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G. Grynberg, F. Biraben, E. Giacobino, B. Cagnac. Doppler-free two-photon spectroscopy of neon. II. Line intensities. *Journal de Physique*, 1977, 38 (6), pp.629-640. 10.1051/jphys:01977003806062900 . jpa-00208622

HAL Id: jpa-00208622

<https://hal.science/jpa-00208622>

Submitted on 1 Jan 1977

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Classification
Physics Abstracts
 2.630 — 5.235

DOPPLER-FREE TWO-PHOTON SPECTROSCOPY OF NEON. II. LINE INTENSITIES

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(Reçu le 9 février 1977, accepté le 4 mars 1977)

Résumé. — Nous présentons dans cet article le principe du calcul des intensités des composantes hyperfines d'une raie d'absorption à deux photons et nous comparons les résultats du calcul à nos résultats expérimentaux. Dans la première partie de l'article nous décomposons l'opérateur transition à deux photons sur une base d'opérateurs tensoriels irréductibles. Cet opérateur est en général la somme de deux opérateurs, l'un scalaire, l'autre quadripolaire. Nous en déduisons les règles de sélection pour l'absorption à deux photons ainsi que les formules permettant de calculer l'intensité des composantes hyperfines d'une raie d'absorption à deux photons. Nous donnons également la matrice densité dans l'état excité après le processus d'excitation à deux photons, ce qui permet de calculer l'intensité des raies de fluorescence. Nous étudions enfin les grandeurs intervenant dans l'élargissement par collision d'une raie d'absorption à deux photons. Dans la seconde partie nous présentons les spectres hyperfins expérimentaux obtenus dans l'atome de néon 21 pour les transitions entre le métastable $3s[3/2] 2$ et les niveaux excités $4d'[3/2] 2$, $4d'[5/2] 2$ et $4d[3/2] 2$. Ces transitions sont intéressantes parce que les moments cinétiques extrêmes de la transition étant égaux, l'opérateur transition à deux photons comporte une partie isotrope et une partie quadripolaire. Nous montrons que les rapports expérimentaux entre les parties scalaires et quadripolaires de la transition sont très différents d'une transition à l'autre. Nous montrons enfin qu'un calcul théorique utilisant les formules de la première partie permet de rendre compte de ces rapports.

Abstract. — We report in this paper the principle of the calculation of the hyperfine components of a two-photon absorption line and we compare the results of the calculation with some of our experimental results. In the first part of the paper, the two-photon transition operator is expanded on a tensorial irreducible set basis. That operator is generally the sum of two operators, one scalar and the other one quadrupolar. We deduce from it the selection rules for two-photon absorption and the formulae which permit one to calculate the intensities of the hyperfine components of a two-photon absorption line. We also report the density matrix in the excited state obtained after the two-photon excitation process, which permits one to calculate the fluorescence lines. At last we present the atomic quantities involved in the collision broadening of a two-photon absorption line. In the second part, we present the experimental hyperfine spectra obtained on the neon 21 atom for the transitions between the $3s[3/2] 2$ metastable level and the $4d'[5/2] 2$, $4d'[3/2] 2$ and $4d[3/2] 2$ excited levels. We show that the experimental ratios between the scalar and the quadrupolar parts are very different from one transition to another. At last we compare these ratios with theoretical values obtained using the formulae of the first part. We find a good agreement between experimental and theoretical values.

In a preceding paper [1] we have reported measurements of hyperfine structure in neon using Doppler-free two-photon spectroscopy. These measurements need an unambiguous interpretation of the hyperfine spectrum. We present in this paper how to calculate the intensity of each component of this spectrum.

The paper is divided in two parts. In the first part, we investigate in more detail the two-photon operator we have introduced before [2]. We show how this operator can be used in order to find the selection rules and to predict the line intensities. We show also that the atomic quantities involved in the shift and broadening of spectral lines are related to this operator. In the second part we present some hyperfine spectra in neon and we show how we can interpret them using

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the theory developed in the first part. We are in that paper mostly interested by the complex case where the experimental spectrum is the sum of two spectra [3], one which is of the scalar type, the second which is of the quadrupolar type ⁽¹⁾.

1. Application of the irreducible tensorial operator formalism to Doppler-free two-photon spectroscopy. —

1.1 TWO-PHOTON TRANSITION OPERATOR. — 1.1.1 Two-photon transition operator when the two photons have the same frequency. — At resonance, and for the Doppler-free line, the two-photon transition probability between levels g and e is equal to [2] :

$$\Gamma_g = \frac{n_1 n_2 \omega^2}{\varepsilon_0^2 \Gamma_e} \times \left| \sum_r \frac{\langle e | \mathbf{D} \cdot \boldsymbol{\varepsilon}_1 | r \rangle \langle r | \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 | g \rangle + \langle e | \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 | r \rangle \langle r | \mathbf{D} \cdot \boldsymbol{\varepsilon}_1 | g \rangle}{\hbar(\omega - \omega_r)} \right|^2 \quad (1)$$

The incoming and return waves have the same circular frequency ω , and polarizations $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$. The numbers of photons in the two involved modes are n_1 and n_2 . Γ_e is the width of the excited state e , $\mathbf{D}$ is the electric dipole operator and $\hbar\omega_r$ is the energy of the intermediate state r . We have chosen the origin for the energies so that the energy of level g is zero.

Formula (1) is demonstrated using perturbation theory to the second order. It follows that the result is restricted to the case where :

— The energy defects $\hbar(\omega - \omega_r)$ are much larger than the natural widths Γ_r and the Doppler widths of the r - g transitions.

— The transition rate Γ_g is much smaller than the natural width of the excited state Γ_e . The results are only valid in the non-saturation limit.

By introducing the symmetrical two-photon transition operator $Q_{\varepsilon_1 \varepsilon_2}^S$, defined by

$$Q_{\varepsilon_1 \varepsilon_2}^S = \frac{1}{2} \left[\mathbf{D} \cdot \boldsymbol{\varepsilon}_1 \frac{1}{\hbar\omega - \mathcal{H}_0} \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 + \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 \frac{1}{\hbar\omega - \mathcal{H}_0} \mathbf{D} \cdot \boldsymbol{\varepsilon}_1 \right] \quad (2)$$

$\mathcal{H}_0$ being the hamiltonian of the atom.

Formula (1) becomes

$$\Gamma_g = \frac{4 n_1 n_2 \omega^2}{\varepsilon_0^2 \Gamma_e} |\langle e | Q_{\varepsilon_1 \varepsilon_2}^S | g \rangle|^2. \quad (3)$$

⁽¹⁾ The results presented in that paper are taken from the thesis of G. Grynberg (Paris, avril 1976, C.N.R.S. AO 12497). Other results dealing with the two-photon operator and its experimental application in Doppler-free two-photon spectroscopy are presented there. Some of the results of the first part have been recently and independently published by Flusberg, Mossberg and Hartmann (ref. [4]).

To find formula (1) from formula (3), one has to introduce a closure relation $\left(\sum_r |r\rangle \langle r| = 1 \right)$ between

$\mathbf{D} \cdot \boldsymbol{\varepsilon}_1$ and $\frac{1}{\hbar\omega - \mathcal{H}_0}$ in the definition of $Q_{\varepsilon_1 \varepsilon_2}^S$.

Formulae (1) and (3) are strictly equivalent, the summation over all the relay levels r is included in the operatorial form of $Q_{\varepsilon_1 \varepsilon_2}^S$.

It clearly appears that the selection rules for the two-photon transitions and the intensity of the components can be deduced from the study of $Q_{\varepsilon_1 \varepsilon_2}^S$.

As already mentioned in [2], the $Q_{\varepsilon_1 \varepsilon_2}^S$ operators are symmetrical in the exchange of the polarizations $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$. This property is related to the fact that the incoming and return waves have the same pulsation. If the experiment is done with two sources of different frequencies [5], this property is no longer true. The study of this case is done in the appendix; it is then shown that the selection rules derived below are not valid for waves of different frequency.

The $Q_{\varepsilon_1 \varepsilon_2}^S$ operators form a set of tensorial operators of rank inferior or equal to 2. Indeed $Q_{\varepsilon_1 \varepsilon_2}^S$ is obtained by coupling twice the vectorial operator $\mathbf{D}$ and once the scalar operator $(\hbar\omega - \mathcal{H}_0)^{-1}$. Moreover, $Q_{\varepsilon_1 \varepsilon_2}^S$ is a symmetrical operator ($Q_{\varepsilon_1 \varepsilon_2}^S = Q_{\varepsilon_2 \varepsilon_1}^S$), hence the $Q_{\varepsilon_1 \varepsilon_2}^S$ operators have components only on the tensorial operators of rank 0 and 2.

1.1.2 Standard components of $Q_{\varepsilon_1 \varepsilon_2}^S$. — It is interesting to introduce the standard components, Q_q^k of these operators. Let D_q be a standard component of the electric dipole operator $\mathbf{D}$:

$$\mathbf{D} = \sum_q (-)^q D_{-q} \mathbf{e}_q \quad (4)$$

with

$$\begin{aligned} \mathbf{e}_0 &= \mathbf{e}_z \\ \mathbf{e}_{\pm 1} &= \mp \frac{1}{\sqrt{2}} (\mathbf{e}_x \pm i \mathbf{e}_y) \end{aligned} \quad (5)$$

Q_q^k is equal to

$$Q_q^k = \sum_{q_1 q_2} \langle kq | 11 q_1 q_2 \rangle D_{q_1} \frac{1}{\hbar\omega - \mathcal{H}_0} D_{q_2}. \quad (6)$$

For every set of polarizations $\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2$ of the incoming and return waves 1 and 2, there exist coefficients $a_q^k(\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2)$ satisfying :

$$Q_{\varepsilon_1 \varepsilon_2}^S = \sum_{k,q} a_q^k(\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2) Q_q^k. \quad (7)$$

When waves 1 and 2 have standard polarizations q_1 and q_2 , one obtains by reversing relation (6)

$$a_q^k(q_1, q_2) = \frac{1}{2} [\langle kq | 11 q_1 q_2 \rangle + \langle kq | 11 q_2 q_1 \rangle]. \quad (8)$$

It can be noticed that the symmetry properties of the Clebsch-Gordan coefficients permit one to show again that the $k = 1$ component is zero. (On the other hand, it is obvious that there is no component of rank k larger than 2.)

When the polarizations are not standard ones, they can be expanded on the standard polarizations :

$$\varepsilon_i = \sum_q (-)^q \varepsilon_{-q}^{(i)} e_q \quad i = 1, 2. \quad (9)$$

One then obtains

$$a_q^k(\varepsilon_1, \varepsilon_2) = \sum_{q_1, q_2} (-)^{q_1+q_2} \varepsilon_{-q_1}^{(1)} \varepsilon_{-q_2}^{(2)} a_q^k(q_1, q_2). \quad (10)$$

Taking into account the properties of the $a_q^k(q_1, q_2)$ coefficients given before, one finds again that only the tensorial orders 0 and 2 appear in the sum written in (7).

If we take the direction of the light beam as the quantification axis, we obtain using (8) :

$$\begin{aligned} a_{\pm 2}^2(\varepsilon_1, \varepsilon_2) &= \varepsilon_{\mp 1}^{(1)} \cdot \varepsilon_{\mp 1}^{(2)} \\ a_{\pm 1}^2(\varepsilon_1, \varepsilon_2) &= 0 \\ a_0^2(\varepsilon_1, \varepsilon_2) &= -\frac{1}{\sqrt{6}} (\varepsilon_1 \cdot \varepsilon_2) \\ a_0^0(\varepsilon_1, \varepsilon_2) &= -\frac{1}{\sqrt{3}} (\varepsilon_1 \cdot \varepsilon_2). \end{aligned} \quad (10bis)$$

1.1.3 Remark on the definition of the tensorial order of $Q_{\varepsilon_1 \varepsilon_2}^S$. — We have just shown that the two-photon transition operator has tensorial components of rank 0 and 2 only. Strictly speaking, this result is only valid if the tensorial order is related to the total angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. Indeed, $[\hbar\omega - \mathcal{H}_0]^{-1}$ is scalar only with respect to the total angular momentum $\mathbf{F}$.

Nevertheless, in most usual cases, the conclusions of § 1.1 remain valid if one considers the electronic angular momentum $\mathbf{J}$. This is true as long as the hyperfine structure of the relay-levels r (involved in formula (1)) is very small compared to the energy defect $\hbar \Delta\omega$, of the one-photon transition. This result can be interpreted in the following way : because of the uncertainty relation, the atom stays in level r during a time of the order of $1/\Delta\omega$; during this time the electronic and nuclear spins can not be coupled. In the following, we will always suppose that this condition is verified.

In the same way, for an atom presenting LS coupling, if the fine structure of the r relay-levels is small compared to the energy defect $\hbar \Delta\omega$, the decomposition of $Q_{\varepsilon_1 \varepsilon_2}^S$ in two tensors of rank 0 and 2 with respect to L is possible.

1.1.4 Decomposition of $Q_{\varepsilon_1 \varepsilon_2}^S$ on a basis of irreducible tensorial operators. — In many problems involv-

ing two-photon transitions between levels α and β , it is simpler to use the following operator :

$${}^{\alpha\beta}Q_{\varepsilon_1 \varepsilon_2}^S = P(\alpha J_\alpha) Q_{\varepsilon_1 \varepsilon_2}^S P(\beta J_\beta) \quad (11)$$

$P(\alpha J_\alpha)$ and $P(\beta J_\beta)$ are the projectors on the subspaces defined by the quantum numbers α , J_α and β , J_β .

As we show below, it often occurs that ${}^{\alpha\beta}Q_{\varepsilon_1 \varepsilon_2}^S$ has a definite rank (either scalar or quadrupolar), when $Q_{\varepsilon_1 \varepsilon_2}^S$ has components on operators of rank 0 and 2 :

— if the angular momenta of the ground and excited states are different ($J_\alpha \neq J_\beta$), the scalar operator will not be able to couple these levels

$$J_\alpha \neq J_\beta \Rightarrow {}^{\alpha\beta}Q_{\varepsilon_1 \varepsilon_2}^S \text{ is of rank 2}$$

— if the angular momenta of both considered levels are equal, and inferior or equal to 1/2, only the scalar operator will be able to couple them

$$J_\alpha = J_\beta \text{ and } J_\beta = 0 \text{ or } 1/2 \Rightarrow Q_{\varepsilon_1 \varepsilon_2}^S \text{ is of rank 0.}$$

These conclusions are absolutely general and do not depend on the exciting polarizations ε_1 and ε_2 .

For many calculations that we present in the following, it is useful to separate in the two-photon transition operator between levels α and β , ${}^{\alpha\beta}Q_{\varepsilon_1 \varepsilon_2}^S$, the reduced matrix element from the angular part. Such a decomposition is easily done by using the $T_q^k(\alpha J_\alpha, \beta J_\beta)$ operators defined by :

$$\begin{aligned} T_q^k(\alpha J_\alpha, \beta J_\beta) &= \sum_{m_\alpha m_\beta} (-)^{J_\beta - m_\beta} \times \\ &\times \langle J_\alpha J_\beta m_\alpha - m_\beta | k q \rangle | \alpha J_\alpha m_\alpha \rangle \langle \beta J_\beta m_\beta |. \end{aligned} \quad (12)$$

These operators form a basis of irreducible tensorial operators [6]. One easily finds

$$\begin{aligned} {}^{\alpha\beta}Q_{\varepsilon_1 \varepsilon_2}^S &= \sum_{k=0,2} \sum_q \frac{\langle \alpha J_\alpha || Q^k || \beta J_\beta \rangle}{\sqrt{2k+1}} \times \\ &\times a_q^k(\varepsilon_1, \varepsilon_2) T_q^k(\alpha J_\alpha, \beta J_\beta). \end{aligned} \quad (13)$$

1.2 SELECTION RULES. — **1.2.1 Selection rules on the J quantum number.** — Since the $Q_{\varepsilon_1 \varepsilon_2}^S$ operator has two tensorial components, one of order 0, the other of order 2, the use of the Wigner-Eckart theorem between the initial and final levels of the transition, e and g implies the following selection rules :

$$\begin{aligned} |J_e - J_g| &\leq 2 \\ \left. \begin{aligned} J_g = 0 &\rightarrow J_e = 1 \\ J_e = 1 &\rightarrow J_g = 0 \end{aligned} \right\} &\text{forbidden.} \end{aligned}$$

This last condition may seem surprising; indeed an atom can undergo a transition between these levels in a stepwise excitation : for example, the 7^3S_1

level of mercury can be excited from the fundamental level 6^1S_0 by absorbing one photon at $2\,537\text{ \AA}$ ($6^1S_0 \rightarrow 6^3P_1$) then one photon at $4\,358\text{ \AA}$ ($6^3P_1 \rightarrow 7^3S_1$). The reason for the absence of two-photon transition between these levels is that *there is always a destructive interference between several paths*; let us suppose for example that one of the waves is σ^+ polarized, and the other σ^- polarized; the transition between the 6^1S_0 and 7^3S_1 ($m=0$) levels can be done by two paths

$$6^1S_0 \rightarrow 6^3P_1, \quad m=1 \rightarrow 7^3S_1, \quad m=0 \quad (1)$$

$$6^1S_0 \rightarrow 6^3P_1, \quad m=-1 \rightarrow 7^3S_1, \quad m=0. \quad (2)$$

A straightforward calculation shows that the probability amplitude of path (1) is equal and of opposite sign to that of path (2). It is thus directly shown that the probability of absorbing two photons of the same frequency from level 6^1S_0 to level 7^3S_1 is zero.

This property is specifically related to the fact that both exciting photons have the same frequency; this property disappears if the two photons have different frequencies ω_1 and ω_2 ; the energy denominators are then respectively $(\omega_1 - \omega_r)$ and $(\omega_2 - \omega_r)$ for each path: one of the path is then favoured with respect to the other. In other words, the two-photon transition operator is no more symmetrical, and it contains a part of rank 1 which can couple the 6^1S_0 and 7^3S_1 levels (cf. appendix).

1.2.2 Selection rules on the F quantum number. — In a general way, the selection rules on F are the same as that we have just found on J :

$$|F_e - F_g| \leq 2$$

$$F_g = 0 \rightarrow F_e = 1 \quad \text{and} \quad F_g = 1 \rightarrow F_e = 0$$

forbidden.

Nevertheless, it often occurs (cf. § 1.1.1) that only one of the two parts of the $Q_{\varepsilon_1\varepsilon_2}^S$ operator, either the scalar operator Q_0^0 , or the quadrupolar operator Q_0^2 can couple the levels J_e and J_g ; in that case, the intensities of the hyperfine components and the selection rules will be those of the scalar or quadrupolar operators.

Particularly, if the transition occurs between levels with the same angular momentum ($J_e = J_g$), J_g being equal to 0 or $1/2$, then ${}^{eg}Q_{\varepsilon_1\varepsilon_2}^S$ is a scalar operator. Hence, one can deduce that, in that case, the following selection rules hold for hyperfine structure components [2]:

$$\Delta F = 0 \quad (F_e = F_g)$$

$$\Delta m_F = 0 \quad (m_{F_e} = m_{F_g}).$$

When the fundamental level is not polarized and when there is no magnetic field, the intensity of each hyperfine structure component is proportional to the degeneracy ($2F_g + 1$) of the F_g level, since in the case of a

scalar excitation, the transition probability is the same for all the Zeeman sublevels m_F .

On the contrary, if the transition is made between levels with different angular momenta ($J_e \neq J_g$), ${}^{eg}Q_{\varepsilon_1\varepsilon_2}^S$ is a quadrupolar operator and the selection rules, as well as the hyperfine structure component intensities are those of a quadrupolar electric transition.

If the transition is made between levels with the same angular momentum, $J_g = J_e$, J_g being equal or superior to 1, we shall have to take into account both the quadrupolar and scalar operators, except if the symmetry of the excitation (for example two σ^+ polarized waves) implies that only the quadrupolar operator appears in expression (7). One then expects very different relative intensities of the hyperfine components according as the polarization is linear or circular.

1.3 CALCULATION OF THE LINE INTENSITIES. —

1.3.1 Absorption probability on a $J_g \rightarrow J_e$ transition. — We perform the calculation of the absorption line intensities in zero magnetic field and supposing that the fundamental level is not polarized.

At resonance ($\delta\omega = 0$) the absorption probability on the Doppler-free line (3) is equal to:

$$\Gamma_g = \frac{A}{2J_g + 1} \sum_{m_g, m_e} |\langle eJ_e m_e | {}^{eg}Q_{\varepsilon_1\varepsilon_2}^S | gJ_g m_g \rangle|^2$$

with

$$A = \frac{4n_1 n_2 \omega^2}{\varepsilon_0^2 \Gamma_e}. \quad (14)$$

Using the expansion of ${}^{eg}Q_{\varepsilon_1\varepsilon_2}^S$ (13) and the orthogonality relation of the Clebsch-Gordan coefficients, one finds:

$$\Gamma_g = \frac{A}{2J_g + 1} \sum_{k=0,2} \frac{|\langle eJ_e \| Q^k \| gJ_g \rangle|^2}{2k+1} \times \left(\sum_q |a_q^k(\varepsilon_1, \varepsilon_2)|^2 \right). \quad (15)$$

One can notice that if ${}^{eg}Q_{\varepsilon_1\varepsilon_2}^S$ has a definite rank, formula (16) ensures a complete separation between the part concerning the light excitation

$$\left(\sum_q |a_q^k(\varepsilon_1, \varepsilon_2)|^2 \right)$$

and the atomic part (reduced matrix element).

Using the values (10bis) of the $a_q^k(\varepsilon_1, \varepsilon_2)$ coefficients, the $\sum_q |a_q^k(\varepsilon_1, \varepsilon_2)|^2$ can be expressed in a simple form [4]:

$$|a_0^0(\varepsilon_1, \varepsilon_2)|^2 = \frac{1}{3} |\varepsilon_1 \cdot \varepsilon_2|^2 \quad (16)$$

$$\sum_q |a_q^2(\varepsilon_1, \varepsilon_2)|^2 = \frac{1}{2} + \frac{1}{2} |\varepsilon_1 \cdot \varepsilon_2^*|^2 - \frac{1}{3} |\varepsilon_1 \cdot \varepsilon_2|^2$$

(The last formula can be demonstrated by expanding the following products : $|\epsilon_1 \cdot \epsilon_2|^2$, $|\epsilon_1 \cdot \epsilon_2^*|^2$ and $(\epsilon_1 \cdot \epsilon_1^*)(\epsilon_2 \cdot \epsilon_2^*) = 1$.)

1.3.2 *Intensities of the various hyperfine components $F_g \rightarrow F_e$ of a same transition $J_g \rightarrow J_e$.* — Assuming that the nucleus has a nuclear spin I , the absorption probability on the $F_g \rightarrow F_e$ component of the two-photon transition between the levels of quantum numbers J_g and J_e is easily deduced from (15) :

$$\Gamma_{J_g F_g \rightarrow J_e F_e} = \frac{A}{2 F_g + 1} \sum_{k=0,2} \times \times \frac{|\langle e J_e I F_e \| Q^k \| g J_g I F_g \rangle|^2}{2 k + 1} \sum_q |a_q^k(\epsilon_1, \epsilon_2)|^2. \quad (17)$$

In comparison with (15), we have replaced $(2 J_g + 1)$ by $(2 F_g + 1)$: we have thus normalized the population of level F_g to 1. In most cases, the hyperfine structure is small compared to the thermal energy and the population of a hyperfine sublevel is proportional to its degeneracy. If n_0 is the number of atoms in the ground state, the number of atoms in level F_g is equal to

$$n(F_g) = \frac{2 F_g + 1}{(2 J_g + 1)(2 I + 1)} n_0. \quad (18)$$

The number of atoms excited per unit time, that is, the measured intensity $I_{J_g F_g \rightarrow J_e F_e}$ of the absorption line, can than be deduced from (17) and (18)

$$I_{J_g F_g \rightarrow J_e F_e} = n(F_g) \Gamma_{J_g F_g \rightarrow J_e F_e} = n_0 \frac{2 F_g + 1}{(2 J_g + 1)(2 I + 1)} \Gamma_{J_g F_g \rightarrow J_e F_e}. \quad (19)$$

The knowledge of these quantities is obviously essential in the experiments to identify the lines and thus determine the hyperfine structure intervals.

Formula (17) can be transformed by using the relation between the reduced matrix elements $\langle e J_e I F_e \| Q^k \| g J_g I F_g \rangle$ and $\langle e J_e \| Q^k \| g J_g \rangle$ [7]

$$\Gamma_{J_g F_g \rightarrow J_e F_e} = A(2 F_e + 1) \sum_{k=0,2} \left\{ \begin{matrix} J_e & J_g & k \\ F_g & F_e & I \end{matrix} \right\}^2 \times \times \frac{|\langle e J_e \| Q^k \| g J_g \rangle|^2}{2 k + 1} \sum_q |a_q^k(\epsilon_1, \epsilon_2)|^2. \quad (20)$$

This formula is considerably simplified if the $^{eg}Q_{\epsilon_1 \epsilon_2}^S$ operator is either scalar or quadrupolar.

In the case of a scalar operator, using (19) and (20) and replacing by its value the «6j» coefficient corresponding to $k = 0$, one finds that the intensities of the hyperfine components are proportional to

$$I_{J_g F_g \rightarrow J_e F_e}^{(0)} \sim (2 F_g + 1) \delta_{F_g F_e} \delta_{J_e J_g}. \quad (21)$$

One finds the result of § 1.2.2 again : the transition is made between levels of same F , the intensity of

each component is proportional to the degeneracy of the initial level $(2 F_g + 1)$, and the relative intensities do not depend on the ϵ_1 and ϵ_2 polarizations.

When J_e is different from J_g , all the $^{eg}Q_{\epsilon_1 \epsilon_2}^S$ operators are of rank 2 independent of the polarizations ; the relative intensities of the various hyperfine structure components do not depend on the ϵ_1 and ϵ_2 polarizations. The intensity of one component is obtained from (19) and (20) ; it is proportional to [8] :

$$I_{J_g F_g \rightarrow J_e F_e}^{(2)} \sim (2 F_g + 1)(2 F_e + 1) \left\{ \begin{matrix} J_e & J_g & 2 \\ F_g & F_e & I \end{matrix} \right\}^2. \quad (22)$$

If J_e is equal to J_g and superior or equal to 1, $^{eg}Q_{\epsilon_1 \epsilon_2}^S$ may be of rank 2 for a particular choice of the polarizations and a mixture of operators of rank 2 and 0 for another choice. In the latter case, the spectrum is the superposition of quadrupolar and an isotropic spectrum. The relative intensity of the two spectra is characterized by the ratio [3] :

$$R(g, e) = \frac{|\langle e J_e \| Q^0 \| g J_g \rangle|^2}{1/5 |\langle e J_e \| Q^2 \| g J_g \rangle|^2}. \quad (23)$$

Using (20) and (23), one finds that the intensity of a hyperfine component in the general case is proportional to

$$I_{J_g F_g \rightarrow J_e F_e} \sim (2 F_g + 1) \times \times \left[R(g, e) \delta_{F_g F_e} + (2 F_e + 1) \left\{ \begin{matrix} J_e & J_g & 2 \\ F_g & F_e & I \end{matrix} \right\}^2 \right]. \quad (24)$$

In the following section, we describe how to calculate the ratio $R(g, e)$.

1.3.3 *Relation between the matrix elements of Q^k and the matrix elements of the electric dipole.* — We calculate the matrix elements of the Q_q^k operators from (6) :

$$\begin{aligned} \langle J_e m_e | Q_q^k | J_g m_g \rangle &= \sum_{q_1 q_2} \langle k q | 11 q_1 q_2 \rangle \times \\ &\times \sum_{r J_r} \langle J_e m_e | D_{q_1} | J_r m_r \rangle \frac{1}{\hbar(\omega - \omega_r)} \\ &\times \langle J_r m_r | D_{q_2} | J_g m_g \rangle. \end{aligned}$$

Applying the Wigner-Eckart theorem to the Q_q^k , D_{q_1} , and D_{q_2} operators, and using the relations between the «6j» and «3j» coefficients [7], one finds :

$$\begin{aligned} \frac{\langle e J_e \| Q^k \| g J_g \rangle}{\sqrt{2 k + 1}} &= (-)^{J_g + J_e + k} \sum_{r J_r} \times \\ &\times \frac{\langle e J_e \| D \| r J_r \rangle \langle r J_r \| D \| g J_g \rangle}{\hbar(\omega - \omega_r)} \left\{ \begin{matrix} J_e & J_g & k \\ 1 & 1 & J_r \end{matrix} \right\}. \end{aligned} \quad (25)$$

As shown in formula (25) the ratio $R(g, e)$ defined by formula (23) depends on the relay-levels r . If the *one intermediate-level approximation* can be used which means that there is only one very close relay-level $|rJ_r\rangle$ which contributes to the two-photon transition probability, $R(g, e)$ takes the simple value $R(g, e; J_r)$:

$$R(g, e; J_r) \simeq \frac{1}{3(2J_g + 1) \left\{ \begin{matrix} J_e & J_g & 2 \\ 1 & 1 & J_r \end{matrix} \right\}^2} \quad (26)$$

But it often occurs that this approximation cannot be applied. Particularly if several intermediate levels r have energies not too different from the energy of one photon $\hbar\omega$ the measurement of the ratio $R(g \rightarrow e)$ provides information on the respective influence of these various levels in the calculation of the transition probability. In the second part of this paper, we illustrate these considerations with the example of transitions in neon : we compare in that case the value of $R(g, e)$ measured experimentally with the prediction of a theoretical calculation performed from formulae (23) and (25).

1.3.4 Density matrix of the excited state. — Up to now, we have been only interested in the intensities of the *absorption* lines; but one of the main advantages of the two-photon transitions is that they can be detected on the fluorescence light at a wavelength λ_{er} different from the exciting wavelength. Now, the fluorescence intensity in a given direction not only depends on the *population* of the excited state (that we have just calculated), but also on its *polarization*. We must then know the various terms of the excited state density matrix that are obtained immediately after the excitation process (*pumping* matrix). Before calculating the density matrix, we mention that the experimental part of the paper (Section 2) can be understood without any reference to these calculations.

Developing the evolution operator up to the second order, one finds the pumping matrix ρ_e in the excited state as a function of the stationary density matrix ρ_g in the ground state :

$$\rho_e = A {}^{eg}Q_{\varepsilon_1\varepsilon_2}^S \rho_g {}^{eg}Q_{\varepsilon_1\varepsilon_2}^{S+} \quad (27)$$

where A is defined by (14).

Using the expansion of ${}^{eg}Q_{\varepsilon_1\varepsilon_2}^S$ on the irreducible tensorial operators (13) and the properties of these operators [6], one finds :

$$\begin{aligned} \rho_e = A \sum_{\substack{k=0,2 \\ k'=0,2 \\ q,q'}} \frac{\langle eJ_e \parallel Q^k \parallel gJ_g \rangle}{\sqrt{2k+1}} \times \\ \times \frac{\langle eJ_e \parallel Q^{k'} \parallel gJ_g \rangle^*}{\sqrt{2k'+1}} (-)^{J_g+J_e-q'} \\ \times a_q^k(\varepsilon_1, \varepsilon_2) a_{-q'}^{k'*}(\varepsilon_1, \varepsilon_2) \\ \times T_q^k(eJ_e, gJ_g) \rho_g T_{q'}^{k'}(gJ_g, eJ_e) \end{aligned} \quad (28)$$

We defined new quantities which are independant of the atomic states and characterize the radiation field :

$${}^{kk'}\varphi_Q^K = \sum_{qq'} (-)^{k'-q'} a_q^k(\varepsilon_1, \varepsilon_2) a_{-q'}^{k'*}(\varepsilon_1, \varepsilon_2) \times \langle KQ \parallel kk' qq' \rangle \quad (29)$$

Let $\rho_{q_e}^{k_e}$ and $\rho_{q_g}^{k_g}$ be the coefficients of the pumping matrix and of the stationary density matrix of the ground state on a basis of irreducible tensorial operators :

$$\begin{aligned} \rho_e &= \sum_{k_e q_e} \rho_{q_e}^{k_e} T_{q_e}^{k_e}(eJ_e, eJ_e) \\ \rho_g &= \sum_{k_g q_g} \rho_{q_g}^{k_g} T_{q_g}^{k_g}(gJ_g, gJ_g) \end{aligned} \quad (30)$$

With these notations, it can easily be deduced from (28)

$$\begin{aligned} \rho_{q_e}^{k_e} &= A \sum_{\substack{kk' \\ KQ \\ k_g q_g}} {}^{kk'}\varphi_Q^K \rho_{q_g}^{k_g} \sqrt{2K+1} \sqrt{2k_g+1} \times \\ &\times \langle k_e q_e \parallel k_g K q_g Q \rangle \left\{ \begin{matrix} J_e & J_g & k \\ J_e & J_g & k' \\ k_e & k_g & K \end{matrix} \right\} \\ &\times \langle eJ_e \parallel Q^k \parallel gJ_g \rangle \langle eJ_e \parallel Q^{k'} \parallel gJ_g \rangle^* \end{aligned} \quad (31)$$

When the ground state is not polarized, only $\rho_{q_g}^{k_g} = \rho_g^0$ is non zero and formula (31) is considerably simplified :

$$\begin{aligned} \rho_{q_e}^{k_e} &= A \sum_{k,k'} {}^{kk'}\varphi_{q_e}^{k_e} \frac{(-)^{J_e+J_g+k'+k_e}}{2J_g+1} \left\{ \begin{matrix} k & k' & k_e \\ J_e & J_e & J_g \end{matrix} \right\} \times \\ &\times \langle eJ_e \parallel Q^k \parallel gJ_g \rangle \langle eJ_e \parallel Q^{k'} \parallel gJ_g \rangle^* \end{aligned} \quad (32)$$

1.3.5 Collision broadening of a two-photon absorption line. — The broadening and shift of the spectral lines with pressure in the limit of the impact approximation have been well known since the theoretical work of Anderson [9] and Baranger [10]. The generalization of these results to the broadening of Raman lines has been developed by Fiutak and Van Kranendonk [11]. The problems of Raman effect and two-photon transitions being closely related to each other, it is easy to extend the latter results.

The extension of the results obtained in a single-photon excitation are rather simple if the energy defect $\hbar\Delta\omega_r$ is sufficiently large. More precisely $\hbar\Delta\omega_r$ has to be large compared to :

1) The Doppler width of the $g \rightarrow r$ one quantum transition.

2) The relaxation rates of the D_{gr} and D_{re} dipoles moments.

We need the first assumption to avoid the problem of stepwise excitation and velocity changing collisions. The second assumption is used to avoid the problem of the perturbation of the line due to collisions in the

intermediate state. It can be understood using the uncertainty principle : the atom spends only a time of the order of $1/\Delta\omega$, in the intermediate state and the phase-shifts produced by the collisions because of the perturbation of the intermediate state are then very small [11]. If the energy defect $\hbar \Delta\omega$, is not large enough, the problem is more complicated ; such a situation has been investigated by Omont and co-workers [12] in the case of Raman scattering and by Berman [13] for two-photon absorption. However it must be pointed out that this last situation is uncommon in usual two-photon spectroscopy. To observe it one has to approach the intermediate state using the technique of Bjorkholm and Liao [5].

In usual single-photon excitation, the width of the line is related to the relaxation rate of the electric dipole moment. If $\hbar \Delta\omega$, is large enough, the corresponding operator for two-photon absorption is ${}^{eg}Q_{\epsilon_1\epsilon_2}^S$. Unlike the electric dipole, the ${}^{eg}Q_{\epsilon_1\epsilon_2}^S$ has no definite rank ; in the general case, it can be decomposed on a quadrupolar and on a scalar operator. The broadening and shift of the line will then be that of the optical scalar and of the optical quadrupole. As the relaxation may act differently on these two quantities, it is possible that the line shape appears as the superposition of two lorentzian curves. In fact, this case occurs rather unusually because :

- it often occurs that ${}^{eg}Q_{\epsilon_1\epsilon_2}^S$ has a definite rank, and there is then only one broadening constant ;
- even if ${}^{eg}Q_{\epsilon_1\epsilon_2}^S$ is a sum of two tensors, when the interaction potential is much more important in the excited state than in the ground state, all the multipolar moments of the transition have almost the same broadening. Particularly, the isotropic and the quadrupolar part presenting the same broadening, the absorption line will still be a lorentzian curve [6].

2. Intensity of the hyperfine components in the neon case. — We present in the second part of the paper experimental results about the intensities of the hyperfine components for several two-photon transitions in neon. The experiments are performed on the odd isotope ${}^{21}\text{Ne}$ (whose nuclear spin is equal to $3/2$). The neon case is interesting because there are cases where ${}^{eg}Q_{\epsilon_1\epsilon_2}^S$ has a definite rank and there are cases where it is the superposition of a scalar and a quadrupolar operator. We compare then the experimental and theoretical values of the ratio between the matrix elements of the scalar and the quadrupolar parts of the two-photon excitation operator.

2.1 DESCRIPTION OF THE EXPERIMENT. — We have investigated several two-photon transitions between the $3s[3/2] 2$ metastable state and the levels of the $4d$ configuration. The experimental set-up has been described in a preceding paper [1]. We just note that the present experiments have been performed with identical linear polarization for the two oppositely propagating beams. This is necessary in order to

obtain an excitation which contains both a scalar and a quadrupolar part ⁽²⁾. The optical isolation in all these experiments has been performed by Faraday rotation (for more details, see ref. [1]).

The neon cell contains about 0.6 torr of pure ${}^{21}\text{Ne}$. At this pressure the relaxation process in the excited state are rather important and it is not possible to calculate the fluorescence using the density matrix obtained just after the excitation process (formula (32)) and neglecting the collisions in the excited state. To perform an exact calculation, it is necessary to know the relaxation constants of the population and the alignment of each hyperfine sublevel as well as the transfer towards all the near sublevels. In fact, the alignment being destroyed faster than the total population of the excited state, we have compared the experimental fluorescence spectrum with the intensities calculated for an absorption spectrum. In other words, we assume that the collisions sufficiently depolarize the excited state. Indeed we have verified that the relative intensities of the hyperfine components are practically the same if the neon pressure in the cell is equal to 1 torr.

2.2 EXPERIMENTAL RESULTS. — The electronic angular momentum J of the $3s[3/2] 2$ metastable level is equal to 2. If the two-photon transition reaches a level of angular momentum $J \neq 2$, the transition is purely quadrupolar and the relative intensities of the hyperfine components are given by formula (22). We have already presented two spectra of this type in neon : $3s[3/2] 2 \rightarrow 4d'[5/2] 3$ (ref. [8]) and

$$3s[3/2] 2 \rightarrow 4d'[3/2] 1$$

(ref. [1]).

The problem is more difficult if the angular momentum of the excited state is also equal to $J = 2$. We present here the results for the $4d[3/2] 2$, $4d'[5/2] 2$ and $4d'[3/2] 2$ excited levels. In these cases from the comparison between the intensities of the scalar and the quadrupolar parts of the spectrum, we deduce the experimental value of $R(g, e)$.

The experimental spectra are represented on figures 1, 2 and 3 ⁽³⁾. We have represented on figure 1a the experimental recording for the transition reaching $4d[3/2] 2$, the theoretical intensities for a quadru-

⁽²⁾ Formulae (16) show that for the same linear polarization, we have $|a_0^2(\epsilon, \epsilon)|^2 = 1/3$ and $\sum_q |a_q^2(\epsilon, \epsilon)|^2 = 2/3$ whereas in the case of the same circular polarization $a_0^2(\epsilon, \epsilon) = 0$ and

$$\sum_q |a_q^2(\epsilon, \epsilon)|^2 = 1.$$

⁽³⁾ From the positions of the resonances, we deduce the hyperfine constants of the excited levels. The corresponding values for the $4d'[3/2] 2$ and $4d'[5/2] 2$ levels have been reported in ref. [1]. The values obtained for $4d[3/2] 2$ and for some others levels of the $4d$ configuration will be presented in K. Beroff's thesis of 3rd cycle (Paris, 1977) and in a forthcoming publication.

polar spectrum (Fig. 1b) and for an isotropic spectrum (Fig. 1c) are plotted below. The presence of the $F_g = 3/2 \rightarrow F_e = 3/2$ resonance in the experimental spectrum obviously demonstrates the existence of an isotropic spectrum because that transition is forbidden in a quadrupolar excitation (due to the vanishing of the Wigner 6j coefficient $\left\{ \begin{smallmatrix} 2 & 3/2 & 3/2 \\ 3/2 & 2 & 2 \end{smallmatrix} \right\}$). From the intensities of the resonances we deduce :

$$R(3s[3/2] 2, 4d[3/2] 2) = 1.76 \pm 0.25 .$$

In the case of the transition reaching $4d'[5/2] 2$, there is also a scalar component in the experimental spec-

FIG. 1. — a) Experimental recording of the $3s[3/2] 2-4d[3/2] 2$ two-photon excitation in ^{21}Ne (the frequency scale corresponds to the atomic energy. This value is twice larger than the one measured on the laser scale). b) Theoretical intensities for a quadrupolar absorption. From left to right, the components (F_g, F_e) are : $(5/2, 1/2)$, $(3/2, 1/2)$, $(7/2, 3/2)$, $(5/2, 3/2)$, $(1/2, 3/2)$, $(7/2, 5/2)$, $(5/2, 5/2)$, $(3/2, 5/2)$, $(1/2, 5/2)$, $(7/2, 7/2)$, $(7/2, 5/2)$. c) Theoretical intensities for a scalar absorption. From left to right, the components (F_g, F_e) are : $(1/2, 1/2)$, $(3/2, 3/2)$, $(5/2, 5/2)$ and $(7/2, 7/2)$.

FIG. 2. — a) Experimental recording of the $3s[3/2] 2-4d'[5/2] 2$ two-photon excitation in ^{21}Ne . b) Theoretical intensities for a quadrupolar absorption. From left to right the components (F_g, F_e) are : $(5/2, 7/2)$, $(1/2, 5/2)$, $(3/2, 5/2)$, $(7/2, 7/2)$, $(5/2, 5/2)$, $(1/2, 3/2)$, $(3/2, 1/2)$, $(5/2, 3/2)$, $(7/2, 5/2)$. c) Theoretical intensities for a scalar absorption. From left to right, the components (F_g, F_e) are : $(7/2, 7/2)$, $(5/2, 5/2)$, $(3/2, 3/2)$ and $(1/2, 1/2)$.

trum (Fig. 2) but its value is much smaller than in the previous case

$$R(3s[3/2] 2, 4d'[5/2] 2) = 0.24 \pm 0.06 .$$

For the last spectrum ($3s[3/2] \rightarrow 4d'[3/2] 2$), the spectrum appears to be purely quadrupolar (Fig. 3). The expected positions of the $F_g = 3/2 \rightarrow F_e = 3/2$ and $F_g = 1/2 \rightarrow F_e = 1/2$ resonances are shown with

FIG. 3. — a) Experimental recording of the $3s[3/2] 2-4d'[3/2] 2$ two-photon excitation in ^{21}Ne . The expected positions of the $F_g = 3/2, F_e = 3/2$ and $F_g = 1/2, F_e = 1/2$ lines are shown with arrows. b) Theoretical intensities for a quadrupolar absorption. The lines are labelled according to their F_g, F_e numbers.

arrows. Taking into account the signal to noise ratio, we can deduce an upper limit for $R(3s[3/2] 2, 4d'[3/2] 2)$:

$$R(3s[3/2] 2, 4d'[3/2] 2) < 0.10 .$$

We now compare these experimental values with a theoretical calculation.

2.3 COMPARISON WITH THEORY. — We calculate in this section the theoretical values of R using the formulae which have been found in the first part of the paper.

The first possible approach is to take into account only the closest intermediate state and to use the formula (26). For the three levels under consideration the closest intermediate state has a $J = 2$ angular momentum. (It is the $2p_6$, in Paschen notation, for the transition reaching $4d[3/2] 2$ and the $2p_4$ for the transitions reaching $4d'[3/2] 2$ and $4d'[5/2] 2$.) It follows that one should find the same value of R , equal to 2.9, in the three cases. The agreement between that value and the experimental results is clearly very bad, particularly in the case of the transitions reaching the two levels of the $4d'$ subconfiguration. The exact calculation needs the summation (25) over all the relay states. It is necessary to know the wave functions of the initial, relay and final states. The levels of the $4d$ configuration and the metastable $3s[3/2] 2$ are with a rather good precision pure Racah states. We perform the calculation using pure Racah states for these levels and we show afterwards that the slight mixing between $4d'[3/2] 2$ and $4d'[5/2] 2$ we have discussed in a preceding paper [1] leads to a small change of the theoretical value of R .

In theory, one has to perform the summation over all the relay levels. In fact, it is sufficient to perform the summation over all the levels of the $2p^5 3p$ configuration, the energy defects of the levels of the other configurations are much larger and it can be shown that their contribution can be neglected with a good approximation.

For the levels of the $2p^5 3p$ configuration, it is important to precisely describe their wave functions. The angular momenta of the core being equal to $3/2$ for the metastable level and $1/2$ for the levels of the $4d'$ subconfiguration, the two-photon excitation is only possible if the intermediate states are not pure Racah states. The wave functions of the levels of the $2p^5 3p$ configuration are derived from the data of S. Liberman [14]. These wave functions are decomposed on the pure Racah's coupling basis :

$$| 2p_i, J_i \rangle = \sum_{j_1, K} \alpha_i(j_1, K) | 3p; j_1, K, J_i \rangle . \quad (33)$$

The values of $\alpha_i(j_1, K)$ are given in table I. In table II, we report the values of the energy defects $\hbar(\omega - \omega_i)$ which appear in the calculation of R (see formulae (23) and (25)), $\hbar\omega_i$ is the energy difference between the energy levels $2p_i$ and $3s[3/2] 2$.

TABLE II

Energy defects for the two-photon transitions reaching the $4d[3/2] 2$, $4d'[5/2] 2$ and $4d'[3/2] 2$ excited levels. In each compartment of the table, the energy defect $\hbar\omega - \hbar\omega_i$, expressed in cm^{-1} , is given. $\hbar\omega$ is the photon energy and $\hbar\omega_i$ is the energy difference between the relay state $2p_i$ and $3s[3/2] 2$.

Relay level	Excited level		
	$4d[3/2] 2$	$4d'[5/2] 2$	$4d'[3/2] 2$
$2p_2$	— 511.7	— 120.1	— 119.1
$2p_4$	— 331.8	59.9	60.9
$2p_5$	— 245.4	146.3	147.3
$2p_6$	210.8	602.6	603.6
$2p_7$	405.1	796.8	797.8
$2p_8$	702.5	1 094.2	1 095.2
$2p_9$	869.7	1 261.4	1 262.4
$2p_{10}$	2 268.9	2 660.7	2 661.7

TABLE I

Relay states wavefunctions. In each compartment of the table, we have reported the $\alpha_i(j_1, K)$ coefficient of formula (33). All the levels of the $2p^5 3p$ configuration, except the $2p_1$ and $2p_3$ which have a zero electronic angular momentum, can be considered as possible relay states.

	$j_1 = 1/2 \ K = 1/2$	$j_1 = 1/2 \ K = 3/2$	$j_1 = 3/2 \ K = 1/2$	$j_1 = 3/2 \ K = 3/2$	$j_1 = 3/2 \ K = 5/2$
$2p_2 \ (J = 1)$	0.88	0	— 0.47	0	0
$2p_4 \ (J = 2)$	0	0.90	0	0.41	— 0.15
$2p_5 \ (J = 1)$	0	0.82	0	0.57	0
$2p_6 \ (J = 2)$	0	— 0.33	0	0.87	0.37
$2p_7 \ (J = 1)$	0	— 0.57	0	0.82	0
$2p_8 \ (J = 2)$	0	0.28	0	— 0.28	0.92
$2p_9 \ (J = 3)$	0	0	0	0	1
$2p_{10} \ (J = 1)$	0.47	0	0.88	0	0

To calculate R it is convenient to define a new quantity :

$$\langle e; j_e, K_e, J_e \parallel q^k \parallel g; j_g, K_g, J_g \rangle = \frac{\langle e; j_e, K_e, J_e \parallel Q^k \parallel g; j_g, K_g, J_g \rangle}{\sqrt{2k+1} \langle e \parallel \mathbf{d} \parallel 3p \rangle \langle 3p \parallel \mathbf{d} \parallel g \rangle} \quad (34)$$

In that expression, we have isolated the reduced matrix elements of the electric dipole of the external electron.

Then using formula (23), by decoupling the angular momenta in $\langle e; j_e, K_e, J_e \parallel \mathbf{d} \parallel g; j_g, K_g, J_g \rangle$, we deduce :

$$\begin{aligned} \langle e; j_e, K_e, J_e \parallel q^k \parallel g; j_g, K_g, J_g \rangle &= (-1)^{1+k+j_e+j_g+2K_e+2J_g+J_e} \sqrt{(2J_g+1)(2J_e+1)(2K_g+1)(2K_e+1)} \times \\ &\times \left[\sum_{i,K,K'} (-1)^{J_i+2K'} \begin{Bmatrix} J_e & J_g & k \\ 1 & 1 & J_i \end{Bmatrix} \frac{\alpha_i(j_e, K) \alpha_i(j_g, K')}{\hbar(\omega - \omega_i)} (2J_i+1) \sqrt{(2K+1)(2K'+1)} \right. \\ &\times \left. \begin{Bmatrix} J_e & J_i & 1 \\ K & K_e & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} J_i & J_g & 1 \\ K_g & K' & \frac{1}{2} \end{Bmatrix} \begin{Bmatrix} K_e & K & 1 \\ l & l_e & j_e \end{Bmatrix} \begin{Bmatrix} K' & K_g & 1 \\ l_g & l & j_g \end{Bmatrix} \right] \quad (35) \end{aligned}$$

In the present case, l_g, l and l_e are equal to 0, 1 and 2.

We can remark that if all the energy defects $\hbar(\omega - \omega_i)$ were equal, the two-photon transition probability between $3s[3/2] 2$ and the levels of the $4d'$ subconfiguration ($j_e = 1/2$) would be equal to 0. Indeed $\sum_i \alpha_i(1/2, K) \alpha_i(3/2, K')$ is a scalar product of two orthogonal vectors because the transformation from the set of eigenfunctions $|3p; j_1, K; J_i\rangle$ to the set $|2p_i; J_i\rangle$ is a unitary transformation. The two-photon transition between $3s[3/2] 2$ and the levels of the $4d'$ subconfiguration are only possible because :

- 1) the energy defects are small compared to the structure of the $2p^5 3p$ configuration ;
- 2) the levels of the $2p^5 3p$ configuration are not pure Racah states.

It may also look surprising to have a scalar excitation between $3s[3/2] 2$ and the levels of the $2p^5 4d$ configuration since the optical electron jumps from an s level to a d level. The fact that the reduced matrix element of q^0 is not vanishing corresponds also to the fact that the energy defects are small compared to the structure of the $2p^5 3p$ configuration and the rank of the two-photon operator has to be compared with the total angular momentum J (cf. § 1.1.3).

If the excited states $4d[3/2] 2$, $4d'[3/2] 2$ and $4d'[5/2] 2$ are taken as pure Racah states, we find using formulae (23), (34) and (35) :

$$R_{th}(3s[3/2] 2, 4d[3/2] 2) = 2.17$$

$$R_{th}(3s[3/2] 2, 4d'[5/2] 2) = 0.5$$

$$R_{th}(3s[3/2] 2, 4d'[3/2] 2) < 10^{-2}.$$

The two last values are slightly changed if we take into account the mixing between $4d'[3/2] 2$ and

$4d'[5/2] 2$ which has been demonstrated in a preceding paper [1]. We have found that :

$$\begin{aligned} |4d'[5/2] 2\rangle &\simeq \cos \theta |4d; 1/2, 5/2, 2\rangle - \sin \theta |4d; 1/2, 3/2, 2\rangle \\ |4d'[3/2] 2\rangle &\simeq \sin \theta |4d; 1/2, 5/2, 2\rangle + \cos \theta |4d; 1/2, 3/2, 2\rangle \end{aligned}$$

with $\sin \theta \simeq 0.2$.

From that we deduce :

$$\begin{aligned} \langle 4d'[5/2] 2 \parallel q^k \parallel 3s[3/2] 2 \rangle &\simeq \\ &\simeq \cos \theta \langle 4d; 1/2, 5/2, 2 \parallel q^k \parallel 3s; 3/2, 3/2, 2 \rangle - \\ &- \sin \theta \langle 4d; 1/2, 3/2, 2 \parallel q^k \parallel 3s; 3/2, 3/2, 2 \rangle \end{aligned}$$

and a similar relation for $\langle 4d'[3/2] 2 \parallel q^k \parallel 3s[3/2] 2 \rangle$.

It follows that the corresponding theoretical values of R are :

$$R_{th}(3s[3/2] 2, 4d'[5/2] 2) = 0.29$$

$$R_{th}(3s[3/2] 2, 4d'[3/2] 2) = 0.01.$$

These values are in very good agreement with the experimental measurements. The small value obtained for $R(3s[3/2] 2, 4d'[5/2] 2)$ and $R(3s[3/2] 2, 4d'[3/2] 2)$ corresponds to a destructive interference on the scalar part of the two-photon operator due to the various possible paths whereas the same interference is constructive in the case of the quadrupolar part. For the transition which reaches $4d[3/2] 2$, the $2p_6$ relay state has a leading influence and the interference effects are less important.

3. Conclusion. — In the first part of the paper we have described a tensorial formalism suited to the problems involved in two-photon spectroscopy. We have shown the interest of splitting the two-photon operator in its scalar and quadrupolar parts. In most cases, only one part of the two-photon operator can couple the ground state to the excited state but when the two parts can couple these states, the calculation of the spectrum often needs the knowledge of the intermediate state wavefunctions because the interference effects are not the same for the scalar and quadrupolar operators.

In the second part we have presented experiments on neon and we have compared these experiments with the theory derived in the first part of the paper. We have shown the importance of the intermediate states for the selection rules and for the relative intensities in a hyperfine spectrum. In addition the theoretical formulae have been applied to these spectra and have yielded a good agreement with the experimental results.

Appendix : The two exciting photons have different frequencies. — We study here the case when the atom undergoes a transition between the fundamental level g and the excited state e by absorbing two photons of frequencies ω_1 and ω_2 different from each other. Such an experimental scheme has been used by Bjorkholm and Liao [5]; its interest lies in the fact that one can increase the transition probability by a great deal by coming close to a relay-level; its major drawback is that it appears a residual Doppler effect proportional to $(\omega_1 - \omega_2)$.

In that case, the probability of absorbing two photons is

$$\Gamma_g = \frac{n_1 \omega_1 n_2 \omega_2}{\varepsilon_0^2 \Gamma_e} \times \left| \sum_r \left[\frac{\langle e | \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 | r \rangle \langle r | \mathbf{D} \cdot \boldsymbol{\varepsilon}_1 | g \rangle}{\hbar(\omega_1 - \omega_r)} + \frac{\langle e | \mathbf{D} \cdot \boldsymbol{\varepsilon}_1 | r \rangle \langle r | \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 | g \rangle}{\hbar(\omega_2 - \omega_r)} \right] \right|^2. \quad (\text{A.1})$$

The polarizations of the photons are $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$ and the numbers of photons in the two modes are n_1 and n_2 .

Let us define $Q_{e_2 e_1}(\omega_1)$, the transition operator associated with the absorption of photons $(\varepsilon_1, \omega_1)$ and $(\varepsilon_2, \omega_2)$

$$Q_{e_2 e_1}(\omega_1) = \mathbf{D} \cdot \boldsymbol{\varepsilon}_2 \frac{1}{\hbar\omega_1 - \mathcal{H}_0} \mathbf{D} \cdot \boldsymbol{\varepsilon}_1. \quad (\text{A.2})$$

The two-photon operator $Q_{e_1 e_2}(\omega_1, \omega_2)$ can then be written

$$Q_{e_1 e_2}(\omega_1, \omega_2) = \frac{1}{2} [Q_{e_2 e_1}(\omega_1) + Q_{e_1 e_2}(\omega_2)]. \quad (\text{A.3})$$

The transition probability Γ_g is then

$$\Gamma_g = \frac{4 n_1 \omega_1 n_2 \omega_2}{\varepsilon_0^2 \Gamma_e} |\langle e | Q_{e_1 e_2}(\omega_1, \omega_2) | g \rangle|^2. \quad (\text{A.4})$$

The $Q_{e_1 e_2}(\omega_1, \omega_2)$ operators can be expanded on tensorial operators of rank 0, 1 and 2. Nevertheless, if the polarizations $\boldsymbol{\varepsilon}_1$ and $\boldsymbol{\varepsilon}_2$ are the same, the component of rank 1 (antisymmetrical one) is zero and most of the results of § 1 can be generalized without problems. Particularly the selection rules we have then obtained are not modified. On the contrary, it must be pointed out that if the spectrum is the superposition of an isotropic spectrum and of a quadrupolar one, the relative intensities of these two spectra will in general vary, when ω_1 is varied, the sum $\omega_1 + \omega_2$ remaining constant. For instance, the destructive interference between the various possible paths for the isotropic part of the $3s[3/2] 2 \rightarrow 4d[3/2] 2$ transition of Neon (cf. § 2) disappears if slightly different frequencies are used.

As before it is interesting to introduce the standard components $Q_q^k(\omega_1)$ and $Q_q^k(\omega_2)$ defined by

$$Q_q^k(\omega_i) = \sum_{q_1 q_2} \langle kq | 11 q_1 q_2 \rangle D_{q_1} \frac{1}{\hbar\omega_i - \mathcal{H}_0} D_{q_2} \quad i = 1, 2. \quad (\text{A.5})$$

If the exciting polarizations are standard polarizations, one obtains, by using the symmetry relations of the Clebsch-Gordan coefficients :

$$Q_{q_1 q_2}(\omega_1, \omega_2) = \sum_{k, q} \langle kq | 11 q_1 q_2 \rangle \times \left[\frac{(-)^k}{2} Q_q^k(\omega_1) + \frac{1}{2} Q_q^k(\omega_2) \right]. \quad (\text{A.6})$$

If the polarizations are not standard ones, it can be derived, in the same way as in (7) :

$$Q_{e_1 e_2}(\omega_1, \omega_2) = \sum_{kq} a_q^k(\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2) \times \left[\frac{(-)^k}{2} Q_q^k(\omega_1) + \frac{1}{2} Q_q^k(\omega_2) \right]. \quad (\text{A.7})$$

The $a_q^k(\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2)$ coefficients take the same value as in formula (10) for $k = 0$ or 2 . But it now appears coefficients $a_q^1(\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2)$ corresponding to $k = 1$. One can then use the formulae giving the line intensities of § 1 provided that Q^k is replaced by

$$\frac{1}{2} [Q^k(\omega_2) + (-)^k Q^k(\omega_1)].$$

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