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STUDY OF DIATOMIC MOLECULES. II. INTENSITIES

Jean-Louis Féménias

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Partie II: Intensités," Canadian Journal of Physics,
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16. Abstract Theory of perturbations, giving the diatomic effective Hamiltonian, is used for calculating actual molecular wave functions and intensity factors involved in transitions between states arising from Hund's coupling cases a,b, intermediate a-b, and c tendency. The Herman and Wallis corrections are derived, without any knowledge of the analytical expressions of the wave functions, and generalized to transitions between electronic states with whatever symmetry and multiplicity. A general method for studying perturbed intensities is presented using primarily modern spectroscopic numerical approaches. The method is used in the study of the ScO optical emission spectrum.

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STUDY OF DIATOMIC MOLECULES. II. INTENSITIES

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I. Introduction

We have already had the opportunity to develop some ideas   /1775*
about the fine study of intensities, in the spectroscopy of dia-
tomic molecules [9,11]. The problems taken up essentially con-
cern evaluation of intensity factors in hyperfine coupling, which
is complex indeed, but pure coupling. We recently became inter-
ested in study of the effect of a light mixture on the intensity
factors, reduced to classical factors [12]. Spin decoupling type
perturbations were accounted for numerically, in a rigorous manner.

Everyone knows that this type of perturbation is neither the
only one nor the most important one. Herman and Wallis [14] have
shown that, even in the $^1\Sigma$ states, there are nonnegligible per-
turbations, due to rotational-vibrational interaction.

In fact, purely theoretically, any perturbation introduced
into the diatomic Hamiltonian [8b] is reflected in the intensities,
by way of modification of the basic wave functions and, therefore,
the matrix elements of the electric dipole moment.

In this article, we plan to classify the different types of
intensity perturbations and to clarify their effects, by general-
izing the calculations of the transitions between electron   states,
of distinct multiplicity or not, and any values of Λ. This

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*Numbers in the margin indicate pagination in the foreign text.

work will be done by integrating the calculations in a homogenous, global presentation of diatomic problems, started in the preceding article [8b].

After a general examination of the intensity problem, justifying the interest which should be given to this field of diatomic spectroscopy (Section II), we inventory and classify the various types of perturbations (Section III), before taking up the general calculation of the Herman and Wallis function [14] (Section IV). Comparison of our calculations with previous results and application to the ScO molecule complete this study (Section V).

II. General Examination of the Problem
A. Basic Formula and Notations

The basic formula used in the study of spectral intensities is given in numerous works and articles (for example Herzberg [15] and Tatum [22], and it can be summarized by

$$I(i \rightarrow f) = f(v) \mathcal{N}(i) m(i \rightarrow f)$$

(1)

where:

$f(v)$ is a simple function of the frequency of the transition from initial state i to final state f, in the form kv^4 for an emission line and $k'v$ for an absorption line, k and k' being con- /1776 stants, depending on the units and experimental conditions;

$\mathcal{N}(i)$ is the number of particles in initial level i; we shall not dwell on bold problems, which require rigorous determination [2]; it frequently is approached through a Boltzmann factor which, in electron spectra in particular, is retained much more as a good phenomenological model, than as an interpreter of a mathematically established statistical distribution;

$m(i \rightarrow f)$, finally, is the square of the modulus of the matrix element of the operator which connects the i and f levels; this

operator frequently is the electric dipole moment **M**, but it can
also be the magnetic dipole, electric quadrupole, etc., moment;
in this study, we shall reason by using **M**.

B. Sensitivity of Intensities

It is well known that, when an elementary molecular level
(rotational or hyperfine) is perturbed, the greatest effect fre-
quently is concentrated on the intensity of the corresponding
spectral lines. More than that, in some cases, the continuity
of the line intensities is broken, while no displacement of the line
is detected (see, for example, Fig 3 of the study of TiN by Dunn
et al [7]).

For example, we consider two transitions to the same final
level of the wave function $|x>$. The initial levels are perturbed,
and we shall observe $\underline{a}$ and $\underline{b}$ ($\underline{a}>\underline{b}$), $|a>$ and $|b>$ respectively,
their unperturbed energies and wave functions. Notations **A** and
B, $|\underline{A}>$ and $|\underline{B}>$ designate the corresponding (actual) perturbed
energies and wave functions. The Hamiltonian of the interaction
is written

$$H = \begin{pmatrix} a & c \\ c & b \end{pmatrix}$$

(2)

with $\underline{c}<<\underline{a}$, $\underline{b}$ and, likewise, $\underline{c}<<\underline{a}-\underline{b}$. Therefore, we are in the case
of a slight, localized perturbation or, again, in that of a rota-
tional-vibrational type perturbation leading to the centrifugal
effect, or of a spin type decoupling which transforms an ($\underline{a}$) coup-
ling into a ($\underline{b}$) coupling when $\underline{J}$ increases [8b]. It is noted that
these examples correspond to very general, if not inevitable,
effects.

The problem of numerical determination of elements $\underline{a}$, $\underline{b}$ and
$\underline{c}$, from experimental $\underline{A}$ and $\underline{B}$ data is now readily solved in rotational
studies [1]. We sometimes **turn back, in order to give the**

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expansions of A and B as a function of a, b and c. It can be shown that

$$A = a \left[1 + \frac{c^2}{a(a-b)} + \frac{c}{a} O(\varepsilon^3) \right]$$

$$B = b \left[1 - \frac{c^2}{b(a-b)} + \frac{c}{b} O(\varepsilon^3) \right]$$

(3)

with $\varepsilon = c/(a-b)$ and where $O(\varepsilon^n)$ represents all the terms of order ε^p, $p \geq n$.

Likewise, it can be seen that

$$|A\rangle = N[|a\rangle + \varepsilon |b\rangle + O(\varepsilon^3)|b\rangle]$$

$$|B\rangle = N'[- \varepsilon |a\rangle + |b\rangle + O(\varepsilon^3)|a\rangle]$$

(4)

where $N^{-2} = 1 + \varepsilon^2 + O(\varepsilon^4)$.

Thus, the observed line intensities are, respectively,

$$I_A = K_A |\langle x ||M||A\rangle|^2$$

$$I_B = K_B |\langle x ||M||B\rangle|^2$$

(5)

with K integrating factors f and $\mathcal{N}$. If the theoretical unperturbed intensities are noted

$$i_a = K_a |\langle x ||M||a\rangle|^2$$

$$i_b = K_b |\langle x ||M||b\rangle|^2$$

(6)

with

$$K_a \simeq K_A \quad K_b^\circ \simeq K_B$$

(7)

obvious, by assuming $i_a \simeq i_b \simeq i$ for simplification, the following is obtained

$$I_A \simeq N^2 \left(1 + \frac{c}{a-b} \right)^2 i$$

$$\simeq i[1 + 2\varepsilon + O(\varepsilon^3)]$$

(8)

$$I_B \simeq N^2 \left(1 - \frac{c}{a-b} \right)^2 i$$

$$\simeq i[1 - 2\varepsilon + O(\varepsilon^3)]$$

A comparison of (3) and (8) shows that the effect of the perturbation is of the first order of ε on the intensities, while it is only second order on energies, hence, on the positions of the lines.

C. The Experimental Counterpart

Unfortunately, this sensitivity of the intensities is not confined to factor m(i→f), which expresses the internal quantum structure of the molecule, but it also is found in statistical factor N(i), which is subject to external effects, such as pressure, temperature and mode of excitation.

We shall not dwell on these problems which are troublesome in the framework of this study, but the source of numerous data in study of the effects of collisions, excitation and deexcitation. We simply say that they lead to experimental difficulties, which explains why studies of intensity are conducted with relatively rough precision in interactions and order of perturbation, necessary to interpretation of a position spectrum [8b].

In the interpretation, when the Boltzmann distribution is too hypothetical to preserve intact   all the physical content of the experimental data, it often is possible to eliminate $N(i)$. Either, in certain very particular cases (the beginning of splitting), the variations are disregarded [9], or, more often, the work is done with relative intensities (see, for example, [4,12]). Despite the mediocre precision of the data, the positive interest which this means of study offers appears here.

Within the framework of the study we have undertaken on diatomic molecules, we intend to examine the intensity problem, along the line of calculation of the perturbations presented elsewhere [8b].

III. Intensities and Perturbations

A. General

In the technique of perturbation presented in Féménias [8b], we saw how the Hamiltonian $\underline{H}$ of a diatomic molecule could be reduced to a block-diagonal form, each block corresponding to level $\underline{J}$ of vibrational level $\underline{v}$ of electron state $\underline{n}\Lambda$, the block dimensions being $(2\underline{S}+1)\times(2\underline{S}+1)$, where $2\underline{S}+1$ is the multiplicity of state $\underline{n}\Lambda$. Level $\underline{n}\Lambda\underline{v}$ thus constitutes Hilbert subspace $\mathscr{H}_0$, in the particular form of the projection technique of Jørgensen [17].

This restriction is accompanied by modification of the base functions. Thus, if $|\Psi^{(0)}\rangle = |\underline{n}(\underline{L})\Lambda\underline{S}\Sigma\underline{v}\Omega\underline{J}M\rangle$ represents one function of type (a), which constitutes the initial base where the Hamiltonian is calculated, $\underline{U}|\Psi^{(0)}\rangle$ represents the corresponding function in the base where $\underline{H}$ is a block diagonal. The expression of $\underline{U}$ is given by expansion by orders of perturbation, the first terms of which are [17]

$$
\begin{aligned}
&\text{order } : 0: U_0 = P_0 \\
&\text{order } : 1: U_1 = \frac{Q_0}{a} V P_0 \\
&\text{order } : 2: U_2 = \frac{Q_0}{a}\left\{ V \frac{Q_0}{a} V - \frac{Q_0}{a} V P_0 V \right\} P_0 \\
&\qquad\qquad\qquad - \frac{1}{2} P_0 V \frac{Q_0}{a^2} V P_0
\end{aligned}
\tag{9}
$$

$\underline{V}$, $\underline{P}_0$, $\underline{Q}_0/\underline{a}^{\underline{n}}$ being defined in Féménias (8b).

The last stage of the calculation is carried out by numerical diagonalization of each block $\underline{n}\Lambda\underline{J}$.

We then have two types of perturbation of initial function $|\Psi^{(0)}\rangle$, external perturbations and internal perturbations of $\mathscr{H}_0$.

B. External Perturbations

They correspond to perturbations of $|\Psi^{(0)}\rangle$ by __exterior__ levels or states of $\mathscr{H}_0$.

1. Vibrational Perturbations

They are due to the effects of levels $\underline{v}' \neq \underline{v}$ on level $\underline{v}$ in the interior of state $\underline{n}\Lambda$, and they originate in the anharmonicity of the oscillator and of vibrational-rotational and anharmonic-rotational interactions. The effect of anharmonicity and vibrational-rotational interaction has been studied, in the case of vibrational-rotational spectra, by numerous authors, the first of whom are Herman and Wallis [14]. More particularly, the rotational-vibrational interaction (centrifugal effect, Féménias [8b]) was discussed by Bunker, in a series of articles, of which we only give the most recent [5].

2. Electron Perturbations

They are due to the effects of the $\underline{n}'\Lambda'\underline{v}'$ levels on the $\underline{n}\Lambda\underline{v}$ level, and they are generally disregarded in the usual intensity study. However, we note that they are responsible for the existence of "extra lines" in the localized perturbation zones and the "forbidden transitions," such as the $\underline{A}'^2\Lambda-\underline{X}^2\Sigma$ transition of ScO, recently observed by Chalek and Gole [6].

Indirectly, they come into play in the slight difference   /1778
which exists between one component Λ and another, in the mixing coefficients of the spin components of a $^{2\underline{S}+1}$ state (Λ and $\underline{S} \neq 0$) [10,12], of which we shall now speak.

C. Internal Perturbations

They correspond to a mixture of different functions $\underline{U}|\psi^{(0)}\rangle$

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of the substates of a $\underline{n}\Lambda\underline{v}$ multiplet, during the final numerical diagonalization.

This type of perturbation has the tremendous advantage that it can be treated in a quasi-exact manner, by using the numerical mixing coefficients provided by the final diagonalization (of which the actual precision is not to be emphasized) and which takes into account the finest interactions, such as the spin-spin, spin-rotation, etc., interactions. An example of the treatment of these perturbations (of the "spin decoupling" type) is given by Féménias et al [12].

It is quite clear that this decoupling is connected with the choice of $\mathscr{H}_0$.   If two strongly bound states $^2\Pi$ and $^2\Sigma$ are treated as a complex [8b], the concepts of external and internal perturbations are modified, and the effect of level $\underline{v}$ on state $^2\Sigma$ on level $\underline{v}$ of state $^2\Pi$ is classed in the set of internal perturbations [12].

In what follows, we obviously are only interested in external perturbations, which alone present difficulties in theoretical treatment.

IV. General Calculation of External Perturbations
A. Calculation Conditions

We shall not limit ourselves to study of the $^1\Sigma$ states, like Herman and Wallis [14], but we shall consider the general case of $^{2\underline{S}+1}\Lambda$ states. Besides, our calculation will concern general transitions between two separate or nonseparate electron states $\underline{n}'\Lambda'$ and $\underline{n}\Lambda$.   On the other hand, we shall limit ourselves to calculation of the first order perturbation, and we shall use as the perturber [8b]

$$V = h + A(r)LS + B(r)[R^2 - L_\perp{}^2]$$

where $\quad h = h_{\text{anharm}} = \sum_{k=3}^{\infty} w_3 q^3$ $\qquad$ (10)

$$q = r - r_e$$

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Disregarding the spin-rotation and spin-spin terms is due to a
desire for clarity, and their introduction does not raise any
theoretical difficulty. However, we note that these interactions
are largely negligible in such a calculation. Finally, we limit
external perturbations to vibrational perturbations, which are the
only ones detectable in the present problems. This explains the
absence of $\underline{h}_{ev}$ [8b] in $\underline{V}$.

To the extent that the problem of emission (or absorption) is
considered in the absence of any external field, and if there is
no interest in a particular polarization of the slit, the problem
is reduced to evaluation of the reduced matrix element of electric
dipole moment $\underline{M}$, between the inital level and the final level, both
of which are perturbed, $\underline{M}^{(1)}$ (i;f) [10]. This evaluation should
be made as a function of matrix elements $\underline{M}$, between pure type ($\underline{a}$)
wave functions.[1] These elements have already been calculated,
with and without nuclear spin [8a]. We use the simplest of them
as the base of the calculation

$$M_c(a, a) = \langle n'(L')\Lambda'S'\Sigma'v'\Omega'J'\|M\|n(L)\Lambda S\Sigma v\Omega J\rangle \tag{11}$$

$$= (-1)^{\Omega'-J'}[(2J'+1)(2J+1)]^{1\cdot 2}\begin{pmatrix} J' & 1 & J \\ -\Omega' & s & \Omega \end{pmatrix}\langle n'(L')\Lambda'S'\Sigma'v'|\mu_s|n(L)\Lambda S\Sigma v\rangle$$

---

[1]Just like study of the Hamiltonians [8b], evaluation of the inten-
sities is done here in base $\underline{a}$, following the convention of Hougen
[16]. If the study concerns coupling states $\underline{b}$, intermediate $\underline{a}$-$\underline{b}$ or
tendency $\underline{c}$, the use of numerical mixing coefficients at the end of
the calculation (section III C) will permit the desired intensity
factor to be obtained with the greatest precision, since, in fact,
electron states which answer to cases of pure coupling are rare,
and a mixture of components is often unavoidable. However, the cal-
culation can be done with matrix elements $\underline{M}$, between type $\underline{b}$ functions,
or type $\underline{a}$ and $\underline{b}$ functions; this causes no difficulty, since the
"pure" intensity factors between the classic or hyperfine coupled
states $\underline{a}$, $\underline{a}_\alpha$, $\underline{a}_\beta$, $\underline{b}$, $\underline{b}_{\beta J}$, $\underline{b}_{\beta S}$, $\underline{b}_{\beta N}$ have been theoretically evaluated
[8a].

where the selection rule $\Delta\Sigma=0$ of an $a \rightarrow a$ transition is taken into account. Henceforth, we designate it $\underline{M}^{(0)}$ (1;f) or $\underline{M}^{(0)}(\underline{n}\Sigma\underline{v}J:\underline{n}'\Sigma\underline{v}'\underline{J}')$.

The modulus of the square of $\underline{M}^{(1)}(\underline{n}\Sigma\underline{v}J:\underline{n}'\Sigma\underline{v}'\underline{J}')$ gives us the desired intensity factor.

B. Evaluation of Perturbed Intensity Factor

We designate $|\psi^{(1)}\rangle$ or $|\underline{n}(\underline{L})\Lambda\underline{S}\Sigma\underline{v}\Omega J M\rangle_1$ the wave function of the initial corrected first order state. It is expressed by (9)

$$|n(L)\Lambda S\Sigma v\Omega JM\rangle_1 = |n(L)\Lambda S\Sigma v\Omega JM\rangle$$
$$+ \lambda \sum_{v_1 \neq v} \frac{\langle v_1|h|v\rangle + \langle v_1|A|v\rangle\Lambda\Sigma + \langle v_1|B|v\rangle[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2]}{h\omega(v - v_1)}$$

$$\times |n(L)\Lambda S\Sigma v_1 \Omega JM\rangle - \lambda \sum_{v_1 \neq v} \frac{\langle v_1|B|v\rangle}{h\omega(v - v_1)}\{[(S+\Sigma)(S-\Sigma+1)(J+\Omega)(J-\Omega+1)]^{1/2}$$

$$\times |n(L)\Lambda S \Sigma - 1 v_1 \Omega - 1 JM\rangle + [(S-\Sigma)(S+\Sigma+1)(J-\Omega)(J+\Omega+1)]^{1/2}$$

$$\times |n(L)\Lambda S \Sigma + 1 v_1 \Omega + 1 JM\rangle\} \qquad (12)$$

or

$$|\Psi^{(1)}\Sigma\Omega v\rangle = |\Psi^{(0)}\Sigma\Omega v\rangle + \lambda\left[\sum_{v_1 \neq v} a(v_1,v) + b(v_1,v)J(J+1)\right]|\Psi^{(0)}\Sigma\Omega v_1\rangle$$

$$- \lambda \sum_{v_1 \neq v} b(v_1,v)\{[(S+\Sigma)(S-\Sigma+1)(J+\Omega)(J-\Omega+1)]^{1/2}|\Psi^{(0)}\Sigma - 1 \Omega - 1 v_1\rangle$$

$$+ [(S-\Sigma)(S+\Sigma+1)(J-\Omega)(J+\Omega+1)]^{1/2}|\Psi^{(0)}\Sigma + 1 \Omega + 1 v_1\rangle\} \qquad (13)$$

with

$$a(v_1,v) = \frac{\langle v_1|h|v\rangle + \langle v_1|A|v\rangle\Lambda\Sigma + \langle v_1|B|v\rangle[S(S+1) - \Omega^2 - \Sigma^2]}{h\omega(v - v_1)}$$

$$b(v_1,v) = \frac{\langle v_1|B|v\rangle}{h\omega(v - v_1)}$$

We shall designate all the symbols relative to the final state.

Thus, reduced matrix element $\underline{M}$ is given by

$$\langle\Psi^{(1)}||M||\Psi^{(1)}\rangle = M^{(0)}(n\Sigma vJ;n'\Sigma v'J')\{1 + \lambda \sum_{v_1 \neq v} [a(v_1,v) + b(v_1,v)J(J+1)] \rho(v_1,v)$$

$$+ \lambda \sum_{v_1' \neq v'} [a'(v_1',v') + b'(v_1',v')J'(J'+1)] \rho(v,v_1')\}$$

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with

$$\rho(v_1, v_2') = \frac{M^{(0)}(n\Sigma v_1 J; n'\Sigma v_2' J')}{M^{(0)}(n\Sigma v J; n'\Sigma v' J')}$$

perturbations of $\Delta\Sigma = \pm 1$ only appear in the second order in the matrix element. We assume

$$\alpha = \sum_{v_1 \neq v} a(v_1, v)\rho(v_1, v'), \qquad \beta = \sum_{v_1 \neq v} b(v_1, v)\rho(v_1, v')$$

$$\alpha' = \sum_{v_1' \neq v'} a'(v_1', v')\rho(v, v_1'), \qquad \beta' = \sum_{v_1' \neq v'} b'(v_1', v')\rho(v, v_1') \qquad (15)$$

and we thus obtain the general form of the first order element

$$M^{(1)}(n\Sigma v J; n'\Sigma v' J') = M^{(0)}(n\Sigma v J; n'\Sigma v' J')[1 + \lambda\alpha + \lambda\alpha' + \lambda\beta J(J+1) + \lambda\beta' J'(J'+1)] \qquad (16)$$

The intensity factor is given by

$$m^{(1)}(n\Sigma v J; n'\Sigma v' J') = m^{(0)}(n\Sigma v J; n'\Sigma v' J')[1 + 2\lambda\alpha + 2\lambda\alpha' + 2\lambda\beta J(J+1) + 2\lambda\beta' J'(J'+1)] \qquad (17)$$

The expression between brackets is customarily given by $\underline{F}(\underline{J})$, replacing $\underline{J}'$ by $\underline{J}$, $\underline{J}\pm 1$, according to the type of splitting ($\underline{P}$, $\underline{Q}$, $\underline{R}$) studied, and it is called the factor or function of Herman and Wallis [14]. We note that ratios ρ defined in (14) do not depend on $\underline{J}$. In fact, by using (11),

$$\rho(v_1, v_2') = \frac{M^{(0)}(n\Sigma v_1 J; n'\Sigma v_2' J')}{M^{(0)}(n\Sigma v J; n'\Sigma v' J')} = \frac{\langle n'(L)\Lambda' S'\Sigma v_2' |\mu_s| n(L)\Lambda S\Sigma v_1 \rangle}{\langle n'(L)\Lambda' S'\Sigma v' |\mu_s| n(L)\Lambda S\Sigma v \rangle} \qquad (18)$$

In the second order of perturbation theory, the factor of Herman and Wallis [14] is much more complex, as can be foreseen in the expression for $\underline{U}_2$ (9), which is comparable to the third order of perturbation theory applied to $\underline{H}$ [8b]. The degree of the polynomial of $\underline{J}(\underline{J}+1)$ and $\underline{J}'(\underline{J}'+1)$, which gives $\underline{F}(\underline{J})$, will increase, and the coefficients will interpose matrix elements $\underline{M}$ between functions $|\psi^{(0)}\Sigma\pm 1\rangle$, which already appear in (13). The calculation, although tedious, offers no difficulty in principle, but it will not be dealt with here.

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V. Applications

We propose two applications of this general calculation: first, to find the relations of Herman and Wallis [14] in the case of a rotational-vibrational spectrum; then, to use formula (17) in study of an electron spectrum and more precisely verify that the effect of Herman and Wallis is actually negligible, in the case of the $\underline{A}^2\Pi(\underline{v}=0) \to \underline{X}^2\Sigma(\underline{v}=0)$ transition of ScO, a study of which has been presented elsewhere [12]. These two applications will essentially permit us to review a certain number of approximations and evaluations of coefficients in current usage.

We start by evaluating coefficients $\underline{a}$, $\underline{a}'$, $\underline{b}$ and $\underline{b}'$, defined in (13).

A. Expansions and Approximate Relations

Let the following be evaluated

$$\frac{\langle v_1|B(r)|v \rangle}{\hbar\omega(v - v_1)} (v_1 \neq v)$$

Function $B(r)$ is known exactly, since

$$B(r) = \frac{h}{2\mu r^2} = \frac{h}{2\mu r_e^2}\left(1 + \frac{q}{r_e}\right)^{-2} \simeq B_e - 2\frac{B_e}{r_e}q + 3\frac{B_e}{r_e^2}q^2 - 4\frac{B_e}{r_e^3}q^3 \tag{19}$$

with $\underline{B_e}=\hbar/2\mu \underline{r_e}^2$, $\underline{q}=\underline{r}-\underline{r_e}$, $\underline{r_e}$ is the internuclear distance at equilibrium [16]. Therefore, we have, in the third order of $\underline{q}$, by using (29) in Femenias [8b]

$$
\begin{aligned}
b(v_1, v) = \frac{\langle v_1|B(r)|v \rangle}{\hbar\omega(v - v_1)} &= -\frac{2B_e}{\hbar\omega r_e}\xi v^{1/2}\left[1 - 6\frac{\xi^2}{r_e^2}v\right] && \text{if } v_1 = v - 1 \\
&= +\frac{2B_e}{\hbar\omega r_e}\xi(v + 1)^{1/2}\left[1 + 6\frac{\xi^2}{r_e^2}(v + 1)\right] && \text{if } v_1 = v + 1 \\
&= +\frac{3B_e}{2\hbar\omega r_e^2}\xi^2[v(v - 1)]^{1/2} && \text{if } v_1 = v - 2 \\
&= -\frac{3B_e}{2\hbar\omega r_e^2}\xi^2[(v + 1)(v + 2)]^{1/2} && \text{if } v_1 = v + 2
\end{aligned}
\tag{20}
$$

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$$= -\frac{4B_c}{3\hbar\omega r_c^3}\,\xi^3\,[v(v-1)(v-2)]^{1/2} \qquad \text{if } v_1 = v - 3$$

$$= +\frac{4B_c}{3\hbar\omega r_c^3}\,\xi^3\,[(v+1)(v+2)(v+3)]^{1/2} \qquad \text{if } v_1 = v + 3 \tag{20}$$

where

$$\xi = \hbar/\sqrt{2\mu\hbar\omega}.$$

The same type of relation can be obtained in evaluation of $\qquad$ /1781
$[<v_1|h|v>]/[\hbar\omega(v-v_1)]$, by using the expansion of h (10). We some-
times note here that this expansion only begins in order 3 of q
and that its coefficients are less easy to obtain by spectroscopic
measurements ((41) in Fémènias [8b]). We will have occasion to
return to these difficulties in subsection C of this section.

By retaining only the first term $w_3 q^3$, the following is
obtained

$$\frac{\langle v_1|h|v\rangle}{\hbar(v-v_1)} = \frac{3w_3\xi^3}{\hbar\omega}\,v^{3/2} \qquad \text{if } v_1 = v - 1$$

$$= -\frac{3w_3\xi^3}{\hbar\omega}\,(v+1)^{3/2} \qquad \text{if } v_1 = v + 1 \tag{21}$$

$$= \frac{w_3\xi^3}{3\hbar\omega}\,[v(v-1)(v-2)]^{1/2} \qquad \text{if } v_1 = v - 3$$

$$= -\frac{w_3\xi^3}{3\hbar\omega}\,[(v+1)(v+2)(v+3)]^{1/2} \qquad \text{if } v_1 = v + 3$$

$$= 0 \qquad \text{if } v_1 = v \pm 2$$

The expansion of $A(r)$ by powers of q is noted

$$A(r) = A(r_c) + A_1 q + A_2 q^2 + A_3 q^3 \tag{22}$$

and, hence, we obtain, for values of $a(v_1, v)$ (13)

$$a(v-1,v) = \frac{\xi v^{1/2}}{\hbar\omega}\left\{3w_3\xi^2 v + [A_1 + 3A_3\xi^2 v]\Lambda\Sigma \right.$$
$$\left. -\frac{2B_c}{r_c}\left[1 + 6\frac{\xi^2}{r_c^2}v\right][S(S+1) - \Omega^2 - \Sigma^2]\right\} \tag{23}$$

$$a(v+1,v) = -\frac{\xi(v+1)^{1/2}}{\hbar\omega}\left\{3w_3\xi^2(v+1) + [A_1 + 3A_3\xi^2(v+1)]\Lambda\Sigma \right.$$
$$\left. -\frac{2B_c}{r_c}\left[1 + 6\frac{\xi^2}{r_c^2}(v+1)\right][S(S+1) - \Omega^2 - \Sigma^2]\right\}$$

$$a(v-2,v) = \frac{\xi^2[v(v-1)]^{1/2}}{2h\omega}\left\{A_2\Lambda\Sigma + \frac{3B_e}{r_e^2}[S(S+1) - \Omega^2 - \Sigma^2]\right\}$$

$$a(v+2,v) = -\frac{\xi^2[(v+1)(v+2)]^{1/2}}{2h\omega}\left\{A_2\Lambda\Sigma + \frac{3B_e}{r_e^2}[S(S+1) - \Omega^2 - \Sigma^2]\right\}$$

$$a(v-3,v) = \frac{\xi^3}{3h\omega}[v(v-1)(v-2)]^{1/2}\left\{w_3 + A_3\Lambda\Sigma - \frac{4B_e}{r_e^3}[S(S+1) - \Omega^2 - \Sigma^2]\right\}$$

$$a(v+3,v) = -\frac{\xi^3}{3h\omega}[(v+1)(v+2)(v+3)]^{1/2}\left\{w_3 + A_3\Lambda\Sigma - \frac{4B_e}{r_e^3}[S(S+1) - \Omega^2 - \Sigma^2]\right\}$$

In the case of $\underline{A}$ also, the customary spectroscopic data do not allow coefficients $\underline{A}_1$, $\underline{A}_2$, $\underline{A}_3$,...to be obtained easily. Therefore, we take a simple case, to evalute the term $[<\underline{v}_1|\underline{A}(\underline{r})|\underline{v}>]/[\underline{h}\omega(\underline{v}-\underline{v}_1)](\underline{v}_1\neq\underline{v})$. We know that the variation of $\underline{A}$ with $\underline{r}$ is expressed by the appearance of parameters $\underline{A}_J$ and $\underline{A}^0$ in the diatomic Hamiltonian [8b]. By assuming that these parameters are essentially due to perturbations by the two closest vibrational levels of $\underline{v}$, $\underline{v}'=\underline{v}\pm1$, and by reasoning in a similar manner for $\underline{D}$, the following relations are easily obtained

$$Y^2 - X^2 \simeq A^0 \qquad\qquad (24) \quad \underline{/17}$$

$$y^2 - x^2 \simeq - Dh\omega \qquad\qquad (25)$$

$$Yy - Xx \simeq A_J h\omega$$

with

$$X = \langle v+1|A|v\rangle \simeq \xi(v+1)^{1/2}[A_1 + 3A_3\xi^2(v+1)] \quad x = \langle v+1|B|v\rangle$$

$$Y = \langle v-1|A|v\rangle \simeq \xi v^{1/2}[A_1 + 3A_3\xi^2 v] \qquad\qquad y = \langle v-1|B|v\rangle$$

Parameter $\underline{A}^0$ is generally unobtainable numerically, since it is included in source energy $\underline{T}$ (8b); meanwhile, Merer [19] has evaluated it

$$A^0 \simeq - A_J^2/D \qquad\qquad (26)$$

The fourth equation necessary for solution of this system is obtained, by using the matrix elements of the expansion of $\underline{B}$ (19), (20). We note that, for the $\underline{v}=0$ levels, $\underline{y}=\underline{Y}=0$, and system (25) is sufficient for determination of $\underline{X}$ and $\underline{x}$. Besides, system (25) is also sufficient for $\underline{v}\neq0$, if $\underline{A}_3$ is disregarded.

It goes without saying that these last relations are only to provide approximate values, which permit justification of the working hypotheses or to theoretically confirm some observations (see Section V C). They have the same mathematical value as the third order expansions of $\underline{q}$ which lead to (20) and (23).

B. Rotational-Vibrational Spectra. The Problem of Herman and Wallis [14]

We take the case where the initial and final electron states are identical, and we evaluate the various terms which occur in (17). For that, we use the expansions of $\underline{a}(\underline{v}_1,\underline{v})$ and $\underline{b}(\underline{v}_1,\underline{v})$, given in (20) and (23) but, also, the expansions of the spherical tensor components $\mu_{\underline{s}}(\underline{r})(\underline{s}=0,\pm 1)$ of $\underline{M}$, in Oxyz molecular coordinates [10]

$$\mu_s(r) = \sum_{i=0}^{i} \mu_{si} q^i \quad s = 0, \pm 1 \tag{27}$$

Ratios $\rho(\underline{v}_1,\underline{v'}_2)$, defined in (18), are then written, retaining only the quantum numbers of interest in this case,

$$\rho(v_1, v_2') = \frac{\langle n\Lambda v_2'|\mu_s|n\Lambda v_1\rangle}{\langle n\Lambda v'|\mu_s|n\Lambda v\rangle} = \frac{\langle v_2'|\mu_0|v_1\rangle}{\langle v'|\mu_0|v\rangle} \simeq \frac{\langle v_2'|\mu_{00} + \mu_{01}q|v_1\rangle}{\langle v'|\mu_{00} + \mu_{01}q|v\rangle} \tag{28}$$

The arbitrary stop in expansion of the $\underline{q}$ term is explained, only by our desire to compare our results with those of Herman and Wallis [14]. It is evident that, a priori, no connection exists between the orders of expansion of $\mu_{\underline{s}}$, $\underline{A}(\underline{r})$, $\underline{B}(\underline{r})$ and $\underline{h}$anharm, if it is not a power of $\underline{q}$.

The sequence of calculation is evident, and we give no more details of it. Application of the various relations (15), (20), (23), (28) and (17) will permit the following result, peculiar to to transitions $\underline{v} \to \underline{v}' = \underline{v}+1$, to be obtained without difficulty

$$
\begin{aligned}
m^{(1)}(n\Sigma vJ; n\Sigma\ v+1\ J') = m^{(0)}(n\Sigma vJ; n\Sigma\ v+1\ J') \Big\{ 1 - \frac{2\xi^3}{\hbar\omega}(v+1)^{1/2}(A_2\Lambda\Sigma + \frac{3B_e}{r_e^2} \\
\times [S(S+1) - \Omega^2 - \Sigma^2])\frac{\mu_{01}}{\mu_{00}} + \frac{4B_e}{\hbar\omega r_e}\xi(v+1)^{1/2}\Big[1 + 6\frac{\xi^2}{r_e^2}(v+1)\Big][J(J+1) - J'(J'+1)] \\
- \frac{3B_e\xi^3}{\hbar\omega r_e^2}(v+2)(v+1)^{1/2}\frac{\mu_{01}}{\mu_{00}}J(J+1) + \frac{3B_e\xi^3}{\hbar\omega r_e^2}v(v+1)^{1/2}\frac{\mu_{01}}{\mu_{00}}J'(J'+1)\Big\}
\end{aligned}
\tag{29}
$$

where $\underline{r_e}$ can be replaced by $\xi(\omega/\underline{B_e})^{1/2}$. The application to the 0→1 and 1→2 transitions, dealt with by Herman and Wallis [14], is immediate, but it will not be detailed here. On the other hand, some remarks can be made on this subject.

Herman and Wallis [14] arranged their terms by increasing powers of $\gamma=2\underline{B_e}/\omega$, and the preceding calculation permits these terms to be found, up to order γ^1; some γ^2 terms also appear in the present calculation. On the other hand, beside the missing γ^2 /17?3 terms, the total absence of terms due to anharmonicity ($\underline{w_3}$) can be noted, with a single look at expression (29), while these terms appear in Herman and Wallis.

If the expansion of (17) is extended to the γ^2 terms, some purely centrifugal contributions of γ^2 of Herman and Wallis can be found but, obviously, no anharmonic contribution. Actually, taking account of the λ^2 terms in (17) is disputable, for these terms are theoretically of the second order and, therefore, they should only be taken into account, if the wave functions are expanded to the second order (9). It can be verified that, in this case, the calculation makes the anharmonic contributions of Herman and Wallis appear.

The explanation of these phenomena is simple: in the meaning of the calculations presented here, the initial functions used by Herman and Wallis are already perturbed, because the linear and quadratic distortions of $\underline{B}$ are taken into account from the beginning of their calculation (Herman and Wallis [14], Eq. 7). The perturbation introduced by these authors is only relative to the $\underline{q}^3$ terms of $\underline{hanharm}$ and $\underline{B}(\underline{r})$. Therefore, the first order of Herman and Wallis corresponds to a higher order of this calculation (actually, an order intermediate between our first and second orders). Besides, Herman and Wallis make terms analogous to our λ^2 contributions appear in $\underline{F}(\underline{m})$. As an example, the $\theta^2\gamma^2\underline{m}^2$ terms of the 0→1 and 1→2 transitions, which is justified in their calculation, because their expansion is carried out by powers of γ.

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We conclude that it is impossible to compare our orders and those of Herman and Wallis and that only a comparison of individual terms has meaning. We simply note that expression (29), more general than that of Herman and Wallis, since it is applicable to any Λ multiplet for an arbitrary y, permits the first terms of the expansion of these authors to be found, without any previous knowledge of the analytical form of the wave functions. We also emphasize that the spin-orbit correction constant is especially small, since it makes the second coefficient of the expansion of $\underline{A}(\underline{r})$, $\underline{A}_2$, come into play. Finally, and above all, we stress the fact that the effect of anharmonicity only comes into play in the <u>second order</u> of perturbation theory, the essential effect of the first order being due to centrifugal phenomena [5].

The problem then arises, of knowing if it occurs for a $\underline{y} \rightarrow \underline{y} + 2$ transition, where the anharmonic effects are large [14]. A calculation similar to the preceding one permits the following to be obtained

$$
m^{(1)}(n\Sigma v J; n\Sigma\, v + 2\, J') = (2J' + 1)(2J + 1)\left(\begin{array}{ccc} J' & 1 & J \\ -\Omega & 0 & \Omega \end{array}\right)^2 \mu_{01}\, \frac{2\xi^2}{\hbar\omega}[(v + 1)(v + 2)]^{1/2}
$$
$$
\times \left\{ 2\xi^2(w_3 + A_3\Lambda\Sigma - 4\frac{B_e}{r_e}[S(S + 1) - \Omega^2 - \Sigma^2]) + \frac{B_e}{r_e}\left([J(J + 1) - J'(J' + 1)]\right. \right.
$$
$$
\left. \times \left[2 + \frac{\xi^2}{r_e^2}\left(\frac{22v}{3} + 10\right) - \frac{3}{2r_e}\frac{\mu_{00}}{\mu_{01}}\right] - 2\frac{\xi^2}{r_e^2}J'(J' + 1)\right) \right\}
$$
(30)

where the angular portion deduced from (11) has been explained. The same remarks can be repeated here, for higher orders of $\gamma = 2\underline{B}_e/\omega$. For the first terms, like Herman and Wallis, we find the constant contribution of anharmonicity, which occurs here in our first order. This order, the variation of the factor of Herman and Wallis with $\underline{J}$ and $\underline{J'}$, is only due to centrifugal effects.

The same type of calculation could be repeated without difficulty, in the more general case, for the $\underline{y} \rightarrow \underline{y} + 3$, $\underline{y} \rightarrow \underline{y} + 4$, etc., the case which happens in following the expansions of $\underline{h}_{anharm}$, $\underline{B}(\underline{r})$

and $\underline{A}(\underline{r})$. But, there is interest here in adjusting the orders of
Herman and Wallis, since it quantitatively determines the degree
to which expansion of these quantities imposes the introduction of
a higher order of perturbation of the wave functions. The expres-
sions of an arbitrary order of the most general factors of Herman
and Wallis, therefore, can theoretically be calculated without dif-
ficulty, unless it is the somewhat less tedious nature of the
expansions.

C. Electron Spectra

1. Franck-Condon and "r-centroid" Factors

In the case of electron spectra, the problem is complicated
by the fact that the vibrational functions depend on the electron
nature of each state, by means of $\underline{r}_e$ and the location and shape of
each potential energy curve. This affects the radial portion of
$\underline{M}^{(0)}(\underline{n}\Sigma\underline{v}J; \underline{n}'\Sigma\underline{v}'J')$ in (16), i.e., $\langle\underline{n}'(\underline{L}')\Lambda'\underline{S}'\Sigma\underline{v}'|\mu_{\underline{s}}|\underline{n}(\underline{L})\Lambda\underline{S}\Sigma\underline{v}\rangle$ or
$\langle\underline{n}'(\underline{L}')\Lambda'\underline{v}'|\mu_{\underline{s}}|\underline{n}(\underline{L})\Lambda\underline{v}\rangle$(11). This element is written

$$\langle v'|(\langle n'(L')\Lambda'|\mu_s(r)|n(L)\Lambda\rangle)|v\rangle = \langle v'|R_{es}(r)|v\rangle \qquad (31)$$

while remembering that the electron functions depend parametrically
on $\underline{r}$ [8b] and by assuming

$$\langle n'(L')\Lambda'|\mu_s(r)|n(L)\Lambda\rangle = R_{es}(r) = \text{Component } \underline{s} \text{ of the "electron tran-} \qquad (32)$$
sition moment."

To the extent that $\underline{R}_{es}(\underline{r})$ varies little with $\underline{r}$, there is

$$\langle n'(L')\Lambda'v'|\mu_s|n(L)\Lambda v\rangle \simeq R_{es}q_{vv'}. \qquad (33)$$

$\underline{q}_{vv'}$ being an integral of the overlap of pure vibrational functions,
called the Franck Condon factor [15].

If it is not possible to disregard the variation of $\underline{R}_{es}$ with
$\underline{r}$, it is possible to carry out a limited expansion around a value
$\overline{\underline{r}}$. Therefore, the problem is to select this value. Thus, we have

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$$R_{cs}(r) = R_{cs}(\bar{r}) + (r - \bar{r})\left(\frac{\partial R_{cs}}{\partial r}\right)_{\bar{r}} + \sum_{k=2}^{\infty}\frac{(r - \bar{r})^k}{k!}\left(\frac{\partial^k R_{cs}}{\partial r^k}\right) + ... \tag{34}$$

Consequently,

$$\langle n'(L')\Lambda'v'|\mu_s|n(L)\Lambda v\rangle = R_{cs}(\bar{r})q_{vv'} + \left(\frac{\partial R_{cs}}{\partial r}\right)_{\bar{r}}\langle v'|r - \bar{r}|v\rangle + \sum_{k=2}^{\infty}\frac{1}{k!}\left(\frac{\partial^k R_{cs}}{\partial r^k}\right)_{\bar{r}}\langle v'|(r - \bar{r})^k|v\rangle \tag{35}$$

It seems natural enough to select a value for $\bar{r}$, which cancels the first term of this expansion. Therefore, the following is assumed

$$\bar{r} = \frac{\langle v'|r|v\rangle}{\langle v'|v\rangle} = \quad \text{"r-centroid" of the } n\Lambda r \rightarrow n'\Lambda'v' \text{ transition} \tag{36}$$

This is the procedure of Halevi [13]. Therefore,

$$\langle n'(L')\Lambda'v'|\mu_s|n(L)\Lambda v\rangle = R_{cs}(\bar{r})q_{vv'}\left[1 + \sum_{k=2}^{\infty}\frac{1}{k!R_{cs}(\bar{r})}\left(\frac{\partial^k R_{cs}}{\partial r^k}\right)_{\bar{r}}\mathscr{S}_k\right] \tag{37}$$

with

$$\mathscr{S}_k = \frac{\langle v'|(r - \bar{r})^k|v\rangle}{\langle v'|v\rangle} = \quad \text{moment of order } \underline{k}$$

This relation, associated with formula (11) and (16), permits the expression of $\underline{M}^{(1)}(\underline{n}\Sigma\underline{v}J;\underline{n'}\Sigma\underline{v'}J')$ in the general case, therefore, also the intensity factor $\underline{m}^{(1)}(\underline{n}\Sigma\underline{v}J;\underline{n'}\Sigma\underline{v'}J')$.

We note that, in the first order of perturbation theory, the last term of (12), the $\underline{J}^{\pm}\underline{S}_{\mp}$ term, does not come into play. There are no first order $\Delta\Sigma\neq0$ transitions. There is only a risk of these transitions appearing in the second order, for type a states.[2] In the case of $\underline{a}$-$\underline{b}$ or $\underline{b}$-$\underline{b}$ transitions, the $\Delta\Sigma=0$ rule is broken, by means of mixtures of different Σ functions in each state, introduced by the mixing parameters.

---

[2]Do not confuse this effect, from the $\underline{v_1}\neq\underline{v}$ and $\underline{v_1'}\neq\underline{v'}$ levels, with the "direct" spin decoupling effect, due to perturbations between the levels of different Σ, but of the same value of $\underline{v}$ (or $\underline{v'}$). The latter is accounted for directly by the mixing parameters (see Section III C).

Therefore, the calculation procedure is theoretically simple.

First stage: analog of the "transformation of Van Vleck" [23] or of Jørgensen [17, 8b]: establishment of the expressions of wave functions (13) and of matrix element $\underline{M}(i;f)$, perturbed in the first or second order. The first order essentially causes centrifugal perturbations and the second, anharmonic perturbations, as well as "secondary" spin decoupling effects (perturbation of the $\Sigma\underline{v}$ level by a $\Sigma'\underline{v}_1$ level, $\Sigma'=\Sigma\pm 1$ and $\underline{v}_1\neq\underline{v}$).

Second stage: these expression still depend on values of $\underline{M}^{(0)}$ $(i;f)$ and on ratios ρ, in which the "$\underline{r}$-centroids", the Franck-Condon factors and moments of order $\underline{k}$ come into play. As to the "r-centroids," an account of their general properties is found in Schamps [20]. Besides, there are numerous articles in the literature on the "$\underline{r}$-centroids" of individual molecules. The Franck-Condon factors for a hundred systems of 72 diatomic molecules have been cataloged in McCallum et al [18]. As to moments $\mathcal{S}^k$, they occur mainly with hydrides.

Third stage: matrix elements $\underline{M}(i;f)$ are now externally perturbed. The calculation is ended, by introducing internal perturbations, i.e., mixtures of components Σ of the $\underline{v}'$ level under study, due to "direct" spin decoupling. This last stage has been illustrated by Féménias et al [12], in the case of $\underline{A}^2\Pi\rightarrow\underline{X}^2\Sigma$ and $\underline{B}^2\Sigma\rightarrow\underline{X}^2\Sigma$ systems of ScO.

2. Application to ScO

We shall use the preceding theoretical expansion to verify the hypothesis we made in a preceding study of the ScO spectrum [12], to find out if the effects of Herman and Wallis can be disregarded in the interval of values of $\underline{J}$ under study. Our calculation will be carried out for the (0,0) band of the $\underline{A}^2\Pi_{3/2}\rightarrow\underline{X}^2\Sigma$ transition of ScO. The use of (12), (16), (21) and the notations

introduced in (25) gives

$$M^{(1)}(A^2\Pi_{3/2}\, v = 0\, J;\, X^2\Sigma\, v = 0\, J) \simeq M^{(0)}(A^2\Pi_{3/2}\, v = 0\, J;\, X^2\Sigma\, v = 0\, J)$$

$$\times \left\{ 1 - \frac{1}{\hbar\omega}\left[3w_3\xi + \frac{X}{2} - \frac{7}{4}x \right]\rho(1,0) - \frac{1}{\hbar\omega'}\left[3w_3'\xi'^3 + \frac{x'}{4} \right]\rho(0,1) \right. \tag{38}$$

$$\left. - \frac{x}{\hbar\omega}\rho(1,0)\, J(J+1) - \frac{x'}{\hbar\omega'}\rho(0,1)J'(J'+1) \right\}$$

Useful data on ScO are presented in Table 1, and they result in
the following values

$$x \simeq 2.5 \times 10^{-2}\,\text{cm}^{-1};\quad x' \simeq 2.4 \times 10^{-2}\,\text{cm}^{-1}$$

$$X \simeq -1.12\,\text{cm}^{-1} \tag{39}$$

$$\frac{\xi^3 w_3}{\hbar\omega} \simeq 1.45 \times 10^{-2}\,\text{cm}^{-1};\quad \frac{\xi'^3 w_3'}{\hbar\omega'} \simeq 1.20 \times 10^{-2}\,\text{cm}^{-1}$$

We draw attention to the manner in which the anharmonicity
constants have been derived. Equation (41) of Féménias [8b]
permits a relation among $\omega_e x_e, w_3$ and w_4 to be obtained. We have
disregarded w_4 and extracted w_3. It is quite evident that the
contribution of w_4 greatly risks being of the same order of magni-
tude as that of $(5/2)w_3^2/\mu\omega^2$; consequently, the values obtained in
(39) for the anharmonic effect can only be used as simple, rather
rough orders of magnitude.

TABLE 1.   NUMERICAL DATA ON
S O MOLECULE [3,6] (cm^{-1}.)

Parameter	State	
	$A^2\Pi_{3/2}$	$X^2\Sigma$
D	0.69×10^{-6}	0.59×10^{-6}
A_J	$\sim 10^{-4}$	—
ω_e	881.6	975.7
$x_e\omega_e$	5.5	4.2

Numerical application results in

$$m^{(1)}(A^2\Pi_{3/2}\, v = 0\, J;\, X^2\Sigma\, v = 0\, J') = m^{(0)}(A^2\Pi_{3/2}\, v = 0\, J;\, X^2\Sigma\, v = 0\, J)\{1 - [7.5\rho(1,0) \tag{40}$$

$$+ 7.2\rho(0,1)]10^{-2} - [5.7\rho(1,0)J(J+1) + 5\rho(0,1)J'(J'+1)]10^{-5}\}$$

With the lack of any supplementary information on ScO and based on the appearance of our spectra [21], we _increase_ $\rho(1,0)$ and $\rho(0,1)$ by 1, and the (1,0) and (0,1) bands appear slightly weaker than the (0,0) band. Under these conditions, the factor of Herman and Wallis becomes

$$F(J,J') = 1 - 14.7 \times 10^{-2} - [5.7J(J+1) + 5J'(J'+1)]10^{-5} \qquad (41)$$

When a ratio of the line to line intensity is set up, it is seen in this expression that the difference between the Herman and Wallis factors in the numerator and denominator is on the order of magnitude of the coefficients of $\underline{J}(\underline{J}+1)$ and $\underline{J'}(\underline{J'}+1)$ /1786 multiplied by $4\underline{J}$ at the maximum, while retaining only the largest terms; therefore, if $\underline{J}$ does not exceed 50, this difference is on the order of 1% and its effect is negligible, compared with the observed spin decoupling effect (ratio on the order of 4) which explains why we have not previously taken account of $\underline{F}(\underline{J},\underline{J'})$ in this type of study [12]. In a "temperature curve," i.e., $\ln(\underline{I}(\underline{J})/\underline{m}(^0))$ vs. $\underline{J}(\underline{J}+1)$, where $\underline{I}(\underline{J})$ is the measured intensity of band $\underline{J}$ (without specifying the line) the correction to be applied, $\ln \underline{F}(\underline{J},\underline{J'})$ is on the order of $\ln 0.6$, for $\underline{J}=50$, thus, 0.5 to the initial value, which is on the order of 1 for the lines under study. This effect is large and, accordingly, completely observable. The total lack of deviation causes us to think that our increase of $\rho(1,0)$ and $\rho(0,1)$ is essential and that it must not be expected that these ratios ratios are greater than 0.25, such a value giving a scarcely observable (but not observed) deviation, at the limit of our measurements. The effect of Herman and Wallis [14] is, therefore, quite negligible in our preceding study of ScO [12].

However, this latter aspect of the calculation brings out, in a very clear way, the existing interconnection between studies of position and intensity, and it shows how the remarkable precision of numerical adjustments of frequencies can be used, to obtain the advantage of the great sensitivity of the intensities. To

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minimize the intensity factor error permits the statistical data to be made more reliable, so that intensities can be derived. This results in a better understanding of extramolecular phenomena, such as excitation and collision.

VI. Conclusion

Our entire study has, thus, permitted us to set up a method of calculation of actual diatomic wave functions and intensity factors, which can be developed to any precision, parallel to the method of calculation of Hamiltonians [8b].

This method requires practically no prior knowledge, since the expansion is carried out with wave functions, the analytical form of which is not defined. Besides, the calculation can be carried out for any transition between any st ᵗes or levels. As to the "mixing coefficients", required for the final calculation, they can be obtained rather simply, from constants derived from analysis of rotation, when this analysis has not been carried out according to actual numerical diagonalization techniques.

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