Multichannel quantum defect theory analysis of the Rydberg spectrum of Na₂

M. Ch. Bordas, M. Broyer, J. Chevalere, P. Labastie, S. Martin

► To cite this version:

M. Ch. Bordas, M. Broyer, J. Chevalere, P. Labastie, S. Martin. Multichannel quantum defect theory analysis of the Rydberg spectrum of Na₂. Journal de Physique, 1985, 46 (1), pp.27-38. 10.1051/jphys:0198500460102700 . jpa-00209943

HAL Id: jpa-00209943

<https://hal.science/jpa-00209943>

Submitted on 1 Jan 1985

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

33.80E — 33.80K — 33.10

Multichannel quantum defect theory analysis of the Rydberg spectrum of Na₂

M. Ch. Bordas, M. Broyer, J. Chevalere, P. Labastie and S. Martin

Laboratoire de Spectrométrie Ionique et Moléculaire (*), Université Lyon I,
Campus de La Doua, 69622 Villeurbanne Cedex, France

(Reçu le 26 juin 1984, accepté le 25 septembre 1984)

Résumé. — Les séries de Rydberg *ns* et *nd* de la molécule Na₂ ont été excitées par double résonance optique pour $15 < n < 80$ et $4 < J < 45$. Les spectres observés sont analysés par la théorie du défaut quantique à plusieurs voies. Les énergies et les intensités de toutes les raies mesurées expérimentalement sont calculées théoriquement en utilisant comme paramètres les défauts quantiques des différentes raies et les constantes moléculaires de l'ion. L'accord entre les raies théoriques et expérimentales est remarquable et les principaux effets observés dans les spectres sont interprétés par une image physique simple (effet stroboscopique). L'éventualité d'un mélange s-d est également envisagée et on montre qu'il est négligeable à la précision de nos mesures. Finalement des quasi-profiles de Fano sont observés pour les très grandes valeurs de *J*.

Abstract. — The *ns* and *nd* Na₂ Rydberg states have been excited by Optical-Optical Double Resonance for $15 < n < 80$ and $4 < J < 45$. The observed spectra are analysed in terms of the Multi-Channel Quantum Defect Theory. The intensities and the energies of all the measured lines are theoretically calculated using as parameters the quantum defects of the various series and the molecular constants of the Na₂⁺ ion. The agreement between experimental and theoretical lines is remarkable and the main effects observed in the spectra are interpreted by a simple physical picture (stroboscopic effect). The possibility of s-d mixing is also investigated and we show that it can be neglected within the accuracy of our measurement.

1. Introduction.

Since the pioneering work of Schawlow [1], numerous experiments have demonstrated that Rydberg spectra of molecules could be observed by laser optical-optical double resonance (O.O.D.R.). The Rydberg states of Na₂ [1-4], NO [5], K₂ [6, 7], Li₂ [8, 9] have been studied using this method. In a recent paper [10], we have reported observation of Na₂ Rydberg states for very high *n* values up to *n* = 70. This enabled us to study the *l*-uncoupling occurring in the *ns* and *nd* series as a function of the rotational quantum number *J*. A perturbative model was developed to treat this phenomenon and appeared sufficient to interpret the main features of the spectra. However, this model was not able to reproduce the observed intensity of all the lines, and moreover, it is completely unable to treat the interaction of a Rydberg series with an other one at high *n* values (quasi continuum), or with a real continuum. As demonstrated by Fano in a famous paper on H₂ [11],

these Rydberg spectra must be analysed by the multichannel quantum defect theory (M.Q.D.T.) introduced for atoms by Seaton [12]. This theory has then proved to be greatly efficient for treating various problems in H₂ [13, 14] and NO [15]. In this paper we present a M.Q.D.T. analysis of Na₂ Rydberg spectra. Section 2 is devoted to the theoretical calculation, and section 3 to the experimental results.

2. M.Q.D.T. applied to Na₂.

2.1 M.Q.D.T. IN MOLECULES. — In molecular Rydberg states, when the energy is high enough, the electron velocity can become smaller than the nuclear velocity, so that the Born-Oppenheimer (B.O.) approximation is no longer valid. This effect could be treated by a perturbative model in a B.O. basis set, but the great number of levels involved in Rydberg series leads to a complicated calculation. This difficulty can be overcome by M.Q.D.T.

M.Q.D.T. takes advantage of the fact that the potential seen by the optical electron is Coulombic at sufficiently large distances from the ionic core.

(*) L.A. CNRS n° 171.

In fact, in this region, the wavefunction can be expanded in terms of products of an ionic core state function $|vN^+\rangle$ with a Coulombic function of the outer electron variables $Y_m^l(\theta, \phi) M_{v(v, N^+)} l(r)$. Here, v is the vibrational quantum number of the ion, N^+ its angular momentum, $v(v, N^+)$ is the principal quantum number of the electron defined as

$$E = E_{vN^+} - \frac{Ry}{[v(v, N^+)]^2} \quad (1)$$

where Ry is the Rydberg constant, E is the total energy and E_{vN^+} is that of the ion, namely,

$$E_{vN^+} = T_\infty(v) + B^+(v) N^+(N^+ + 1). \quad (1')$$

$B^+(v)$ and $T_\infty(v)$ are respectively the rotational constant and the vibrational term of the ion. Notice that this form of the wavefunction corresponds to Hund's case d coupling.

On the other hand, at small distances from the core, the electron motion is strongly coupled to that of the nuclei, and the B.O. approximation applies. This means that the internuclear distance R is a good quantum number and that A , the projection of l onto the internuclear axis, is also a good quantum number. The wavefunction is then a sum of terms $\psi_{iAR}(\text{el}) |R\rangle |JM - A\rangle$ where J is the total angular momentum and i is a collective name for the other quantum numbers of the state.

One has now to connect the wavefunctions inside and outside the core. First of all, the angular parts of the functions are connected by a transformation matrix U . The radial parts of the nuclear wavefunctions are connected by the wavefunction $\langle R | v \rangle$. The radial part of the electron wavefunction is only needed outside the core. In this region, M.Q.D.T. shows that this function is phase shifted relative to the function of same energy without core. This phase shift is a real one at $E > E_{vN^+}$ when the electron can go to infinity, and is noted $\pi\mu_{iA}(R)$. For $E < E_{vN^+}$ (closed channel), the phase shift affects the coefficient of the rising exponential at infinity, which is

$\sin \pi v(v, N^+)$ without core; it is now

$$\sin \pi [v(v, N^+) + \mu_{iA}(R)]$$

(for details, the readers are referred to the papers by Seaton [12] and Greene *et al.* [16]).

The wavefunction obtained is a linear combination of the B.O. basis set. The important fact here is that the summation over all the Rydberg states has been implicitly performed, thus eliminating the difficulties of standard perturbation theory (see also Fano [11]).

Another advantage comes from the fact that the quantum defects $\mu_{iA}(R)$ can be generally considered as energy-independent in a first approximation. In fact, in our treatment, we assume that the quantum defects are energy-independent, in agreement with our experimental results.

2.2 THE TRANSFORMATION MATRIX U . — We will limit ourselves to the discrete case and will not consider the vibrational coupling here. This coupling, which is responsible for some of the autoionization processes, is assumed to introduce a negligible shift of the energy levels.

We therefore assume that the μ_{iA} 's are R independent and we disregard vibration. With these assumptions, all the v_{N^+} considered are real quantities and we are in the case

$$E < E_{vN^+} = T_\infty(v) + B^+ N^+(N^+ + 1).$$

If l was a good quantum number, the U matrix would reduce to the familiar transformation matrix from Hund's case a to Hund's case d, which is known for singlet states by standard Racah algebra :

$$U_{AN^+}^{(J)}(l) = \langle lJN^+ 0 | lAJ - A \rangle. \quad (2)$$

For $l = 0$, corresponding to the series $ns^1\Sigma_g^+$:

$$U_{0N^+}^{(J)}(l = 0) = \delta_{JN^+}. \quad (3)$$

For $l = 2$, the matrix splits into two sub-matrix corresponding to the series of $+$ or $-$ symmetry.

For series $nd^1\Sigma_g^+$, $nd^1\Pi_g^+$, $nd^1\Delta_g^+$, the U matrix is :

$$U_{AN^+}^{(J,+)}(l=2) = \begin{array}{c|ccc} & N^+ & & \\ \hline A & & J-2 & J & J+2 \\ \hline 0 & \sqrt{\frac{3J(J-1)}{2(4J^2-1)}} & -\sqrt{\frac{J(J+1)}{(2J-1)(2J+3)}} & \sqrt{\frac{3(J+1)(J+2)}{2(2J+1)(2J+3)}} \\ \hline 1 & \sqrt{\frac{2(J^2-1)}{4J^2-1}} & -\sqrt{\frac{3}{(2J-1)(2J+3)}} & -\sqrt{\frac{2J(J+2)}{(2J+1)(2J+3)}} \\ \hline 2 & \sqrt{\frac{(J+1)(J+2)}{2(4J^2-1)}} & \sqrt{\frac{3(J-1)(J+2)}{(2J-1)(2J+3)}} & \sqrt{\frac{J(J-1)}{2(2J+1)(2J+3)}} \end{array} \quad (4)$$

For the series $nd\ ^1\Pi_g^-$ and $nd\ ^1\Delta_g^-$, we have :

$$U_{AN^+}^{(J;-)}(l=2) = \begin{array}{c|cc} & N^+ & \\ \hline A & & \\ \hline & J-1 & J+1 \\ \hline 1 & \sqrt{\frac{J-1}{2J+1}} & -\sqrt{\frac{J+2}{2J+1}} \\ \hline 2 & \sqrt{\frac{J+2}{2J+1}} & \sqrt{\frac{J-1}{2J+1}} \end{array} \quad (5)$$

Actually, the potential experienced by the Rydberg electron is not spherically symmetric, so that l is not strictly a good quantum number. We therefore have to take into account mixing between different l series of same symmetry.

In Na₂, the Rydberg states converging towards the Na₂⁺ X²Σ_g⁺ state are of g-symmetry for even l values (s, d, g...) and of u-symmetry for odd l values (p, f...). If we consider the four series ($ns\ ^1\Sigma_g^+$, $nd\ ^1\Sigma_g^+$, $nd\ ^1\Pi_g$, $nd\ ^1\Delta_g$) observed in Na₂ [10], s-d or d-g mixing can occur for $^1\Sigma_g^+$ series and d-g mixing for $^1\Pi_g$ and $^1\Delta_g$ series. However, the g series are not seen in our experiment, indicating that coupling to these series is weak. We therefore consider only s-d mixing, which may be important, as shown for the NO molecule [17].

The core state $|i\Sigma_g^+ J\rangle$ is taken as a combination of s or d state

$$\begin{aligned} |\Sigma_1^+\rangle &= c_1 |s\Sigma^+\rangle - c_2 |d\Sigma^+\rangle \\ |\Sigma_2^+\rangle &= c_2 |s\Sigma^+\rangle + c_1 |d\Sigma^+\rangle \end{aligned} \quad (6)$$

with $|c_1|^2 + |c_2|^2 = 1$
and the matrix (4) becomes

$$U_{iA;IN^+}^{(J,+)} = \begin{array}{c|ccccc} & l; N^+ & & & & \\ \hline i; A & & 0; J & 2; J-2 & 2; J & 2; J+2 \\ \hline 1; 0 & c_1 & -c_2 U_{0,J-2}^{(J,+)}(l=2) & -c_2 U_{0,J}^{(J,+)}(l=2) & -c_2 U_{0,J+2}^{(J,+)}(l=2) \\ \hline 2; 0 & c_2 & c_1 U_{0,J-2}^{(J,+)}(l=2) & c_1 U_{0,J}^{(J,+)}(l=2) & c_1 U_{0,J+2}^{(J,+)}(l=2) \\ \hline 1 & 0 & U_{1,J-2}^{(J,+)}(l=2) & U_{1,J}^{(J,+)}(l=2) & U_{1,J+2}^{(J,+)}(l=2) \\ \hline 2 & 0 & U_{2,J-2}^{(J,+)}(l=2) & U_{2,J}^{(J,+)}(l=2) & U_{2,J+2}^{(J,+)}(l=2) \end{array} \quad (7)$$

2.3 EIGENFUNCTIONS AND ENERGY LEVELS.

2.3.1 Fundamental equation. — As explained in paragraph 2.A, each function $\psi_{iA}(\text{el}) |JM - A\rangle$ in the core is connected to the function

$$\sum_{IN^+} U_{iA;IN^+}^{(J)} M_{v_{N^+},l}(r) |IN^+ JM\rangle$$

outside, and the coefficient of rising exponential at infinity in $M_{v_{N^+},l}(r)$ is proportional to $\sin \pi[v(N^+) + \mu_{iA}]$.

The eigenfunctions will be a combination $\sum_{iA} A_{iA} \psi_{iA}(\text{el}) |JM - A\rangle$ and the coefficient of rising exponentials must vanish to satisfy the conditions $\psi = 0$ at infinity. Hence, for a given J -value, the A_{iA} coefficients are solutions of the following system :

$$\sum_{iA} U_{iA;N^+}^{(J)} \sin \{ \pi[v(N^+) + \mu_{iA}] \} A_{iA} = 0 \quad (8)$$

for each l, N^+ .

This system has non trivial solutions when

$$\det [U_{iA;N^+}^{(J)} \sin \{ [v(N^+) + \mu_{iA}] \}] = 0. \quad (9)$$

Equation (9) together with relations (1) determines the discrete energy eigenvalues. It is possible to show that these equations give as many series of levels as rows (or columns) in the U matrix. So, at given J , there are two series of $-$ symmetry and four with $+$ symmetry. However, owing to the interactions between the Rydberg series, no unique labelling scheme of the levels exists. In the present paper, the numbering of the lines is obtained by continuity from the low n values, where the assignments are unambiguous.

2.3.2 Normalization. — It may be shown [16] that the normalization factor for the eigenfunction is

$$\mathcal{N}^{-2} = \sum_{IN^+} v^3(N^+) \left| \sum_{iA} A_{iA} U_{iA;N^+}^{(J)} \times \cos \{ \pi[v(N^+) + \mu_{iA}] \} \right|^2. \quad (10)$$

This equation is valid only if $d\mu/dE \ll v^3$. Since we assume $d\mu/dE = 0$, this condition is fulfilled. The function obtained by (8) and (9) must be multiplied by $\mathcal{N}$. The energy dependence of $\mathcal{N}$ is mainly $v^{-3/2}$, as usual for Rydberg levels.

2.3.3 Low energy values. — At low energy values, the difference between the terms E_{N^+} in relations (1) is negligible so that all the v_{N^+} 's are approximately equal. The terms $\sin \pi[v(N^+) + \mu_{iA}]$ are all equal in one column of the determinant (9) and may be factored out, leading to

$$\prod_{iA} \sin [\pi(v + \mu_{iA})] = 0 \quad (9')$$

whose solutions are

$$v = n - \mu_{i_0 A_0}$$

for each $i_0 A_0$, corresponding to an eigenfunction $\psi_{i_0 A_0}(\text{el}) |JM - A_0\rangle$ in the core and its continuation outside. These eigenfunctions have a pure Hund's case a character corresponding to the validity of B.O. approximation at low energies. In this region, the Rydberg series are noted as usual nl^1A .

In fact, in this approximation, it is possible to obtain the Hund's case a energy levels (where l is a « good » quantum number)

$$E = B[J(J+1) + l(l+1) - 2A_0^2] - \frac{Ry}{(n - \mu_{A_0})^2} \quad (11)$$

This is performed in Appendix I using a first order approximation of equations (1) and (9).

2.3.4 Evolution of coupling with principal quantum number n . — At low n the coupling is Hund's case a but l -uncoupling occurs and one might expect Hund's case d to become valid at sufficiently high n . In fact, this is never true. Jungen *et al.* [13] have shown that equations (8) and (9) (independently of (1)) can never lead to Hund's case d. Moreover, there is a « periodic return » to Hund's case a : when the difference between the terms E_{N^+} in relations (1) is the same as a multiple of the Rydberg levels spacing, the v_{N^+} 's differ by an integer. The terms $\sin \pi(v_{N^+} + \mu_{iA})$ are all equal in absolute value in one column of the determinant (9) and the calculation is the same as in paragraph 2.3.3 : the eigenfunctions have a pure Hund's case a character. This effect is studied in detail in another paper [18] both theoretically and experimentally. It occurs when $k \frac{2 Ry}{v^3} \simeq B_+(4J+2)$ where k is an integer. If ω_{e1}

and ω_N are the classical frequencies of the electronic and nuclear motion respectively, we have $\omega_{e1} = 2 Ry/v^3$ and $\omega_N = 2 B_+(J+1/2)$ and the « periodic return » to Hund's case a is obtained when $k\omega_{e1} = 2\omega_N$ and may be classically interpreted as follows : the electron « sees » the detailed structure of the core only when it passes through it. Hence it « lights » the core like a

stroboscope at frequency ω_{e1} . The internuclear axis seems at rest when it makes an integer number of half turns during an electron period, i.e. when $2\omega_N = k\omega_{e1}$. Since the axis seems at rest, the projection A of l onto this axis is a good quantum number and the coupling is Hund's case a.

2.4 ELECTRIC DIPOLE TRANSITION INTENSITIES.

2.4.1 Calculation of the transition intensities. — In our experiment (to be described below, see § 3.1), a first laser populates a given (v', J') level in the $A^1\Sigma_u^+$ or $B^1\Pi_u$ state and a second one excites the molecule from this level to Rydberg states. In order to compare experimental and theoretical Rydberg spectra, we must calculate the intensities of the transitions between an intermediate state (A or B in our experiments) and Rydberg states. If $|\psi'\rangle$ and $|\psi\rangle$ are respectively the intermediate state and Rydberg state eigenfunctions, the transition intensity is proportional to

$$|\langle \psi' | \mathbf{e} \cdot \mathbf{d} | \psi \rangle|^2. \quad (12)$$

Since $|\psi'\rangle$ has a small spatial extension, one has only to use the core expression of $|\psi\rangle$, which is

$$|\psi\rangle = \mathcal{N} \sum_{iA} A_{iA} |iA\rangle = \mathcal{N} \sum_{iA} A'_{iA} |lA\rangle. \quad (13)$$

Thus the integrals of interest are

$$\langle \psi' | \mathbf{e} \cdot \mathbf{d} | lA \rangle. \quad (14)$$

The calculation of these matrix elements was performed in [10]. The result is a product of an angular term and a radial integral. At the time, it was assumed that the radial integrals were independent on A or A' and computable by an hydrogenic formula. In fact, this is not true since the Na_2 molecule is not exactly equivalent to a hydrogen atom. Indeed, the $3pA^1\Sigma_u^+$ and $3pB^1\Pi_u$ eigenfunctions have little to do with a $3p$ eigenfunction of an H atom ! Therefore we take here radial integrals as parameters $f(l, A)$ depending upon l and A and also upon the intermediate A or B state. Since $|lA\rangle$ is assumed to be energy independent so is $f(l, A)$. In fact, in the region $9 \leq n \leq 15$ we indeed observe variations of μ_{iA} and $f(m, A)$. However the energy range corresponding to $20 \leq n \leq \infty$ is quite narrow and therefore it is reasonable to assume that μ_{iA} and $f(l, A)$ are energy independent. We have :

$$\begin{aligned} A'_{s\Sigma} &= c_1 A_{s1} + c_2 A_{s2} \\ A'_{d\Sigma} &= -c_2 A_{s1} + c_1 A_{s2} \end{aligned} \quad (15)$$

and we can use results of [10] to find

a) $A^1\Sigma_u^+$ intermediate level :

The A state has a $p\Sigma_u^+$ character and we have :

$$I(A^1\Sigma_u^+ v', J' \rightarrow Ryv, J, \varepsilon) = k\mathcal{N}^2(2J+1)(2J'+1)$$

$$\times |\langle v' | v \rangle|^2 \times \left\{ \left[A'_{s\Sigma} f(s\Sigma) \begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + A'_{d\Sigma} f(d\Sigma) \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \right] \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix} \right\}$$

$$+ \frac{1}{\sqrt{2}} A_{dII} f(dII) (1 + \varepsilon(-)^{J'+J'+1}) \begin{pmatrix} 1 & 1 & 2 \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} J' & 1 & J \\ 0 & -1 & 1 \end{pmatrix} \Big\}^2. \quad (16)$$

In (16), $\varepsilon = 1$ for states of + symmetry and $\varepsilon = -1$ for states of - symmetry.

b) B $^1\Pi_u$ intermediate state :

Besides the $3p\Pi_u$ character of the state, the transition intensity depends on the + or - symmetry of B levels populated by the first laser. The results are :

$$I(B \ ^1\Pi_u^+ v', J', \varepsilon' \rightarrow Ry v, J, \varepsilon) = k' N^2 (2J+1) (2J'+1) \times |\langle v' | v \rangle|^2 \times \\ \times \left\{ \frac{1}{\sqrt{2}} (1 + \varepsilon'(-)^{J'+J'+1}) \left[A'_{s\Sigma} f(s\Sigma) \begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} + A'_{d\Sigma} f(d\Sigma) \begin{pmatrix} 2 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} \right] \begin{pmatrix} J & 1 & J' \\ 0 & 1 & -1 \end{pmatrix} \right. \\ \left. + \frac{1}{2} (1 + \varepsilon \varepsilon' (-)^{J'+J'+1}) \left[A_{dII} f(dII) \begin{pmatrix} 2 & 1 & 1 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} J & 1 & J \\ 1 & 0 & -1 \end{pmatrix} + A_{d\Delta} f(d\Delta) \begin{pmatrix} 2 & 1 & 1 \\ -2 & 1 & 1 \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ 2 & -1 & -1 \end{pmatrix} \right] \right\}^2 \quad (17)$$

3. Comparison between theory and experiment for Na₂ Rydberg states.

3.1 EXPERIMENTAL SET UP. — The experimental set up is the same as in reference [10]. Briefly a supersonic sodium beam is crossed at right angles by two superimposed tunable pulsed dye lasers. The first laser selects a well defined rovibrational level v', J' of the A $^1\Sigma_u^+$ or B $^1\Pi_u$ of state Na₂. The second laser excites the Rydberg states (Fig. 1). Beyond the ionization limit the Rydberg states are autoionizing by vibrational coupling and we detect the electrons by means of an electron multiplier. A very small electric field (0.5 to 1 V.cm⁻¹) is sufficient to collect the electrons. This is very important to observe highly excited Rydberg states ($n \simeq 70$) since the Stark effect which enlarges the lines profile varies as n^7 [19]. We will present in a forth-coming paper Stark investigations of the Na₂ Rydberg states. In our system all autoionizing Rydberg states with lifetimes inferior to 1 μ s (or few μ s) are detected, the interaction region being 1 cm long and the Na₂ velocity being about 1 000 m/s. 1 μ s is rather long for a vibrational autoionization lifetime [20] and we have assumed in our theoretical treatment that the number of detected electrons is proportional to the Rydberg states population given by formulae (16) and (17). We do not consider here rotational autoionization [7], but in this case it is possible to observe levels of very long lifetimes. The results concerning rotational autoionization features will be published in a forthcoming paper.

3.2 ASSIGNMENT AND FITTING. — Molecular constants of the Na₂⁺ ground state, and quantum defects of the four observed series $ns \ ^1\Sigma_g^+$, $nd \ ^1\Sigma_g^+$, $nd \ ^1\Pi_g$, $nd \ ^1\Delta_g$ were approximately known from our earlier work [10]. We had only to improve these values, and to check the values of c_1 (in Eq. (6)) and $f(l, \Lambda)$ (in Eqs. (16), (17)). We made this treatment only for $v = 4$, for

Fig. 1. — Principle of the experiment.

which a great number of experimental results were available.

3.2.1 s-d mixing. — Experimentally we observed two series $n\Sigma_1^+$ (quantum defect $\mu_{\Sigma_1} \simeq 0.6$) and $n\Sigma_2^+$ (quantum defect $\mu_{\Sigma_2} \simeq 0.2$). The eigenfunctions of the two levels $n\Sigma_1^+$ and $n\Sigma_2^+$ are developed on s and d states by equation (6). For + symmetry states, (9) is a 4×4 determinant and the energy levels are strongly dependent of s-d mixing, particularly the strongly perturbed $nd\Pi^+$ series. On the contrary the - symme-

try energy levels ($nd\Pi^-$, $nd\Delta_g$) are completely independent on s-d mixing. Therefore it is possible to determine $\mu_{d\Pi}(v)$, $\mu_{d\Delta}(v)$, $B_+(v)$ and $T_\infty(v)$ from $-$ symmetry series. As expected the results are very close to those obtained in reference [10] : for $v = 4$, $\mu_{d\Pi}(4) = -0.01$, $\mu_{d\Delta}(4) = 0.42$, $B_+(4) = 0.112 \text{ cm}^{-1}$, $T_\infty(4) = 39\,953.5 \text{ cm}^{-1}$. These parameters are then used to determine c_1 , $\mu_{s\Sigma}(v)$ and $\mu_{d\Sigma}(v)$. The results are illustrated graphically on figures 2a and 2b : for $n=18$ (Fig. 2a) and $n=22$ (Fig. 2b) we have plotted the energy of P and $R\Sigma_2^+$, P and $R\Pi^+$ lines as a function of J' . For each J' value the energy of the $Q\Pi^-$ line is taken as the origin. On the figures the points are experimental and the curves are calculated for three sets of parameters i) $c_1 = 1$, $\mu_{s_1} = 0.6$, $\mu_{s_2} = 0.22$, ii) $c_1 = 0.9$, $\mu_{s_1} = 0.6$, $\mu_{s_2} = 0.22$, iii) $c_1 = 0.9$, $\mu_{s_1} = 0.60$, $\mu_{s_2} = 0.15$. The experimental results are well represented by the first set of parameters. In fact the quantum defect $\mu_{s_2}^+$ may be determined from the $P\Sigma_2^+$ and $R\Sigma_2^+$ lines at low J values (comparison of i and iii), the perturbation between $\Sigma^+ - \Pi^+$ level being very small at low J' values. Then, the c_1 coefficient may be determined by the lines at high J values (comparison of i and ii), the perturbation of Σ^+ and Π^+ levels being strongly dependent on J' and c_1 . We conclude that $c_1 \simeq 1$, and the s-d mixing is too small to be observed in our experiments. The series $n\Sigma_1^+$ is $n\Sigma^+$ and the series $n\Sigma_2^+$ is $nd\Sigma^+$ as assumed in reference [10].

3.2.2 Assignment of levels. — At low n values, the assignment of each line is not difficult since it is possible to use Hund's case a notation. At higher n values, the spectra become more complex and the assignment is not so easy. For this purpose, we calculated theoretical spectra using the previously determined parameters, and we compared them with the experimental ones. As an example tables II to V show the experimental and theoretical positions of the Q and R lines respectively for $J' = 4$ and $J' = 22$. For each level we give the components of the eigenfunction on the Hund's case a basis set and the various v_{N^+} 's. At low energy where formula (11) is valid, Λ and n are also given and Hund's case a is well verified. At higher n values mixings between the various Λ components occur, and then the periodic return to Hund's case a is observed when the v_{N^+} 's differ by an integer k . In tables II to V, the theoretical line positions are calculated with the previously determined parameters [10] and $c_1 = 1$. The agreement with experimental results is very good.

3.2.3 Intensities. — The observed spectra are very different for the A $^1\Sigma_u^+$ and B $^1\Pi_u$ intermediate states and we will discuss them in two different paragraphs.

a) A $^1\Sigma_u^+$ intermediate state.

The spectra from the A state are very clear for two main reasons. First, since it is a Σ state, the transitions to pure $^1\Delta$ states are forbidden. Second, the Franck-Condon factors between A and Rydberg states are nearly $\delta_{vv'}$, as can be seen from table Ia.

The lines intensities lead to the determination of the

Fig. 2. — Energy of P and $R\Sigma_2^+$, P and $R\Pi^+$ as a function of J' . For each J' value the $Q\Pi^-$ line is taken as the origin. The points are experimental, the curves are calculated for three sets of parameters : — $c_1 = 1$, $\mu_{s_1} = 0.6$, $\mu_{s_2} = 0.22$; --- $c_1 = 0.9$, $\mu_{s_1} = 0.6$, $\mu_{s_2} = 0.22$; - · - $c_1 = 0.9$, $\mu_{s_1} = 0.60$, $\mu_{s_2} = 0.15$: a) $n = 18$; b) $n = 22$.

Table Ia. — Franck-Condon factors for the A ¹Σ_u⁺-highly excited Rydberg state transition (J = 0).

$\nu_{\text{Rydberg}} \backslash \nu_B$	0	1	2	3	4	5	6	7	8
0	.976	.024							
1	.024	.931	.044						
2		.044	.894	.062					
3		.001	.060	.863	.076	.001			
4			.002	.072	.837	.087	.001		
5				.003	.082	.817	.096	.001	
6					.004	.090	.801	.103	.001
7						.005	.095	.790	.108
8							.006	.098	.783

Table Ib. — Franck-Condon factors for the B ¹Π_u-highly excited Rydberg state transition (J = 0).

$\nu_{\text{Rydberg}} \backslash \nu_B$	0	1	2	3	4	5	6	7	8
0	.480	.317	.135	.047	.015	.004	.001		
1	.389	.037	.216	.189	.101	.043	.016	.005	.002
2	.115	.369	.013	.081	.163	.131	.073	.034	.014
3	.015	.230	.240	.082	.011	.103	.129	.095	.053
4		.044	.307	.120	.132	.002	.047	.105	.102
5		.003	.084	.343	.044	.143	.024	.013	.072
6			.006	.128	.347	.008	.125	.053	.000
7				.010	.172	.331	.000	.095	.074
8					.015	.214	.307	.006	.063

$f(l, A)$ coefficients. Here, we have only to know $f(l = 2, \Sigma)$ and $f(l = 2, \Pi)$. Since the transitions to A are forbidden, and the $ns \ ^1\Sigma_g^+$ series is very weak, we take $f(l = 0, \Sigma) = 0$. We find

$$\frac{f(l = 2, \Sigma)}{f(l = 2, \Pi)} = 0.5.$$

As a comparison, the hydrogenic approximation would have given a ratio equal to 1.

b) B ¹Π_u intermediate level.

The Rydberg spectra observed with the B state as intermediate level were recorded with a quadrupole mass spectrometer tuned on the Na₂⁺ mass peak. In this quadrupole the electric extraction field was not well defined and was of the order of 10 to 20 V.cm⁻¹. In such conditions, the n values observed were limited to about $n = 35$. Moreover with the B state the Rydberg spectra are more complicated because the Franck-Condon factors between the B state and the Rydberg states are well spread as illustrated in table Ib.

The spectra recorded with the B state shows a very strong $nd \ ^1\Delta_g$ series, a weaker $ns \ ^1\Sigma_g^+$ series, and we do not observe $nd \ ^1\Pi_g$ and $nd \ ^1\Sigma_g^+$ series. This means that

Table II. — Theoretical and experimental positions of the Q lines for $J' = 4$ (levels of $-$ symmetry). In the stroboscopic fringes the observed lines have a strong Π character.

Level A n	Experim. energy	Theoret. energy	$\nu_{N^+=3}$	$\nu_{N^+=5}$	$ A_{d\Pi} $	$ A_{d\Delta} $
$\Pi \ 22$	39 729.5	39 729.69	22.077	21.979	0.995	0.103
$\Pi \ 23$	748.9	748.95	23.086	22.974	.993	.118
$\Pi \ 24$	765.7	765.86	24.097	23.969	.991	.134
$\Delta \ 25$	774.0	773.85	24.623	24.487	.277	.961
$\Pi \ 25$	781.1	780.78	25.109	24.965	.989	.151
$\Delta \ 26$	787.7	787.77	25.628	25.475	.309	.951
$\Pi \ 26$	794.0	794.02	26.121	25.959	.985	.170
$\Delta \ 27$	800.3	800.15	26.634	26.462	.344	.939
$\Pi \ 27$	806.0	805.80	27.135	26.953	.982	.190
$\Delta \ 28$	811.2	811.20	27.640	27.448	.379	.925
$\Pi \ 28$	816.4	816.35	28.149	27.946	.977	.212
$\Delta \ 29$	821.0	821.12	28.647	28.433	.417	.909
$\Pi \ 29$	826.1	825.83	29.165	28.940	.972	.236
$\Delta \ 30$	830.2	830.05	29.654	29.417	.455	.890
$\Pi \ 30$	834.5	834.38	30.182	29.933	.965	.261
$\Delta \ 31$	838.1	838.12	30.661	30.400	.495	.869
$\Pi \ 31$	842.2	842.11	31.200	30.925	.957	.289
$\Delta \ 32$	845.3	845.43	31.670	31.382	.535	.845
$\Pi \ 32$	849.3	849.12	32.219	31.916	.948	.318
$\Delta \ 33$	852.1	852.09	32.679	32.363	.576	.817
$\Pi \ 33$	855.6	855.52	33.239	32.907	.936	.351
$\Delta \ 34$	858.3	858.15	33.688	33.342	.618	.786
$\Pi \ 34$	861.4	861.35	34.260	33.896	.923	.386
$\Delta \ 35$	863.7	863.70	34.699	34.321	.659	.752
$\Pi \ 35$	867.0	866.69	35.282	34.885	.906	.424
$\Delta \ 36$	868.8	868.79	35.710	35.299	.700	.714
$\Pi \ 36$	871.6	871.59	36.305	35.873	.885	.465
	873.5	873.47	36.722	36.275	.740	.672
	876.2	876.09	37.328	36.859	.861	.509
	878.0	877.78	37.736	37.252	.779	.627
	880.2	880.24	38.353	37.845	.830	.558
	881.6	881.77	38.752	38.228	.817	.577
	884.2	884.07	39.377	38.828	.793	.610
	885.6	885.46	39.769	39.204	.851	.524
	887.8	887.62	40.402	39.810	.747	.665
	889.0	888.88	40.788	40.179	.884	.468
	890.9	890.91	41.427	40.789	.691	.723
	892.2	892.06	41.809	41.153	.913	.409
	894.0	893.95	42.452	41.766	.623	.782
	895.2	895.03	42.833	42.129	.938	.347
	896.8	896.79	43.476	42.740	.542	.841
	898.1	897.80	43.860	43.105	.959	.283
	899.5	899.43	44.500	43.712	.447	.895
	900.5	900.39	44.890	44.081	.976	.217
	902.0	901.89	45.523	44.680	0.338	0.941
	903.0	902.81	45.923	45.058	.989	.151
	905.2	905.08	46.960	46.037	.996	.084
	907.3	907.21	48.000	47.015	1.000	.017
	909.3	909.22	49.043	47.994	0.999	.052
	911.3	911.10	50.089	48.973	.993	.122
	913.0	912.88	51.137	49.951	.981	.194
	913.7	913.71	51.649	50.428	.429	.903
	914.6	914.55	52.188	50.929	.963	.271
	915.3	915.29	52.671	51.378	.543	.840
	916.1	916.13	53.240	51.906	.936	.353
	916.9	916.78	53.695	52.327	.647	.763
	917.6	917.62	54.292	52.879	.897	.442
	918.3	918.20	54.722	53.276	.740	.673
	919.1	919.02	55.344	53.850	.841	.541
	919.5	919.54	55.753	54.226	.819	.573
	920.5	920.34	56.394	54.815	.762	.647
	920.9	920.81	56.788	55.177	.885	.466
	921.6	921.59	57.442	55.776	.653	.758
	922.2	922.03	57.830	56.131	.935	.354
	922.9	922.77	58.485	56.730	.507	.862
	923.3	923.19	58.879	57.089	.971	.240
	924.4	924.30	59.936	58.051	.992	.127
	925.6	925.35	60.999	59.015	1.000	.018
	926.4	926.36	62.029	59.983	0.996	.092
	927.5	927.32	63.142	60.949	.979	.202

the intensity of these two last series is weak but the superposition of several $nd \ ^1\Delta_g$ series corresponding to different vibrational levels ν in the Rydberg states precludes precise measurements. We can however estimate that for the B state

$$\frac{f(l = 0, \Sigma)}{f(l = 2, \Delta)} \simeq 0.5; \quad \frac{f(l = 2, \Pi)}{f(l = 2, \Delta)} \leq 0.2$$

Table III. — *Theoretical and experimental positions of the R lines for $J' = 4$ (levels of + symmetry). In the stroboscopic fringes, the observed lines have a strong Π or Σ character.*

Level Λ n	Experim. energy	Theoret. energy	$\nu_{N'=5}$	$ A_{d\Sigma} $	$ A_{d\Pi} $	$ A_{d\Delta} $
Δ 22	39 721.1	39 720.95	21.568	0.012	0.178	0.984
Σ 22	725.2	725.69	21.788	.908	.410	.089
Π 22	731.2	731.55	22.069	.431	.887	.167
Δ 23	741.5	741.35	22.566	.015	.206	.978
Σ 23	745.2	745.45	22.783	.887	.447	.111
Π 23	750.8	750.88	23.081	.473	.861	.188
Δ 24	759.3	759.22	23.563	.018	.237	.971
Σ 24	763.2	762.77	23.778	.866	.482	.137
Π 24	767.5	767.86	24.096	.513	.832	.210
Δ 25	774.9	774.95	24.560	.021	.271	.962
Σ 25	778.2	778.03	24.772	.842	.513	.167
Π 25	782.4	782.85	25.112	.552	.801	.233
Δ 26	788.8	788.86	25.558	.021	.311	.950
Σ 26	791.3	791.55	25.765	.817	.540	.201
Π 26	795.9	796.15	26.131	.589	.765	.259
Δ 27	801.1	801.23	26.554	.022	.354	.935
Σ 27	803.5	803.58	26.757	.791	.563	.235
Π 27	807.8	807.99	27.150	.625	.726	.287
Δ 28	812.2	812.29	27.551	.020	.403	.915
Σ 28	814.4	814.34	27.748	.764	.582	.280
Π 28	818.4	818.59	28.172	.660	.681	.318
Δ 29	822.1	822.20	28.547	.015	.456	.890
Σ 29	824.0	823.99	28.739	.735	.595	.325
	828.2	828.11	29.195	.693	.629	.353
	831.1	831.13	29.543	.003	.516	.856
	832.8	832.70	29.729	.705	.602	.374
	836.1	836.69	30.208	.724	.567	.393
	839.3	839.20	30.540	.019	.582	.813
	840.4	840.57	30.719	.674	.603	.426
	846.5	846.53	31.538	.053	.651	.757
	847.8	847.72	31.708	.641	.598	.480
	853.3	853.20	32.537	.104	.721	.685
	854.2	854.23	32.698	.608	.586	.536
	859.3	859.31	33.541	.177	.785	.594
	860.1	860.17	33.689	.574	.567	.591
	865.0	864.93	34.550	.269	.832	.485
	865.7	865.62	34.679	.537	.544	.645
	870.2	870.11	35.567	.372	.853	.366
	870.7	870.62	35.670	.505	.510	.696
	875.3	875.22	36.662	.478	.467	.746
	879.3	879.34	37.625	.558	.817	.147
	39 879.6	39 879.46	37.654	0.456	0.410	0.790
	883.3	883.39	38.648	.564	.154	.812
	883.5	883.45	38.664	.638	.766	.074
	887.4	887.26	39.709	.701	.713	.010
	889.3	889.08	40.236	.581	.658	.430
	892.2	892.25	41.211	.517	.747	.418
	895.2	895.19	42.186	.431	.833	.346
	898.1	897.96	43.165	.304	.917	.258
	899.9	899.90	43.893	.950	.208	.235
$k=1$	900.7	900.57	44.153	.111	.983	.145
	902.5	902.46	44.914	.967	.063	.249
	903.2	903.05	45.162	.140	.990	.009
	904.9	904.80	45.909	.922	.325	.213
	905.5	905.44	46.196	.369	.921	.123
	907.1	906.94	46.887	.847	.512	.141
	907.7	907.70	47.248	.529	.814	.242
	909.1	908.94	47.855	.769	.637	.050
	910.9	910.82	48.820	.688	.724	.056

and

$$\frac{f(l=2, \Sigma)}{f(l=2, \Delta)} \leq 0.2.$$

3.2.4 « Stroboscopic fringes » with the $A^1\Sigma_u^+$ intermediate levels. — At low n values, the Rydberg state eigenfunctions are nearly in Hund's case a and we expect P, R lines for transitions $\Sigma' \rightarrow \Sigma$ and P, Q, R lines for the others to be observed, with $\Delta\Lambda = 0, \pm 1$. As n increases, mixing between Σ , Π and Δ levels leads to the possibility of « forbidden » transitions such as $\Sigma' \rightarrow \Delta$. This occurs for $10 < n < 20$ depending on J' . At the same time, Δ -doubling increases and the P, Q, R lines are no longer equally spaced [10]. At higher n , the

Table IV. — *Theoretical and experimental positions of the Q lines for $J' = 22$ (levels of - symmetry). In the stroboscopic fringes the observed lines have a strong Π character.*

Level Λ n	Experim. energy	Theoret. energy	$\nu_{N'=21}$	$\nu_{N'=23}$	$ A_{d\Pi} $	$ A_{d\Delta} $
Π 16	39 583.5	39 582.76	16.116	15.928	0.967	0.275
Δ 17	610.3	610.38	16.671	16.462	.344	.939
Π 17	631.2	631.66	17.139	16.912	.944	.331
Δ 18	654.7	654.45	17.687	17.438	.405	.914
Π 18	673.0	672.65	18.164	17.895	.921	.389
Δ 19	691.6	691.59	18.705	18.411	.470	.883
Π 19	707.9	707.35	19.193	18.876	.892	.453
Δ 20	723.0	723.17	19.724	19.381	.538	.843
Π 20	737.7	736.98	20.226	19.856	.853	.521
Δ 21	750.5	750.26	20.745	20.347	.609	.794
Π 21	762.5	762.49	21.261	20.833	.805	.594
Δ 22	773.7	773.67	21.769	21.310	.680	.733
Π 22	784.3	784.59	22.301	21.808	.743	.669
	794.3	794.05	22.795	22.269	.751	.660
	804.0	803.87	23.344	22.780	.666	.746
	811.9	811.89	23.823	23.226	.820	.573
	820.7	820.77	24.389	23.749	.570	.822
	827.9	827.62	24.856	24.180	.882	.471
	835.7	835.65	25.438	24.714	.453	.892
	841.7	841.57	25.893	25.131	.936	.352
	849.0	848.83	26.487	25.673	.313	.950
	854.5	854.00	26.937	26.081	.976	.217
$k=1$	865.1	865.14	27.987	27.031	.998	.067
	875.2	875.16	29.045	27.981	.995	.096
	884.3	884.22	30.112	28.931	.964	.266
	888.7	888.70	30.686	29.439	.402	.916
	892.4	892.41	31.187	29.881	.899	.439
	896.5	896.28	31.736	30.362	.577	.817
	899.7	899.86	32.269	30.828	.793	.609
	903.5	903.16	32.788	31.280	.734	.679
	906.7	906.62	33.356	31.772	.641	.768
	909.4	909.45	33.846	32.194	.864	.504
	912.7	912.75	34.444	32.708	.435	.901
	915.3	915.21	34.913	33.108	.957	.292
$k=2$	920.7	920.54	35.993	34.025	.999	.049
	925.5	925.47	37.089	34.947	.978	.211
	928.0	927.97	37.684	35.443	.393	.920
	930.0	930.05	38.200	35.872	.884	.468
	932.5	932.18	38.756	36.330	.641	.767
	934.4	934.27	39.321	36.795	.707	.707
	936.1	936.08	39.832	37.213	.838	.545
	938.3	938.15	40.443	37.709	.438	.899
	939.7	939.71	40.922	38.097	.965	.261
	943.1	943.13	42.0344	38.989	.998	.068
	946.5	946.36	43.171	39.891	.915	.403
	39 948.1	39 947.91	43.747	40.344	0.614	0.789
	949.4	949.38	44.323	40.794	.705	.709
	950.8	950.67	44.842	41.199	.858	.514
$k=4$	953.3	953.29	45.958	42.060	.988	.151
	956.0	955.79	47.107	42.934	.967	.255
	957.8	958.17	48.284	43.819	.771	.637
	959.4	959.21	48.825	44.223	.824	.567
$k=5$	961.3	961.27	49.958	45.059	.988	.152
	963.5	963.27	51.133	45.916	.948	.318
	965.4	965.19	52.339	46.783	.674	.739
	966.0	965.98	52.870	47.161	.904	.427
	967.7	967.66	54.039	47.985	.997	.081
	968.5	968.55	54.687	48.437	.407	.914
	969.3	969.30	55.260	48.834	.806	.591
	970.4	970.03	55.826	49.223	.824	.567
	971.2	970.85	56.486	49.674	.316	.949
	971.7	971.46	56.998	50.021	.999	.035
	974.8	974.77	60.004	52.016	1.000	.018
	976.2	976.01	61.265	52.831	0.799	.601
$k=6$	976.7	976.55	61.842	53.199	.857	.516
	977.7	977.65	63.060	53.969	.991	.136
	978.7	978.74	64.354	54.774	.645	.764
	980.3	980.19	66.179	55.886	.907	.422
	981.3	981.15	67.491	56.669	.300	.954
	982.5	982.44	69.366	57.765	.620	.784
	983.6	983.62	71.251	58.840	.820	.572
	984.6	984.73	73.157	59.900	.928	.372
	985.7	985.78	75.089	60.947	.978	.210
	986.7	986.76	77.046	61.980	.995	.100
	987.7	987.67	79.026	62.996	.999	.045

spectrum becomes more complicated because of complete mixing between Λ -eigenfunctions. However, as seen in paragraph 2.3.4), there is a « periodic return » to Hund's case a, at the positions

Table V. — *Theoretical and experimental positions of the R lines for $J' = 22$ (levels of + symmetry). In the stroboscopic fringes the observed lines have a strong Π or Σ character.*

Level A_n	Experim. energy	Theoret. energy	$\nu_{N^+=23}$	$ A_{d\Sigma} $	$ A_{d\Pi} $	$ A_{d\Delta} $
Σ 16	39 571.4	39 571.82	15.730	0.828	0.508	0.235
Π 16	590.8	591.98	16.100	.578	.770	.268
Δ 17	615.2	615.35	16.564	.076	.414	.907
Σ 17	621.5	622.39	16.711	.786	.527	.322
Π 17	641.0	641.22	17.127	.636	.705	.313
Δ 18	659.6	659.32	17.557	.102	.521	.847
Σ 18	664.7	664.74	17.692	.738	.520	.429
	683.0	682.45	18.157	.692	.624	.364
	696.7	696.31	18.547	.126	.647	.752
	701.1	700.61	18.673	.684	.476	.553
	717.8	717.26	19.188	.746	.516	.422
	727.5	727.74	19.534	.130	.783	.608
	731.0	731.33	19.657	.626	.391	.675
	747.0	746.82	20.216	.796	.363	.483
	754.0	754.72	20.520	.088	.906	.413
	758.3	757.86	20.645	.572	.281	.771
	772.0	771.97	21.235	.834	.147	.533
	778.3	778.21	21.513	.016	.986	.167
	780.5	780.94	21.638	.544	.129	.829
	799.5	798.93	22.519	.150	.981	.124
	800.7	801.16	22.636	.548	.041	.835
	811.6	811.67	23.213	.788	.366	.494
	817.1	817.31	23.541	.224	.867	.445
	827.7	827.50	24.171	.718	.560	.415
	833.7	833.46	24.564	.168	.637	.752
	841.7	841.39	25.118	.624	.711	.322
	847.7	847.57	25.576	.072	.377	.924
	853.8	853.73	26.059	.488	.846	.217
	865.1	864.90	27.010	.228	.970	.086
	875.2	875.39	28.003	.214	.974	.080
	882.3	882.46	28.739	.880	.433	.200
	885.5	885.37	29.059	.544	.806	.231
	889.7	889.61	29.545	.174	.505	.845
	890.7	890.77	29.683	.728	.476	.494
	894.7	894.51	30.139	.730	.574	.372
	897.5	897.37	30.502	.206	.824	.528
	898.5	898.47	30.645	.572	.291	.767
	904.5	904.49	31.466	.030	.997	.077
	911.5	911.41	32.497	.318	.846	.428
	928.0	928.35	35.521	.330	.383	.862
	933.5	933.56	36.635	.498	.216	.840

$k \frac{2 Ry}{\nu^3} \simeq B(4J' + 2)$. This is related to a great simplification of the spectra because P, Q, R lines of a given A (but not necessary the same n) are at the same energy for the following reason : assume that the intermediate level has a + symmetry. A $Q\Pi$ line has - symmetry, and hence has a quantum defect μ_{Π} , relative to $N^+ = J - 1 = J' - 1$. A $P\Pi$ line has + symmetry, and a quantum defect μ_{Π} , relative to $N^+ = J = J' - 1$, so that P and Q lines have same quantum defect and same ionization limits and hence coincide. The same property is true for the R lines. This is illustrated on figure 3 with intermediate level $A \ ^1\Sigma_u^+$ ($v' = 4$, $J' = 10$) in this case, only $v = 4$ occurs in Rydberg series, owing to Franck-Condon factors. Further, the Δ lines are forbidden if the eigenfunction is pure Hund's case a function, which is the case when $2 kRy/\nu^3 = B(4J' + 2)$. Moreover Σ lines are weak, so that one observes only one series in these regions. This effect was called « stroboscopic fringes », because it corresponds to interference between Rydberg series converging towards different ionization limits, and because it may be interpreted as stroboscopic effects between electronic and nuclear motions. It must be remarked that the « periodic return » to Hund's case a

Fig. 3. — Comparison between experimental and theoretical curves for $v' = 4$ $J' = 10$ in the A intermediate state. Stroboscopic fringes $k = 1, 2$ and 3 are clearly observed. The laser linewidth was 0.15 cm^{-1} . The levels of the $ndN^+ = J' \pm 1$ are also given.

is general for molecular Rydberg states in the region of high n values except in the H_2 molecule for which the rotational constant B is too high [11, 20]. This effect must lead to strong modifications of the spectra in any case but the particular form of the spectrum illustrated in figure 3 is obviously dependent on the studied transition.

3.2.5 Influence of J' on the spectra. — The most relevant parameter in studying the influence of J' on the spectra is the position of the fringes mentioned above, since they occur at $2 kRy/\nu^3 = B(4J' + 2)$. Figures 3 to 6 show the evolution with J' . For $J' = 4$, one fringe is seen at $n \simeq 45$. For $J' = 10$, there are three fringes at $n \simeq 35$, $n \simeq 45$, $n \simeq 51$. For $J' = 22$, there are also three fringes at $n \simeq 29$, $n \simeq 34$, $n \simeq 40$, but they only extend upon two or three n 's. Figure 7 shows higher n values for $J' \simeq 22$. At these energies, the

Fig. 4. — Same as in figure 3 but for $v' = 4$ $J' = 4$ in the A state. Only one stroboscopic fringe ($k = 1$) is observed for $n \simeq 44-45$.

Fig. 5. — Same as in figure 3 but for $v' = 4$ $J' = 22$ in the A state. The first stroboscopic fringe ($k = 1$) appears for $n \simeq 27-28$.

Fig. 7. — Comparison between experimental and theoretical curves in the region of high n values. The intermediate level was $v' = 4$ $J' = 22$ in the A state.

extend of the fringes is only one intense line, at $n \simeq 52$, 56 and so on. Finally, for $J' = 30$ (Fig. 6), the fringes appear at lower n value ($n \simeq 25$) and they extend on a very short region. All these figures illustrate the very good agreement between theoretical and experimental spectra for both intensities and positions.

Fig. 6. — Same as in figure 3 but for $v' = 4$ $J' = 30$ in the A state. The first stroboscopic fringe ($k = 1$) appears for $n \simeq 24-25$. Due to the high J' value, the fringes extend on a very small energy region.

3.2.6 Quasi-Fano profiles. — In the region of high v_{N^+} values, the main features of our Rydberg spectra can be interpreted by the interaction of two Rydberg series : a very dense series of levels converging towards the $ndN^+ = J' - 1$ limit which forms a quasi-continuum and the levels of the other $ndN^+ = J' + 1$ series. Indeed these two series are the only ones allowed by the approximate selection rule $N^+ = J' \pm 1$ derived in reference [10] for the transitions $ndN^+ \leftarrow A3p^1\Sigma_u^+$. Each line of the series $ndN^+ = J' + 1$

is a quasi-Fano profile filled with the lines of the $ndN^+ = J' - 1$ series. Beyond the $ndN^+ = J' - 1$ ionization limit the quasi-Fano profiles become true ones. This situation is experimentally observed at high J' values when the $ndN^+ = J' - 1$ and $ndN^+ = J' + 1$ limits are well separated. Figure 8 shows such effects for $J' = 45$ in the A state. The signal to noise ratio is too low to resolve experimentally the lines of the $ndN^+ = 44$ inside the quasi-Fano profiles, but we observe their envelope.

Fig. 8. — Quasi-Fano profiles in the region of high n values for $v' = 2$ $J' = 45$ in the A state. Beyond the ionization limit of the $ndN^+ = 44$, the quasi-Fano profiles become true ones. The signal to noise ratio is too low to observe experimentally the lines of the $ndN^+ = J - 1$ series.

4. Conclusion.

The M.Q.D.T. method has proved to be a powerful tool to assign and interpret the Na_2 Rydberg spectra obtained by Optical-Optical Double Resonance.

Indeed the observed interference effects in the electronic dipole transitions are very well reproduced by the theoretical spectra in the region of very high n values ($n \geq 20$). The influence of J' on the spectra is studied in detail both theoretically and experimentally. As J' increases the spectrum is completely modified by l -uncoupling; this effect is interpreted in detail by the M.Q.D.T. theory leading to easy assignment of each line. The experimental parameters (quantum defects, Na₂⁺ molecular constants) obtained by the M.Q.D.T. analysis are in agreement with those obtained by the second order perturbation theory [10]. The improvement of these parameters necessitated a M.Q.D.T. analysis of the vibrational perturbations occurring at lower n values ($10 \lesssim n \lesssim 20$). This treatment will appear in a forthcoming publication.

Appendix I

CALCULATION OF THE ENERGY OF LOW-LYING LEVELS. — At low n values, all v_{N^+} are approximately equal to $n - \mu_{i_0 A_0}$. Hence, we have

$$v_{N^+} = n - \mu_{i_0 A_0} + \varepsilon_{N^+} \quad (\text{A.1})$$

where ε_{N^+} is a small correction.

In the determinant (9) one row is of first order in ε (the line $i_0 A_0$), so that the 0th order can be taken in the other rows. The sinus terms factor out in these rows and the remaining terms are the $U_{i_0 A_0 l N^+}^{(J)}$. The row $i_0 A_0$ is equal to $\pi \varepsilon_{N^+} U_{i_0 A_0 l N^+}^{(J)}$ at first order in the ε_{N^+} 's. We develop determinant (9) along this row $i_0 A_0$. The cofactor of one term ($i_0 A_0, l N^+$) is the same as the cofactor of this term in matrix U , and is equal to $U_{i_0 A_0, l N^+}^{(J)*}$ since U is unitary. We obtain

the equivalent of equation (9) as

$$\sum_{N^+} \varepsilon_{N^+} |U_{i_0 A_0 l N^+}|^2 = 0. \quad (\text{A.2})$$

The ε_{N^+} 's are also given by equations (1) which can be written

$$E = B^+ N^+ (N^+ + 1) - \frac{Ry}{(n - \mu_{i_0 A_0})^2} + \frac{2 Ry}{(n - \mu_{i_0 A_0})^3} \varepsilon_{N^+} + (\varepsilon^2) \quad (\text{A.3})$$

for each N^+ .

Multiplying each equation (A.3) by $|U_{i_0 A_0 l N^+}^{(J)}|^2$, and summing over N^+ , the third term of (A.3) reduces to zero. The second term gives

$$\frac{Ry}{(n - \mu_{i_0 A_0})^2} \det U = \frac{Ry}{(n - \mu_{i_0 A_0})^2}. \quad (\text{A.4})$$

To calculate the first term, we use the fact that :

$$N^+ (N^+ + 1) = \langle l N^+ | N^{+2} | l N^+ \rangle \quad (\text{A.5})$$

and that U is the transformation matrix from $|l N^+ \rangle$ to $|i A \rangle$. Hence, we obtain

$$E = B^+ \langle i_0 A_0 | (N^+)^2 | i_0 A_0 \rangle - \frac{Ry}{(n - \mu_{i_0 A_0})^2} \quad (\text{A.6})$$

since $(N^+)^2 = (\mathbf{J} - \mathbf{l})^2 = J^2 + l^2 - 2 \mathbf{J} \cdot \mathbf{l}$, we have

$$\langle i_0 A_0 | (N^+)^2 | i_0 A_0 \rangle = J(J+1) - 2 A_0^2 + \langle i_0 A_0 | l^2 | i_0 A_0 \rangle$$

and equation (A.6) becomes the same as equation (11) in the particular case where no l -mixing occurs.

References

- [1] CARLSON, N. W., TAYLOR, A. J. and SCHAWLOW, A. L., *Phys. Rev. Lett.* **45** (1980) 18.
- [2] CARLSON, N. W., TAYLOR, A. J., JONES, K. M. and SCHAWLOW, A. L., *Phys. Rev. A* **24** (1981) 822.
- [3] MARTIN, S., CHEVALEYRE, J., VALIGNAT, S., PERROT, J. P., BROYER, M., CABAUD, B. and HOAREAU, A., *Chem. Phys. Lett.* **87** (1982) 235.
- [4] LEUTWYLER, S., HEINIS, T. and JUNG, M., *J. Chem. Phys.* **76** (1982) 4290.
- [5] SEAVER, M., CHUPKA, W. A., COLSON, S. D. and GAU-YACQ, D., *J. Phys. Chem.* **87** (1983) 2226.
- [6] LEUTWYLER, S., HERRMANN, A., WÖSTE, L. and SCHUMACHER, E., *Chem. Phys.* **48** (1980) 253.
- [7] BROYER, M., CHEVALEYRE, J., DELACRETAZ, G., MARTIN, S. and WÖSTE, L., *Chem. Phys. Lett.* **99** (1983) 206.
- [8] EISEL, D. and DEMTRÖDER, W., *Chem. Phys. Lett.* **88** (1982) 481.
- [9] EISEL, D., DEMTRÖDER, W., MÜLLER, W. and BOTSCHWINA, P., *Chem. Phys.* **80** (1983) 329.
- [10] BERNHEIM, R. A., GOLD, L. P. and TIFTON, T., *Chem. Phys. Lett.* **92** (1982) 13.
- [11] MARTIN, S., CHEVALEYRE, J., BORDAS, M. C., VALIGNAT, S., BROYER, M., CABAUD, B. and HOAREAU, A., *J. Chem. Phys.* **79** (1983) 4132.
- [12] FANO, U., *Phys. Rev. A* **2** (1970) 353; FANO, U., *J. Opt. Soc. Am.* **65** (1975) 979.
- [13] SEATON, M. J., *Proc. Phys. Soc.* **88** (1966) 801; SEATON, M. J., *Proc. Phys. Soc.* **88** (1966) 815; SEATON, M. J., *Rep. Prog. Phys.* **46** (1983) 167.
- [14] JUNG, Ch. and ATABEK, O., *J. Chem. Phys.* **66** (1977) 5584.
- [15] JUNG, Ch. and DILL, D., *J. Chem. Phys.* **73** (1980) 3338; RAOULT, M. and JUNG, Ch., *J. Chem. Phys.* **74** (1981) 3388.

- [15] GIUSTI-SUZOR, A. and JUNGEN, Ch., *J. Chem. Phys.* **80** (1983) 986.
- [16] GREENE, C. H., FANO, U. and STRINATI, G., *Phys. Rev. A* **19** (1979) 1485.
- GREENE, C. H., RAU, A. R. P. and FANO, U., *Phys. Rev. A* **26** (1982) 2441.
- [17] JUNGEN, Ch., *J. Chem. Phys.* **53** (1970) 4168.
- [18] LABASTIE, P., BORDAS, M. C., TRIBOLLET, B. and BROYER, M., *Phys. Rev. Lett.* **52** (1984) 1681.
- [19] FABRE, C., Thesis Paris (1980) (unpublished).
- [20] HERZBERG, G. and JUNGEN, Ch., *J. Mol. Spectros.* **41** (1972) 425.
-