FINE STRUCTURE DEPENDENCE OF THE MOLECULAR LINE-BROADENING MECHANISM. APPLICATION TO THE $^2\Pi_{1/2}$ AND $^2\Pi_{3/2}$ STATES OF NO PERTURBED BY Ar AND N_2

J. BONAMY, A. KHAYAR and D. ROBERT

*Laboratoire de Physique Moléculaire, ERA No 834, Faculté des Sciences et des Techniques,
25030 Besançon Cedex France*

Recent precise linewidth measurements show a differential broadening between vibration—rotation lines belonging to the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-bands of NO perturbed by argon or nitrogen. A semiclassical model including anisotropic short-range interactions, using bent trajectories, accounts for the effect. The mechanism causing this effect is discussed.

1. Introduction

An experimental study of the vibration—rotation linewidths of the allowed fundamental bands of nitric oxide was made some time ago by Alamichel and co-workers [1—3]. The interferometric method was not sufficiently sensitive to show a significant difference between either the corresponding lines of the diamagnetic $^2\Pi_{1/2}$ and of the paramagnetic $^2\Pi_{3/2}$ sub-bands. Nevertheless these authors suggested such a possible differential broadening which they estimated through a calculation using the Anderson theory [4,5]. But as they pointed out, such a theory is not so refined as to permit a reliable calculation of this small magnetic effect.

This experiment was reinvestigated by Tejwani et al. [6] and extended to foreign-gas perturbers (N_2 and O_2). The low-resolution spectrometer also prevented observation of any magnetic effect on the linewidths, the Λ doublet of each $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-band being not sufficiently resolved. These authors also calculated the linewidths in the Anderson frame but no attempt was made to calculate a differential broadening between the two sub-bands.

Henry et al. [7] reported the first precise measurements exhibiting the abovementioned magnetic effect for NO perturbed by argon and nitrogen. More precisely, they observed in the fundamental vibrational band an exaltation of the line-broadening coefficient, for a given rotational transition, when passing from the $^2\Pi_{1/2}$ state to the $^2\Pi_{3/2}$ one. These broadening coefficients were deduced from an analysis of high-resolution spectra obtained with a grating spectrometer.

Such results were confirmed by Rohrbeck et al. [8] with two different techniques, by conventional absorption spectroscopy as in ref. [7] using a tunable spin-flip Raman-laser spectrometer, and by Zeeman modulation spectroscopy.

A reliable calculation aiming to account for such a small magnetic effect on the line broadening needs a theory including a realistic description of the close collisions for NO—N_2 and a fortiori for NO—Ar. Indeed for these molecular pairs, the close collisions are very efficient for high rotational levels due to the absence of significant dipolar interaction. A convenient formalism taking into account the short-range interactions has been proposed [9]. The present paper is devoted to an a priori calculation of the line-broadening coefficients for NO—Ar and NO—N_2 in the two $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-bands starting from the theoretical approach of ref. [9] but adapted to the specific NO case.

2. Results and discussion

The semiclassical theory for the present linewidth γ_{fi} calculation for a $v_f J_f \leftarrow v_i J_i$ transition has been developed in ref. [9] where the corresponding analytical expression may be found. This expression allows a realistic estimation of γ_{fi} avoiding any cut-off procedure

by including the anisotropic short-range interaction potential and by using bent trajectories No a priori determination of the anisotropic potential energy is available for NO—Ar and NO—N$_2$ So we have represented it by the superposition of the atom—atom model [10] and of the multipolar interactions (dipole—quadrupole $V_{\mu_1 Q_2}$ and quadrupole—quadrupole $V_{Q_1 Q_2}$). Such a representation has been successfully applied to broadening for several gas mixtures [9,11]. The characteristic parameters tied to these potentials are given in table 1 Figs. 1a and 1b exhibit the behaviour of these potential surfaces for NO—Ar and NO—N$_2$ through the radial dependence of $U_{l_1 l_2 m}(r)$ defined by eq. (33) of ref. [9].

Recall that the electronic ground state of the NO molecule is a $^2\Pi$ state because of an unpaired electron So the expression for γ_{f_i} given in ref [9] for diatomic molecules in a Σ state must be modified to take into account the change of the vibration—rotation states Indeed, the absolute value of the component of the electronic orbital angular momentum along the internuclear axis ($\Lambda = 1$) is strongly coupled to the corresponding spin angular momentum component ($\Sigma = \pm 1/2$). The resulting component for the total electronic angular momentum Ω is 1/2 and 3/2. The $\Lambda-\Sigma$ coupling for NO is intermediate between Hund's cases (a) and (b) [1,2]. The energy level expressions and the wavefunctions for the $^2\Pi$ state of NO were taken from refs [16, 17] Moreover, each level (J, K) is split in a Λ doublet due to the coupling between the rotation of the molecule and the orbital motion of the electrons. Of course the transitions induced by collisions between the various vibration—rotation states in a $^2\Pi$ sub-band must satisfy the usual symmetry rules [14].

The calculated values for the half-width at half intensity γ_{f_i} are given in tables 2 and 3 together with the available experimental data Good consistency is obtained for the observed transitions of both molecular pairs NO—Ar and NO—N$_2$ In particular the increase of γ_{f_i} when passing from the diamagnetic $^2\Pi_{1/2}$ sub-band to the paramagnetic $^2\Pi_{3/2}$ one is reproduced. This differential broadening which is maximum for transitions between low rotational levels vanishes for high rotational ones in accord with the observed behaviour [7] The calculations were made with several sets of energy parameters for the N atom in the NO molecule as it is impossible to decide which ones are better at the present stage [13]. All results are however very close for NO—N$_2$, the maximum difference with respect to results

presented in table 3 being 4% for $J_i = 39/2$. On the contrary, for NO—Ar, only one set of parameters (see table 1) gives results in good accord with experiment. It is interesting to analyze the physical mechanism underlying such behaviour.

For simplicity we first discuss the NO—Ar case. Details of the calculation make it appear that the most efficient collisions are due to the second-order contribution V_2 in the anisotropic potential, mainly through the repulsive part of the corresponding $U_{200}(r)$ coefficient. This is easily understood from fig. 1a since, for all intermolecular distances r, the first-order coefficient $U_{100}(r)$ is less intense than $U_{200}(r)$. In order to present a qualitative analysis of the magnetic effect on the line broadening, only transitions for which the resonance factor argument is nearly zero are considered. Indeed, for low J_i values, all the induced transitions are quasi-resonant due to the low rotational constant of NO (cf table 1) except the transitions induced between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states, but their contribution was found to be negligible Note, concerning the line broadening, that the NO states may be described by symmetric-top wavefunctions ψ_{JKM} with $K = \Omega = 1/2$ and 3/2 for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ electronic states respectively, corresponding to Hund's pure case (a) coupling. This argument no longer stands if one considers the positions or intensities of the rotation lines for which the intermediate coupling description is necessary, especially for high J values. This leads for $^{2,0}S_2[r_c(b)]$ (cf. appendix C of ref. [9]), which is the major contribution to the differential collision cross section, to

$$^{2,0}S_2[r_c(b)] = \tfrac{9675}{5760}(\pi/\hbar v_c')^2$$

$$\times \left\{ \left(\sum_{ij} r_{1i}^2 e_{ij} \right)^2 r_c^{-14}[(2 + D^{(2)})f_8^8(0)] \right.$$

$$- \tfrac{9471}{1720}\left(\sum_{ij} r_{1i}^2 e_{ij} \right)\left(\sum_{ij} r_{1i}^2 d_{ij} \right) r_c^{-20}[(2 + D^{(2)})f_8^{14}(0)]$$

$$\left. + \tfrac{8377677}{1100800}\left(\sum_{ij} r_{1i}^2 d_{ij} \right)^2 r_c^{-26}[(2 + D^{(2)})f_{14}^{14}(0)] \right\} . (1)$$

In this equation r_c and v_c' are parameters tied to the bent trajectory [9] (instead of b and v for a linear trajectory described at constant velocity), r_{1i}, e_{ij} and d_{ij} characterize the atom—atom potential (cf. table 1). The resonance functions $f_n^m(k)$ are defined in appendix A of ref. [9] and are not equal to unity for exact reso-

Table 1
Physical parameters characterizing the NO–Ar and NO–N$_2$ potential energy a)

$$V = V_A + V_E = \sum_{i,j} (d_{ij}/r_{1i,2j}^{12} - c_{ij}/r_{1i,2j}^{6}) + V_{\mu_1 Q_2} + V_{Q_1 Q_2} = 4\pi \sum_{l_1,l_2} \sum_{m=-\inf(l_1,l_2)}^{+\inf(l_1,l_2)} U_{l_1 l_2 m}(r)\, Y_{l_1}^{m}(\theta_1,\varphi_1)\, Y_{l_2}^{-m}(\theta_2,\varphi_2)$$

	ϵ (K) b)	σ (Å) b)	d_{ij} (kcal Å^{12}/mole) c)	e_{ij} (kcal Å^{6}/mole) c)	$|r_{1j}|$, $|r_{2j}|$ (Å) d)	Q (10^{-26} esu) e)	u (10^{-18} csu) e)	B_0 (cm^{-1}) d)
NO–Ar	112 8 (119 4)	3.575 (3 44)	d_{N-Ar} = 1258592 d_{O-Ar} = 912783	e_{N-Ar} = 822 e_{O-Ar} = 746				
NO–N$_2$	118 8 (104.1)	3 578 (3.575)	d_{N-N} = 418679 d_{O-N} = 386754	e_{N-N} = 360 e_{O-N} = 367	$|r_{1N}|$ = 0.614 $|r_{1O}|$ = 0 537 $|r_{2N}|$ = 0 547	Q_{NO} = −1 8 Q_{N_2} = −1 52	μ_{NO} = 0 158	$B_0(NO)$ = 1.6961 $B_0(N_2)$ = 2.01

a) Note that no vibrational constant has been reported in this table due to the negligible dependence of the line-broadening coefficient on the vibrational states for NO (cf ref. [9] for similar cases) This effect has been disregarded in the present calculations
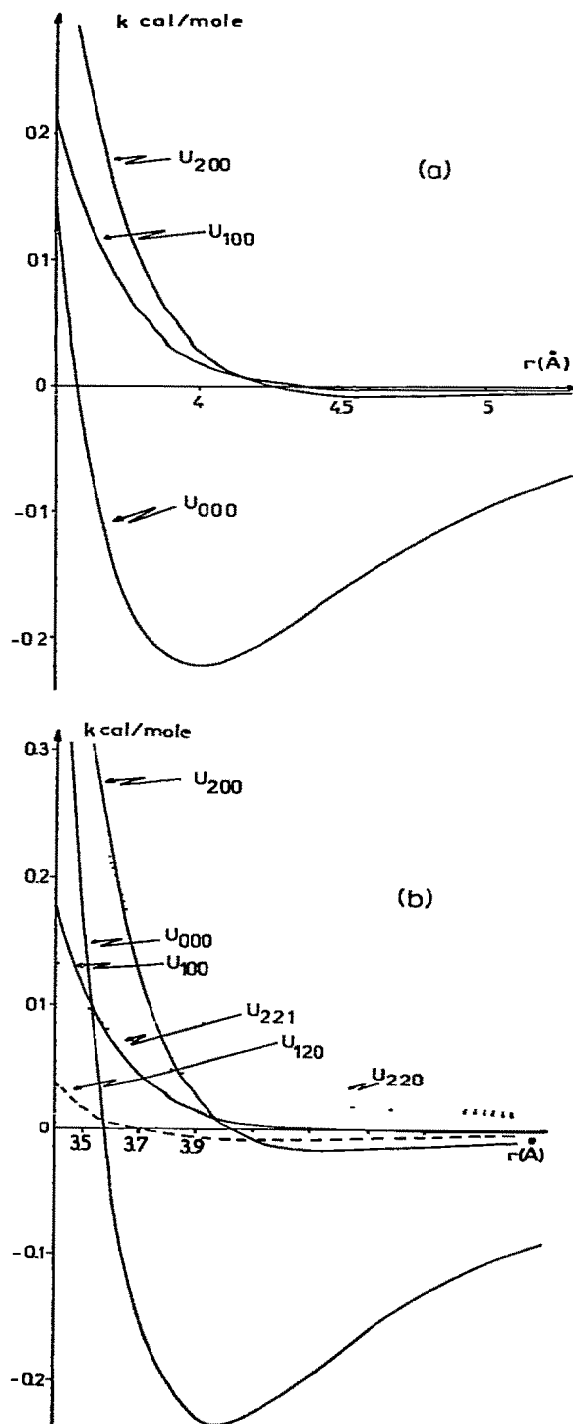b) Values deduced from figs 1a and 1b, and from ref. [12] (..) c) Refs. [12,13]. d) Ref. [14]. e) Ref [15]

Fig 1.

Table 2

Calculated and observed values for the NO–Ar half-width at half intensity γ_{fi} in the R branch (in 10^{-3} cm^{-1} atm^{-1})

J_1	$K = 1/2$			$K = 3/2$		
	a)	b)	c)	a)	b)	c)
1/2	48 7	55 6	55	–	–	–
3/2	47.2	–	(51 5)	47 4	–	–
5/2	46.3	–	(48 5)	47.5	–	–
7/2	45 5	–	45 5	46 5	–	51
9/2	44 9	51 7	(43 5)	45 6	57 3	(49)
11/2	44 5	–	(42)	45	–	(47)
13/2	44 2	–	(39 5)	44 5	–	(45 5)
15/2	43 8	–	(37)	44 1	–	(42 5)
17/2	43 4	–	(36 5)	43 6	–	(42)
19/2	42 8	–	(36)	43	–	(41)
21/2	42 1	–	35 5	42 3	–	40
23/2	41 4	–	(35)	41 6	–	(39 5)
25/2	40 6	–	(35)	40 8	–	(39)
27/2	39 8	–	(35)	40	–	(38)
29/2	39	–	(35)	39 2	–	(37)
31/2	38 2	–	34 5	38 4	–	36 5
33/2	37 3	–	(34 5)	37 5	–	(36)
35/2	36 5	–	(34 5)	36 7	–	(35 5)
37/2	35 7	–	(34)	35 9	–	(35 5)
39/2	34 9	–	(33 5)	35 1	–	(35)
41/2	34 1	–	32	34 2	–	33

a) Calculated values [this work. in Hund's case (a)]
b) Experimental values from ref [8].
c) Experimental values from ref [7] Most of the reported values ( ) have been interpolated from fig 1 of ref [7] The experimental error is $\approx 5\%$

nance due to their dependence on r_c and $v_c'^+$. In eq. (1) the dependence of $^{2,0}S_2[r_c(b)]$ on the optical rotational quantum numbers (J_1 and J_f) appears only through the $D^{(n)}$ factor for $n = 2$ defined by

$$D^{(n)} = (-1)^{J_1 + J_f} 2[(2J_1 + 1)(2J_f + 1)$$
$$\times C(J_1 n J_1, K\ 0\ K)^2 C(J_f n J_f; K\ 0\ K)^2]^{1/2}$$
$$\times W(J_1 J_f J_1 J_f, 1n) \qquad (2)$$

In eq (2) only the Clebsch–Gordan coefficients C depend on the electronic state through the quantum number $K \equiv \Omega = 1/2$ or $3/2$, the Racah coefficient W being K independent. Thus. the variation of the broadening coefficient between the two sub-bands for a given rotational line $J_1 \to J_f$ results from the dependence of $C(J_1\ 2\ J_1, K\ 0\ K)C(J_f\ 2\ J_f, K\ 0\ K)$ on K Table 4 shows the calculated values of $D^{(n)}$ ($n = 1$ and 2) versus J_1 and K for the R branch. As clearly seen in table 4b. the algebraic $D^{(2)}$ values are substantially higher for $K = 3/2$ than for $K = 1/2$ for low J_1 values (by a factor 4 for $J_1 = 3/2$) This difference is less and less important as J_1 increases. As a result of this variation of $D^{(2)}$ versus J_1 and K, the $^{2,0}S_2[r_c(b)]$ contribution to the differential collision cross section

± In ref [9] the resonance function $f_p^D(0)$ has been systematically omitted as a product factor of D in the $^{2,0}S[r_c(b)]$ contribution This error was a typographical omission and was not present in the computational program

Table 3

Calculated and observed values for the NO–N$_2$ half-width at half intensity γ_{fi} in the R branch (in 10^{-3} cm^{-1} atm^{-1})

J_1	$K = 1/2$						$K = 3/2$					
	a)	b)	c)	d)	e)	f)	a)	b)	c)	d)	e)	f)
1/2	68.5	60 1	71 0	65.0	65 0	–	–	–	–	–	–	–
5/2	66.1	54 8	–	–	–	–	68 4	59 3	–	–	–	–
9/2	63 9	51 5	–	58 1	(50)	–	65 8	54 7	–	59 9	(55)	–
19/2	59 4	44.0	–	–	(49.5)	55.0	60 3	45.5	–	–	(54)	60 0
21/2	58 6	42.6	–	–	49 5	–	59 4	43 9	–	–	54	–
33/2	49 4	29 4	52 0	–	(49)	–	50 2	30 3	52 0	–	(52)	–
41/2	39 9	19 3	–	–	46	–	40 7	20 0	–	–	47	–

a) Calculated values (this work) with atom–atom + electrostatic $V_{\mu_1 Q_2}$ and $V_{Q_1 Q_2}$ interactions
b) Calculated values (this work) with *only* the electrostatic interactions
c) Experimental values from ref [6] in which the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components having the same J_1 are assumed to have identical half widths
d) Experimental values from ref. [8]
e) Experimental values from ref [7] Some of the reported values ( ) have been interpolated from fig. 1 of ref. [7]
f) Experimental value from ref [18].

Table 4

Dependence of $D^{(n)}$ on J_i in the R branch for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-bands

	J_i	W	$C_{J_i}C_{J_f}$		$D^{(n)}$	
			$K = 1/2$	$K = 3/2$	$K = 1/2$	$K = 3/2$
(a) $n = 1$	1/2	0 2635	0 1491	–	−0.2222	–
	3/2	0 1870	0 0437	0 3928	−0 0801	−0.7197
	5/2	0 1383	0 0213	0 1917	−0 0408	−0.3674
	7/2	0.1090	0 0127	0.1140	−0 0248	−0 2223
	9/2	0 0898	0.0084	0 0756	−0 0165	−0.1487
	11/2	0.0762	0.0060	0.0539	−0.0119	−0.1065
	13/2	0 0662	0 0045	0 0404	−0.0089	−0 0801
	21/2	0 0434	0 0019	0 0171	−0.0038	−0 0341
	33/2	0 0285	0 0008	0.0073	−0 0016	−0 0146
	41/2	0.0232	0.0005	0 0048	−0.0010	−0 0096
(b) $n = 2$	1/2	0	0	–	0	–
	3/2	0.1528	0.2138	0 0535	−0 3201	−0.0801
	5/2	0 1263	0 2333	0.0350	−0 4083	−0.0613
	7/2	0 1034	0 2402	0.1081	−0 4443	−0.1999
	9/2	0 0867	0.2436	0.1514	−0 4627	−0.2876
	11/2	0.0744	0.2455	0.1779	−0 4735	−0.3431
	13/2	0 0650	0 2437	0.2029	−0.4742	−0.3948
	21/2	0.0430	0 2457	0.2345	−0.4855	−0 4634
	33/2	0 0284	0.2482	0.2433	−0.4932	−0.4835
	41/2	0 0232	0 2487	0 2455	−0.4961	−0.4897

is higher for the vibration–rotation lines belonging to the $^2\Pi_{3/2}$ sub-band than for those belonging to $^2\Pi_{1/2}$ (cf. eq. (1) and table 4b), in good accord with the observed behaviour.

Note here that the $D^{(1)}$ coefficients (cf. table 4a) decrease from $K = 1/2$ to $K = 3/2$ (for a given J_i value) in opposition to $D^{(2)}$. Thus the $^{1,0}S[r_c(b)]$ contribution resulting from the first-order V_1 term in the anisotropic potential hides partially the differential broadening considered here. However the V_1 contribution is small (cf. fig 1a). It appears from the above considerations that the magnitude of this differential broadening between the two sub-bands is connected to the relative contributions of the even and odd spherical harmonics in the intermolecular anisotropic potential (cf. footnote to table 1). Moreover, all the K dependence comes from the $\Delta J = 0$ transitions through the $D^{(n)}$ term. For $n = 1$, these are the induced transitions between the Λ doublets and for $n = 2$, they are elastic transitions. The result of the calculation is that all the $\Delta J = 0$ induced transitions contribute to the broadening by a very small amount (cf. tables 2 and 3).

The above discussion for NO–Ar may easily be ex-
tended to NO–N$_2$. For low J_i values, the electrostatic $V_{\mu_1 Q_2}$ and $V_{Q_1 Q_2}$ interactions dominate the broadening mechanism (cf. table 3). The $V_{\mu_1 Q_2}$ and $V_{Q_1 Q_2}$ potentials would exhibit the same behaviour as V_1 and V_2 respectively. So, the quadrupole–quadrupole interaction, being predominant due to the weak dipole moment of NO (cf. table 1), introduces a differential broadening between the two sub-bands as observed experimentally. In table 3 we report the calculated values including the two abovementioned electrostatic potentials with and without considering the anisotropic atom–atom potential contributions. As may be seen in table 3, these two sets of values exhibit an increasing difference as J_i increases. Recall that all these values are calculated using bent trajectories [9]. Note at this point that a similar calculation performed with straight-line trajectories described at constant velocities and only taking into account the long-range multipolar interactions leads to values closer to the (a) set (cf. ref. [6]). But close collisions are dominant for high J_i values. Thus the last classical trajectory model becomes unrealistic and the corresponding calculated values lose their physical meaning.

Although overall agreement is obtained between the present linwidth calculations and the experimental data, the quantitative differential broadening is discussed further. Indeed, while a number of authors have confirmed the existence of such a differential effect [7,8,18], different values for its amplitude have been measured (for NO–N_2 and $J_i = 9/2$, the experimental effect varies between 3% [8] and 10% [7], the calculated one being 3%). Nevertheless for NO–Ar, if the measured absolute values are significantly different (cf. table 2), the relative differential effect is the same ($\approx 11\%$ for $J_i = 7/2$, the calculated one being 2%). Our calculated values seem to underestimate the differential broadening so the following points are considered. On the one hand, as explained above, the relative contribution of the even and odd components to the anisotropic intermolecular potential appears as determinative for such an effect and the present potential model suffers some uncertainty for NO [13]. On the other hand, the calculation model does not take into account the possible influence of the nature of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ sub-bands for hard collisions (i.e. for impact parameters lower than the kinetic diameter), all the K dependence coming from the weak collisions [cf. eqs. (1) and (2)]. Indeed this model does not include the multiquantum exchanges [9] which may be of importance for hard collisions. A more elaborate model including such exchanges like that of ref. [19], available for the diatom–atom case, might be used to re-examine this point for NO–Ar.

3. Conclusion

The present calculated values and the experimental ones (tables 2 and 3) compare well. More precisely the ne-broadening coefficient γ_{fi} exhibits the correct dedence on the initial rotational quantum number J_i .id the observed increase of the line broadening for a given vibration–rotation line when going from the dia-

magnetic $^2\Pi_{1/2}$ to the paramagnetic $^2\Pi_{3/2}$ is reproduced. The mechanism causing this differential effect has been studied in the present paper. It results for NO–Ar and NO–N_2 from the elastic transitions induced by collisions in the initial and final optical states ($J_i \to J_i; J_f \to J_f$) which depend strongly on the electronic state for low J_i values (cf. table 4).

References

[1] C. Alamichel, Thesis, Paris (1965).

[2] C. Alamichel, J. Phys. 27 (1966) 345.

[3] L. Hochard-Demolliere, C. Alamichel and Ph. Arcas, J. Phys. 28 (1967) 421.

[4] P.W. Anderson, Phys. Rev. 76 (1949) 647.

[5] C.J. Tsao and B. Curnutte, J. Quant. Spectry. Radiative Transfer 2 (1962) 41.

[6] G.D.T. Tejwani, B.M. Golden and E.S. Yeung, J. Chem. Phys. 65 (1976) 5110.

[7] A. Henry, F. Severin and L. Henry, J. Mol. Spectry. 75 (1979) 495.

[8] N. Rohrbeck, R. Winter, W. Herrmann, J. Wildt and W. Urban, Mol. Phys. 39 (1980) 673.

[9] D. Robert and J. Bonamy, J. Phys. 40 (1979) 923.

[10] T.B. Macrury, W.A. Steele and B.J. Berne, J. Chem. Phys. 64 (1976) 1288.

[11] A. Khayar and J. Bonamy, J. Quant. Spectry. Radiative Transfer, to be submitted for publication.

[12] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids, 4th Ed. (Wiley, New York, 1967).

[13] M. Oobatake and T. Ooi, Progr. Theoret. Phys. 48 (1972) 2132.

[14] G. Herzberg, Spectra of diatomic molecules (Van Nostrand, Princeton, 1966).

[15] D.E. Stogryn and A.P. Stogryn, Mol. Phys. 11 (1966) 371.

[16] A. Goldman and S.C. Schmidt, J. Quant. Spectry. Radiative Transfer 15 (1975) 127.

[17] J.A. Miller, C.F. Coll and C.F. Melius, J. Quant. Spectry. Radiative Transfer 21 (1979) 193.

[18] J.A. Sell, J. Quant. Spectry. Radiative Transfer 25 (1981) 19.

[19] E.W. Smith, M. Giraud and J. Cooper, J. Chem. Phys. 65 (1976) 1256.