \int_0^\infty v f(v) dv \int_0^\infty 2\pi b db \{1 - [1 - S_{2,f_2}^{(L)}] \times \exp[-(S_{2,f_2} + S_{2,i_2} + S_{2,f_2}^{(C)})] \cos[S_{2,f_2}' - S_{2,i_2}']\},$$

where  $n_b$  is the numerical density of the perturbing gas,  $f(v)$  is the Maxwell-Boltzmann distribution of relative velocities (in practice, the velocity average is not performed and all calculations are made for the average collision velocity  $\bar{v}$ ),  $\rho_{J_2}$  is the Boltzmann distribution of the perturbing molecules,  $b$  is the impact parameter. The second order  $S_2$  contributions are dynamically related to the interaction between the colliding molecules. They aforementioned have already been defined in previous papers.<sup>12,25</sup>

In its ground state, NO is the  ${}^2\Pi$  state which splits into the two components  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  by spin-orbit interaction, with the  ${}^2\Pi_{1/2}$  levels at lower energy than the  ${}^2\Pi_{3/2}$  levels (normal structure). Moreover, the interaction between the rotational and electronic mo-

tions in the molecule produces  $\Lambda$  doubling for each  $J$  ( ${}^2\Pi_{1/2,3/2}$ ). As the coupling is intermediate between Hund's cases (a) and (b), the real wave functions are linear combinations of the symmetric top wave functions  $\psi({}^2\Pi_{1/2})$  and  $\psi({}^2\Pi_{3/2})$  corresponding to pure Hund's case (a) in which the quantum number  $K$  takes the values  $1/2$  and  $3/2$ , respectively:

$$\tilde{\psi}_{J,1/2,M} = e(J)\psi({}^2\Pi_{1/2}) + d(J)\psi({}^2\Pi_{3/2}),$$

$$\tilde{\psi}_{J,3/2,M} = e(J)\psi({}^2\Pi_{3/2}) - d(J)\psi({}^2\Pi_{1/2}).$$

As  $e(J)$  is nearly 1 [and  $d(J)$  nearly 0] provided the rotational quantum number  $J$  is not too high, Hund's case (a) may be considered as a good approximation for describing the energy levels of the NO molecule.<sup>26</sup> This comes from the fact that the constant  $A_0 = 123.2 \text{ cm}^{-1}$  which represents the magnitude of spin-orbit coupling is higher than the rotational constant  $B_0 = 1.69609 \text{ cm}^{-1}$ .<sup>27</sup> Consequently, the modifications to be brought to the theory<sup>12</sup> due to the  $\Pi$  ground state are minor in the case of NO. The rotational quantum number  $J$  is half-integer with minimum values  $J = 1/2$  or  $J = 3/2$  in the  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  states, respectively, and the Clebsch-Gordan coefficients appearing explicitly in  $S_2(b)$  (cf. Appendix C of Ref. 12) have to be replaced by those of the symmetric top.<sup>25</sup>

In this paper, we establish the temperature dependence of air-broadened NO linewidths in a temperature range of stratospheric interest. For that purpose, a comparison will be first made between measured and calculated widths for NO-NO and NO- $N_2$  systems, in order to test the model. Then  $O_2$ -broadened widths can be confidently calculated. Let us recall that the instability of the NO- $O_2$  system prevents a direct measurement of  $O_2$ -broadened widths. Thus the reliability of the calculation is of crucial importance to predict the temperature dependence of air-broadened widths. A similar study was performed by Tejwani *et al.*<sup>8</sup> in the frame of the Anderson-Tsao-Curnutte theory.<sup>28</sup> Our

TABLE V. Physical parameters characterizing the potential energy.

	$\epsilon$ (K) <sup>a</sup>	$\sigma$ (Å) <sup>a</sup>	$d_{ij}$ (kcal Å <sup>12</sup> /mol) <sup>b</sup>	$e_{ij}$ (kcal Å <sup>6</sup> /mol) <sup>b</sup>	$ r_{1i} ,  r_{2j} $ (Å) <sup>b</sup>	$Q$ (10 <sup>-26</sup> esu) <sup>c</sup>	$\mu$ (10 <sup>-18</sup> esu) <sup>c</sup>	$B_0$ (cm <sup>-1</sup> ) <sup>d</sup>
NO-NO	105.8	3.660	$d_{N-N} = 684\,988$	$e_{N-N} = 455$	$ r_{1N}  = 0.614$ $ r_{10}  = 0.537$	$Q_{NO} = -1.8$		$B_0(NO) = 1.6961$
NO-N <sub>2</sub>	118.8	3.58	$d_{N-O} = 366\,520$	$e_{N-O} = 360$	$ r_{2N}  = 0.548$	$Q_{N_2} = -1.52$	$\mu_{NO} = 0.158$	$B_0(N_2) = 2.01$
NO-O <sub>2</sub>	116.8	3.55	$d_{O-O} = 190\,829$	$e_{O-O} = 285$	$ r_{20}  = 0.603$	$Q_{O_2} = -0.39$		$B_0(O_2) = 1.4377$

<sup>a</sup>Values deduced from the calculated potential surfaces.

<sup>b</sup>Midpoint values from: M. Oobatake and T. Ooi, *Prog. Theor. Phys.* **48**, 2132 (1972).

<sup>c</sup>Recommended values from: D. E. Stogryn and A. P. Stogryn, *Mol. Phys.* **11**, 371 (1966).

<sup>d</sup>Reference 27 and G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1966).

conviction is that this theory, which may give satisfactory results for polar molecules, is no longer valid for instance for NO-O<sub>2</sub> system. Indeed, the quadrupole moment of O<sub>2</sub> being very small ( $\sim 0.4 \times 10^{-26}$  esu cm<sup>2</sup>), the straight path trajectory description is therefore unphysical. In our formalism,<sup>12</sup> the relative translation of the colliding pair takes into account the influence of the isotropic interactions on the trajectory which avoids the unphysical situation in which the molecules interpenetrate.

The remaining problem is to give a correct description of the interaction potential. For low  $J$  values, the long-range quadrupolar interactions are expected to dominate broadening (at least for self- and N<sub>2</sub> broadening), the dipole moment of NO being very weak (see Table II). A more convenient description of the potential valid for high  $J$  values and for weakly interacting molecules, such as NO-O<sub>2</sub>, consists in adding to the electrostatic interactions the so-called atom-atom interactions which include an anisotropic short-ranged

potential. The total potential is written as

$$V = V_A + V_B = \sum_{i,j} \left( \frac{d_{ij}}{r_{1i,2j}^{12}} - \frac{e_{ij}}{r_{1i,2j}^6} \right) + V_{\mu_1\mu_2} + V_{\mu_1Q_2} + V_{\mu_2Q_1} + V_{Q_1Q_2},$$

where the indices  $i$  and  $j$  refer, respectively, to the  $i$ th atom of molecule 1 and the  $j$ th of molecule 2,  $r_{1i,2j}$  is the distance between these two atoms,  $d_{ij}$  and  $e_{ij}$  are the atomic pair energy parameters, and  $\mu$  and  $Q$  are the dipolar and quadrupolar moments of the molecules. The potential may be expressed in terms of the intermolecular distance  $r$ , and of the spherical harmonics  $Y_l^m$  tied to each molecule:

$$V(r, \theta_1, \theta_2, \phi_1 - \phi_2) = 4\pi \sum_{l_1, l_2} \sum_{m=-\min(l_1, l_2)}^{\min(l_1, l_2)} u_{l_1 l_2 m}(r) \times Y_{l_1}^{m_1}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2).$$

The radial functions  $u_{l_1, l_2 m}(r)$  depend explicitly on the intramolecular distances  $r_{1i}$  and  $r_{2j}$  and on the energy

TABLE VI. HWHM (in 10<sup>-3</sup> cm<sup>-1</sup> atm<sup>-1</sup>) for the fundamental band of NO ( $R$  branch) in the <sup>2</sup>Π<sub>3/2</sub> ground state.

$J$	$T$	NO-N <sub>2</sub>				NO-NO	
		295 K		250 K	200 K	295 K	
		a	b	b	b	a	b
2.5		72	71.8	82.3	99.0	118.1	
3.5		68.4					
4.5		68.2					
5.5		67.3	66.7	76.4	92.0	110.3	
6.5		63					
7.5		62.3					
8.5		66.6	63.5	72.8	87.9	106.0	88.5
9.5		63.8					
10.5		62.3			87.7		
11.5		64.2	61.2	69.6	82.9	97.9	
12.5		60.7			90.4		74
13.5		61.8			82.3		70
14.5		60.3	57.5	64.5	74.9	86.3	68
15.5		55.4			82.3		68
16.5		57.8			86.8		67
17.5		60.8	52.5	57.7	65.2	83.2	73.0
18.5		55.7			82.5		66
19.5		53.2					66
20.5		54.2	46.7	50.3	55.2	60.1	62
22.5							65
							63.4

<sup>a</sup>Experimental values (this work).

<sup>b</sup>Calculated values.

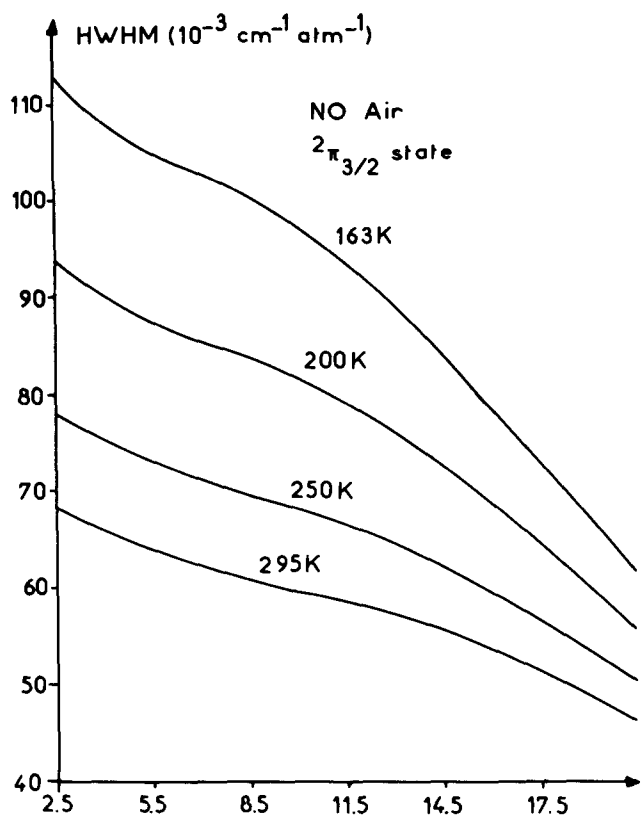


FIG. 2. Air-broadened linewidths of NO; calculated for the  ${}^2\Pi_{3/2}$  subband in the R branch of the fundamental.

parameters  $d_{ij}$  and  $e_{ij}$ . For details, see Refs. 12 and 15. The parameters used for the potential are given in Table II.

## V. RESULTS AND DISCUSSION

In a previous paper,<sup>24</sup> we focused our attention on the differential broadening between vibration-rotation lines belonging to the  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  subbands of NO perturbed by argon or nitrogen. This magnetic effect was first mentioned by Henry *et al.*<sup>7</sup> and confirmed by Rohrbeck *et al.*<sup>9</sup> and Sell<sup>6</sup> but there was not truly agree-

TABLE VII. Calculated HWHM (in  $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$ ) for the fundamental band of NO perturbed by  $\text{O}_2$  (R branch) in the  ${}^2\Pi_{3/2}$  ground state.

$J$	$T$	295 K	250 K	200 K	163 K
2.5		56.3	64.1	76.1	91.0
5.5		51.9	58.6	69.7	83.5
8.5		50.3	56.8	67.7	81.3
11.5		49.4	55.6	65.8	78.2
14.5		48.1	53.9	63.1	74.1
17.5		46.2	51.6	60.0	69.7
20.5		44.1	49.0	56.7	65.2

ment between all authors concerning the absolute magnitude of this effect. From Table II, it appears that our results corroborate those of Henry *et al.*<sup>7</sup> for  $J \leq 10.5$ . For higher  $J$  values, the effect, as deduced from our data, seems to disappear more rapidly as  $J$  increases. However the conclusion of Ref. 24 concerning the possible influence of multiquantum exchanges still holds.

In the following, the calculations will be restricted to the  ${}^2\Pi_{3/2}$ - ${}^2\Pi_{3/2}$  subband (the magnetic effect which will be disregarded, will however be kept in mind).

Our experimental results for  $\gamma_{fi}$  in the  ${}^2\Pi_{3/2}$  fundamental band are compared with the computed linewidths in Table VI. The agreement is satisfactory for  $\text{N}_2$  broadening in the range of temperatures of concern. As the quadrupolar interactions have been found to contribute dominantly to the linewidth, at least for low  $J$  values, it seems that the values chosen for the quadrupolar moments for both NO and  $\text{N}_2$  molecules (Table V) are of correct magnitude. Note that a precise estimation of these constants is of great importance as soon as one aims to predict some linewidths values for which no experimental comparison can be made (NO- $\text{O}_2$  for instance).

Computed values for  $\text{O}_2$  broadened NO linewidths are reported in Table VII. The dominant contribution in this case was found to be due to the short range anisotropic interactions mainly for the intermediate and high

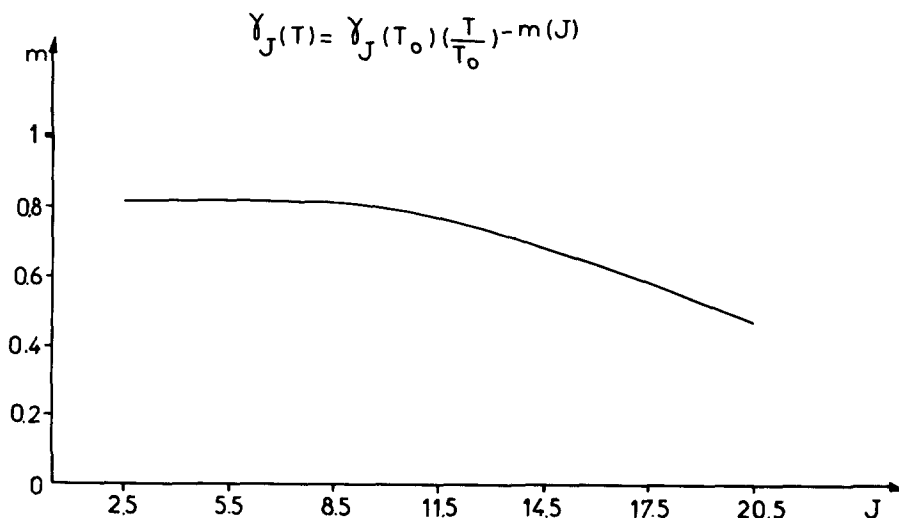


FIG. 3. Power law for the temperature dependence of air-broadened widths of NO: exponent  $m$  vs  $J$ .

$J$  values, the quadrupole–quadrupole interaction being of importance only for the low  $J$  values.

The knowledge of air-broadened linewidths of NO and their dependence on temperature is essential for atmospheric purpose. They have been calculated by using the relation<sup>8</sup>:

$$\gamma_{\text{NO-Air}} = 0.79 \gamma_{\text{NO-N}_2} + 0.21 \gamma_{\text{NO-O}_2} .$$

In Fig. 2, we show the air-broadened linewidths of NO at 163, 200, 250, and 295 K. From these results, it may appear useful to relate  $\gamma_J(T)$  (in  $\text{cm}^{-1} \text{atm}^{-1}$ ) to the experimental  $\gamma_J(T_0)$  ( $T_0$  being the room temperature) by means of the expression<sup>29</sup>:

$$\gamma_J(T) = \gamma_J(T_0) (T/T_0)^{-m(J)} .$$

The parameter  $m(J)$  is deduced from the calculations. Figure 3 shows the variation of the temperature exponent  $m(J)$  with the rotational quantum number  $J$ . This parameter varies from  $m = 0.81$  at  $J = 2.5$  to  $m = 0.47$  at  $J = 20.5$ . At low  $J$ , and in the range of temperatures of concern here (moderate values of the relative energy), the long range electrostatic interactions are more important (quadrupole–quadrupole interaction in  $r^{-5}$ ) while short range dispersion forces (in  $r^{-12}$  to  $r^{-16}$ ) dominate broadening at high  $J$  values. (Let us recall the predominant influence of  $\text{N}_2$  broadening.) Thus, the behavior of the temperature exponent curve (Fig. 3) indicates, at each  $J$  value which is the dominant interaction in the broadening mechanism. In a simple model deduced by Birnbaum from the ATC theory,<sup>30</sup> the HWHM (in  $\text{cm}^{-1} \text{atm}^{-1}$ ) depends on the temperature following the law:

$$\gamma(T) \propto T^{-[n+1/2(n-1)]} ,$$

where  $n$  is the power of  $(1/r)$  in the assumed predominant interaction potential. This leads to  $m = 0.75$  for  $n = 5$  at low  $J$  values and  $m = 0.57$  for  $n = 16$  around  $J = 20.5$ . In spite of the well-known limitations of the ATC theory the results of Fig. 3 roughly follow the above temperature law because of the *limited* range of temperature considered here ( $163 < T < 300$  K).

#### ACKNOWLEDGMENT

This research was supported by the CNRS (RCP No. 453).

- <sup>1</sup>R. D. Blatherwick, A. Goldman, D. G. Murcray, G. R. Cook, and J. W. Van Allen, *Geophys. Res. Lett.* **7**, 471 (1980).
- <sup>2</sup>*Air Pollution*, 2nd ed., edited by A. C. Stern (Academic, New York, 1968), Vol. 3, Chaps. 32–33.
- <sup>3</sup>L. Gray-Young and A. T. Young, *J. Quant. Spectrosc. Radiat. Transfer* **18**, 185 (1977).
- <sup>4</sup>A. Goldman and S. C. Schmidt, *J. Quant. Spectrosc. Radiat. Transfer* **15**, 127 (1975).
- <sup>5</sup>J. R. Gillis and A. Goldman, *Appl. Opt.* **21**, 1161 (1982).
- <sup>6</sup>J. A. Sell, *J. Quant. Spectrosc. Radiat. Transfer* **25**, 19 (1981).
- <sup>7</sup>A. Henry, F. Severin, and L. Henry, *J. Mol. Spectrosc.* **75**, 495 (1979).
- <sup>8</sup>G. D. T. Tejwani, B. M. Golden, and E. S. Yeung, *J. Chem. Phys.* **65**, 5110 (1976).
- <sup>9</sup>W. Rohrbach, R. Winter, W. Herrmann, J. Wildt, and W. Urban, *Mol. Phys.* **39**, 673 (1980).
- <sup>10</sup>L. L. Abels and J. H. Shaw, *J. Mol. Spectrosc.* **20**, 11 (1966).
- <sup>11</sup>J. Y. Mandin, C. Amiot and G. Guelachvili, *Ann. Phys.* **5**, 91 (1980).
- <sup>12</sup>D. Robert and J. Bonamy, *J. Phys.* **10**, 923 (1979).
- <sup>13</sup>G. Guelachvili, *Appl. Opt.* **17**, 1322 (1978).
- <sup>14</sup>N. Lacome, A. Levy, C. Boulet, and J. P. Houdeau, *Appl. Opt.* **21**, 2473 (1982).
- <sup>15</sup>M. Delouis, Thesis, Orsay, 1973.
- <sup>16</sup>J. Y. Mandin, Thesis, Paris, 1981.
- <sup>17</sup>M. Larvor and J. P. Houdeau, *J. Phys. E* **6**, 132 (1973).
- <sup>18</sup>C. Amiot, R. Bacis, and G. Guelachvili, *Can. J. Phys.* **56**, 251 (1978).
- <sup>19</sup>A. Valentin, J. P. Boissy, Ph. Cardinet, A. Henry, Da Wun Chen, and K. N. Rao, *J. Mol. Spectrosc.* **70**, 9 (1978).
- <sup>20</sup>R. S. Lowe, A. R. W. McKellar, and P. Veillette, *J. Mol. Spectrosc.* **88**, 372 (1981).
- <sup>21</sup>R. G. Gordon, *J. Chem. Phys.* **46**, 448 (1967).
- <sup>22</sup>K. W. Nill, F. A. Blum, A. R. Calawa, and T. C. Harman, *Chem. Phys. Lett.* **14**, 234 (1972).
- <sup>23</sup>J. P. Bouanich and C. Brodbeck, *J. Quant. Spectrosc. Radiat. Transfer* **13**, 1 (1973).
- <sup>24</sup>J. Bonamy, A. Khayar, and D. Robert, *Chem. Phys. Lett.* **83**, 539 (1981).
- <sup>25</sup>A. Khayar and J. Bonamy, *J. Quant. Spectrosc. Radiat. Transfer* **28**, 199 (1982).
- <sup>26</sup>L. Hochard-Demolliere, C. Alamichel, and Ph. Arcas, *J. Phys.* **28**, 421 (1967).
- <sup>27</sup>D. B. Keck and C. D. Hause, *J. Mol. Spectrosc.* **26**, 163 (1968).
- <sup>28</sup>P. W. Anderson, *Phys. Rev.* **76**, 647 (1949); C. J. Tsao and B. Curnutte, *J. Quant. Spectrosc. Radiat. Transfer* **2**, 41 (1962).
- <sup>29</sup>P. L. Varghese and R. K. Hanson, *J. Quant. Spectrosc. Radiat. Transfer* **26**, 339 (1981).
- <sup>30</sup>G. Birnbaum, *Adv. Chem. Phys.* **12**, 487 (1967).