TWO-PHOTON TRANSITION PROBABILITIES IN THE OXYGEN
ISELECTRONIC SEQUENCE

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ABSTRACT

The spontaneous emission transition probability for the two-photon transition
$2p^4 \, ^1S_0 \rightarrow 2p^4 \, ^1D_2$ in O I is calculated, and found to be $6.8 \times 10^{-7} \, \text{sec}^{-1}$. Estimates of the probability for the same transition in Ca XIII and Fe XIX yield $1.9 \times 10^{-4} \, \text{sec}^{-1}$ and $1.9 \times 10^{-4} \, \text{sec}^{-1}$, respectively. In all cases the probabilities are much smaller than the electric quadrupole transition probabilities for the same transitions, so that two-photon emission does not contribute significantly to the deexcitation rate of the $\ ^1S_0$ level in any ion of the oxygen sequence.

RESUMEN

Se ha calculado la probabilidad de transición de la emisión espontánea correspondiente a la transición de doble fotón $2p^4 \, ^1S_0 \rightarrow 2p^4 \, ^1D_2$ en O I, obteniendo $6.8 \times 10^{-7} \, \text{sec}^{-1}$. Estimaciones de la probabilidad para la misma transición en Ca XIII y Fe XIX dan $1.9 \times 10^{-4} \, \text{sec}^{-1}$ y $1.9 \times 10^{-4} \, \text{sec}^{-1}$, respectivamente. En todos los casos las probabilidades son mucho menores que las probabilidades de transición de cuádrupolo eléctrico para las mismas transiciones, de forma que la emisión de doble fotón no contribuye significativamente a la velocidad de desexcitación del nivel $\ ^1S_0$ en ningún ión de la secuencia del oxígeno.

INTRODUCTION

The green auroral line of wavelength 5577 Å is due to the electric quadrupole transition $2p^4 \, ^1S_0 \rightarrow 2p^4 \, ^1D_2$ in O I. The transition probability of this line was calculated by Condon, Paschen, Garstang, Yamanouchi and Horie, and Nicolaides, Sinanoglu and Westhaus. It was measured by Omholt, McConkey and Kernahan, Corny and Williams, and Kernahan and Pang (1). The last named authors gave an excellent review of all the results of the earlier investigations. The best Einstein A-value from theoretical electric quadrupole calculations is that of Nicolaides, Sinanoglu and Westhaus (2) who obtained $A = 1.18 \, \text{sec}^{-1}$. This value is in general agreement with the best experimental values: Kernahan and Pang (1) obtained $A = 1.06 \, (\pm 0.32) \, \text{sec}^{-1}$, and Corny and Williams (3) obtained $A = 1.25 \, (\pm 0.05) \, \text{sec}^{-1}$ (after correcting for the 2972 Å transition).

The $^1S_0 \rightarrow ^1D_2$ decay may also take place by spontaneous two-photon emission. This possibility has apparently not been investigated by earlier workers. If the two-photon transition probability were sufficiently large it would contribute to the decay rate of the $^1S_0$ level, and hence to the observed lifetime of that level. However, because two-photon emission forms a continuum, it would not contribute to the intensity of the 5577 Å line. Thus we ask whether the A-value obtained by Corny and Williams by a lifetime experiment is higher than...
the A-value obtained by Kernahan and Pang by an intensity method because the two-photon emission makes a significant contribution to the decay rate of the $^1S_0$ level. In this paper we calculate the two-photon transition probability for the $^1S_0 - ^1D_2$ transition. We shall show that the probability is negligible.

**THEORY**

The basic theory of two-photon spontaneous emission was given by Göppert-Meyer (4). The most important subsequent application of the theory to spontaneous emission transition probabilities was to the 2s–1s transition in hydrogen by Breit and Teller (5), by Spitzer and Greenstein (6), by Kipper (7), and by several later authors whose refinements need not be considered here.

We let a denote the upper state of a two-photon transition and b the lower state. In our problem a is $2p^4 \, ^1S_0$ and b is $2p^4 \, ^1D_2$. Then the spontaneous emission transition probability of $a \rightarrow b$ is

$$ A = \frac{1}{2} \int_0^1 A(y) \, dy \tag{1} $$

where

$$ A(y) = \frac{16\pi^4 \, e^2 \, \nu_{ab} \, \gamma^3 \, (1 - y)^3}{\hbar^2 c^6} \int d\Omega_\alpha \int d\Omega_\beta \, | \nu |^2 \tag{2} $$

and

$$ Y = \sum_c \left\{ \frac{<b \mid (\Sigma_{\tau_s} \cdot e_\beta) \mid c> \cdot \nu_{\alpha c} - \nu_{\alpha c} \nu_{\alpha c}}{\nu_{cb}} \right\} \tag{3} $$

In these equations $\nu_{ab}$ denotes the frequency of the $a \rightarrow b$ transition. c denotes an intermediate state, not necessarily lying between a and b, and the sum over c in (3) is over all possible intermediate states $\Sigma_{\tau_s}$ denotes the sum of $\tau_s$ for all the electrons in the atom. $\nu_{\alpha c}$ is the frequency of the transition $a \rightarrow c$, taken as negative if c is above a; $\nu_{cb}$ is the frequency of the transition $c \rightarrow b$, taken as negative if c is below b. $\alpha$ and $\beta$ denote the two emitted photons, whose propagation vectors $k_\alpha$ and $k_\beta$ are within the solid angle $\Omega_\alpha$ and $\Omega_\beta$, whose polarization vectors are $e_\alpha$ and $e_\beta$, and whose frequencies are $\nu_{\alpha} = \nu_{\beta}$ and $\nu_{\beta} = (1 - y)\nu_{ab}$. The factor 1/2 in equation (1) corrects for the fact that there are two photons and each pair is counted twice.

We have to evaluate the quantity Y. We take the propagation vector $k_\beta$ along the y axis in cartesian coordinates, $k_\alpha$ at an angle $\theta$ to $k_\beta$ in the yz plane. Then we consider the polarization vectors $e_{\alpha 2}$ along the z axis, and $e_{\beta 2}$ along the y axis, $e_{\alpha 1}$ perpendicular to $k_\beta$ in the yz plane and $e_{\beta 1}$ along the x axis. These polarization vectors can be chosen in pairs in four ways. For each combination we evaluate the matrix elements in the numerator of (3). The scalar products, such as $<\tau_s \cdot \epsilon_{\alpha 1}$, are expressed in terms of x, y and z; then x, y and z are expressed in terms of a spherical tensor $<\tau_s^{(11)}$, and the resulting matrix elements are simplified by means of the Wigner–Eckart Theorem. We sum Y over all possible values of the magnetic quantum number of the intermediate state c, and then sum | y |^2 over the four possible polarization combinations, all for each pair of values of the magnetic quantum numbers of the initial and final states. Finally we specialize the resulting formulae to our particular case. For the initial level $a \equiv 2p^4 \, ^1S_0$ we have $M = 0$, for the final level $b \equiv 2p^4 \, ^1D_2$ we have $M = +2, +1, 0, -1, -2$, and for the intermediate states c we must have $J = 1$ so that the pairs of matrix elements in (3) have nonvanishing values for the electric dipole transitions $a \rightarrow c$ and $c \rightarrow b$. We add the five values of | y |^2 for the five combinations of M values. The result of all these calculations is

$$ | y |^2 = \frac{1}{30} (13 + \cos^2 \theta) \begin{vmatrix} \sum P \gamma \frac{1}{\gamma} \nu_{ab} + \nu_{ca} \cr \frac{1}{\nu_{cb} - \nu_{ab}} \end{vmatrix}^2 \tag{4} $$

where

$$ P = (2p^4 \, ^1D_2 \parallel r^{(1)} \parallel \gamma) (\gamma \parallel r^{(1)} \parallel 2p^4 \, ^1S_0) \tag{5} $$

and $\gamma$ denotes all the levels in the atom which have $J = 1$ and which are possible intermediate states. Because the $^1S_0$ and $^1D_2$ levels have even parity we may restrict our choice of intermediate levels to levels of odd parity with $J = 1$. The double vertical bars in the matrix elements in (5) denote that Racah-type reduced matrix elements are used.

The first result of the present paper is contained in (4); the angular correlation factor for the two photons emitted at an angle $\theta$ apart is $(13 + \cos^2 \theta)$. This may be contrasted with the corresponding factor for hydrogen.
which is \((1 + \cos^2 \theta)\). For the total probability in all directions we carry out the integrations over the solid angles \(d\Omega_{\alpha}\) and \(d\Omega_{\beta}\) in (2). We find that

\[
A = \frac{512\pi^6 e^4 a_0^4 \nu_{ab}}{27h^2 c^6} \int_0^1 \psi(y) \, dy \quad [6]
\]

where

\[
\psi(y) = y^3 (1 - y)^3 \left\{ \frac{\nu_{ab}}{\gamma} \sum P \right\} + \frac{\nu_{ab}}{\nu_{ab} + \nu_{ca}}
\]

\[
\nu_{cb} - \nu_{ab}\]

\[
[7]
\]

In these last two formulae we have expressed \(P\) in atomic units and introduced the factor \(a_0^4\) to compensate for this; \(a_0\) is the first Bohr radius. \(\psi(y)\) gives the probability distribution of the two-photon emission, which is a continuum, as a function of the frequency of the photons. Our definition of \(\psi(y)\) is identical to that used by Spitzer and Greenstein (6) and subsequent workers on the hydrogen 2s–1s transition.

We must consider all possible intermediate states. We make the assumption that LS–coupling is strictly valid in the O I spectrum. The results of Garstang (8) for the \(2p^3\) array strongly support this assumption. The only intermediate states which need be considered are of the form \(^1P_1\). There are several possibilities which we consider in turn.

(a) \(2p^3\) (\(^2P\))ns \(^1P_1\)

For intermediate states of this form it may be shown, for example, using the formulae of Rohrlich (9), that the matrix elements in (5) are given by

\[
(2p^4 \ 1D_2 \ || \ r^{(11)} || \ 2p^3 \ (^2P)ns \ 1P_1) = -5^{1/2} \sigma \quad [8]
\]

\[
(2p^4 \ 1S_0 \ || \ r^{(11)} || \ 2p^3 \ (^2P)ns \ 1P_1) = +2^0 \sigma \quad [9]
\]

Any \(n \geq 3\) is possible, including both bound and continuum states. Various \(2p^4\) – \(2p^2\) transitions have been studied by many authors, including Garstang (8), Ott (10), Martinson, Berry, Bickel and Oona (11), Smith, Bromander, Curtis, Berry and Buchta (12), Kelly (13), Druetta and Poulizac (14) and Irwin, Livingston and Kernahan (15). Taking into account all these papers we adopted \(\sigma^2 = 0.13\) for the \(2p^3 - 2p^4(\text{P})\) transitions. When (8) and (9) are substituted in (5) we must remember to change the phase of (9) in accordance with Racah (16, equation 31) when we change the matrix element to be of the form \((2p^4\ 3s^1 \ 1P_1 || r^{(11)} || 2p^4\ 1S_0)\). Thus from (5), (8) and (9) and this extra phase we obtain \(P = +0.58\) for the \(2p^4(\text{P})\) intermediate state. The quantity inside the braces \(\{\}\) in (7) is a very slowly varying function of \(y\), having equal maxima at \(y = 0\) and \(y = 1\) and a minimum at \(y = 0.5\). For ample accuracy in this case we assume a constant value, given by putting \(y = 0.3\): the variation over the whole range of \(y\) for the \(3s\) levels is less than one percent. Then the contribution to the sum over \(\gamma\) in (7) was evaluated and found to be +0.229. In the calculations on \(\text{O I}\) the energies of the levels were taken from Moore (17).

For the higher bound states (4s, 5s, 6s) the Coulomb approximation tables of Oertel and Shomo (18) were used to obtain values of \(\sigma^2\). A rough estimate of the effect of ns states with \(n \geq 7\) was made. All the bound states with \(n \geq 4\) gave an estimated contribution of +0.033 to the sum over \(\gamma\) in (7). This sum is essentially independent of \(\gamma\).

For the continuum states \(2p^3(\text{P})\) we used the tables of Peach (19) to calculate the matrix elements. Her tables included all the resultant states of the \(2p^3(\text{P})\) configuration, and not just that portion which is coupled to a \(^1P_1\) resultant. The appropriate factor was introduced to allow for this; the factor may be derived from general formulae given by Burgess and Seaton (20). For a continuum the sum over \(\gamma\) in (7) is replaced by integration over the energy of the ejected electron. We estimated the contribution of the \(\text{S}_0\) continuum to the sum over \(\gamma\) to be +0.067.

(b) \(2p^3\) (\(^2D\))ns \(^1P_1\)

States of this type have zero matrix elements with the \(2p^4\) \(^1S_0\) level, so they make no contribution to the sum over \(\gamma\) in (7).

(c) \(2p^3\) (\(^2P\))nd \(^1P_1\)

For intermediate states of this type we have

\[
(2p^4 \ 1D_2 \ || \ r^{(11)} || \ 2p^3 \ (\text{P})\text{nd} \ 1P_1) = +2^{-1/2} \sigma \quad [10]
\]

\[
(2p^4 \ 1S_0 \ || \ r^{(11)} || \ 2p^3 \ (\text{P})\text{nd} \ 1P_1) = -(40)^{1/2} \sigma \quad [11]
\]

As before the phase of (11) must be changed when we reverse the order of (11) for insertion in (5). For the \(3d\) state we adopted \(\sigma^2 = 0.0030\) on the basis of Kelly (13).
The contribution to the sum over $\gamma$ in (7) was found to be $+0.004$. Bound nd states with $n > 3$ were neglected. The contribution of the continuum was calculated from the tables of Peach (19) and formulae of Burgess and Seaton (20). After integration over the continuum we obtained a contribution from the ed continuum to the sum over $\gamma$ in (7) to be $+0.168$.

(d) $2s2p^4 np \, ^1P_1$

Intermediate states of this type are possible in principle, but, for $n > 2$, it is found that one or both of the matrix elements in (5) are zero, so that there is no contribution to $P$.

(e) $2s2p^5 \, ^1P_1$

For intermediate states of this type we have

\begin{align*}
(2p^4 \, ^1D_2 \parallel r^{(1)} \parallel 2s2p^5 \, ^1P_1) &= -2^{1/2} \sigma \quad \text{[12]} \\
(2p^4 \, ^1S_0 \parallel r^{(1)} \parallel 2s2p^5 \, ^1P_1) &= -(10)^{1/2} \sigma \quad \text{[13]}
\end{align*}

As before the phase of (13) must be changed when it is inserted in (5). The value of $\sigma^2$ was estimated from the calculations of Nicolaides (21): we adopted $\sigma^2 = 0.25$. His calculations included configuration interaction. The energy used for the $2s2p^5 \, ^1P_1$ state was the estimate of Moore (22). Our final estimate of the contribution to the sum over $\gamma$ in (7) is $-0.244$. It may be noted that this contribution has the opposite sign to those for the other intermediate states: Breit and Teller (5) found a similar effect in hydrogen, for which the contribution of the $2p$ state was of opposite sign to that of the np states with $n > 2$. In principle a contribution also arises from the intermediate state $1s2s^22p^5 \, ^1P_1$, but we believe that this contribution is much smaller than that of the $2s2p^5 \, ^1P_1$ state, and we neglected it.

RESULT

Collecting all the contributions to the sum in (7) we obtain

\[ \psi(y) = 0.066 y^2 (1 - y)^3 \quad \text{[14]} \]

for the probability distribution function of the two-photon continuum. The total transition probability is given by (6), and is $A = 6.8 \times 10^{-7} \text{ sec}^{-1}$

**DISCUSSION**

We note that the form of (14) is significantly different from the form of $\psi(y)$ for hydrogen as tabulated by Spitzer and Greenstein (6). The probability in O I is more strongly concentrated in favour of photons of nearly equal frequency than it is in hydrogen. The difference arises because of the degeneracy of the 2s and 2p states in hydrogen: neither the initial nor the final state in O I is close to any intermediate state.

The transition probability is unexpectedly small, seven orders of magnitude smaller than the 2s -- 1s transition in hydrogen. A factor of about 2000 arises from the smaller $\nu_{ab}$ factor for O I. A factor of about 20 arises because of the absence from the O I spectrum of an intermediate state nearly degenerate with the initial or final state. The remainder of the difference is attributable to the small matrix elements in O I, and in particular to the small numerical factor on the right-hand side of (10). This factor is exceptionally small in this particular case.

The accuracy of our calculations is hard to estimate: probably the largest uncertainty arises from the use of the Coulomb approximation in the quantum-defect method of Peach (19) which we used in our estimation of the continuum matrix elements.

The smallness of the transition probability shows that two-photon transitions do not contribute significantly to the de-excitation of the $^1S_0$ state, and cannot explain the difference between the lifetime and intensity experiments mentioned at the beginning of this paper. Uncertainties in our calculation could not be large enough to vitiate this conclusion.

**THE OXYGEN ISOELECTRONIC SEQUENCE**

It is of interest to examine the behaviour of the transition probability along the oxygen isoelectronic sequence. The frequency $\nu_{ab}$ $\propto Z$, where $Z$ is the nuclear charge. The matrix elements in (5) each behave like $Z^{-1}$, and hence $P$ in (7) behaves like $Z^{-2}$. We must now consider two types of intermediate states. For $2p^4$ ns and $2p^4$ nd states, with $n \geq 3$, including the continuum, $\nu_{ca}$ and $\nu_{cb}$ both behave like $Z^2$. Hence from (7) and (6) we see that $A \propto Z^{-1}$ for large $Z$. For the intermediate state $2s2p^5 \, ^1P_1$ the frequencies $\nu_{cb}$ and $\nu_{ca}$ both behave like $Z$. Hence from (7) and (6) we see that $A \propto Z$. Because the $2s2p^5 \, ^1P_1$ level contributes a term to the sum over $\gamma$ in (7) which has the opposite sign to all the other terms and is initially smaller than the sum of the other terms we expect the transition probability to decrease initially. The sum over $\gamma$ will pass through a zero and change sign.
A will increase again, and for large Z it will behave linearly with Z. For very large Z only the 2s2p$^5$ 1P$^1$ will make a significant contribution to the two–photon transition probability. (However, an accurate calculation of the transition probability for such highly ionized atoms would necessitate consideration of departures from LS–coupling and perhaps relativistic effects. These will introduce additional terms with higher powers of Z.)

We have made estimates of A for the 2p$^4$ 1S$^0$ – 2p$^4$ 1D$^2$ transitions in Ca XIII and Fe XIX using only the 2s2p$^5$ 1P$^1$ intermediate state. The matrix elements for both ions were calculated using the Z–expansion formula of Laughlin and Dalgarno (23). The frequency $\nu_{ab}$ for Ca XIII was taken from Edlén (24) and $\nu_{ca}$ from Fawcett, Burgess and Peacock (25). The frequencies for Fe XIX were calculated from the energies tabulated by Reader and Sugar (26). The transition probabilities obtained were $A = 1.9 \times 10^{-5}$ sec$^{-1}$ for Ca XIII and $A = 1.9 \times 10^{-4}$ sec$^{-1}$ for Fe XIX: for the higher Z the value of A is increasing more rapidly than Z, showing that higher order effects in the energies are significant. For the 2p$^4$ 1S$^0$ level in Ca XIII the electric quadrupole transition 2p$^4$ 1S$^0$ – 2p$^4$ 1D$^2$ has a probability 9 sec$^{-1}$ and the magnetic dipole transition 2p$^4$ 1S$^0$ – 2p$^4$ 3P$^1$ has a probability 7800 sec$^{-1}$, calculated by Mason (27). Fe XIX will have higher transition probabilities. Transition probabilities for ions in the sequence below Ca XIII were given by Malville and Berger (28). Because we used only the 2s2p$^5$ 1P$^1$ intermediate states, and other states give terms with opposite signs in the sum over $\gamma$ in (7), we expect our values to be upper limits on the transition probabilities, apart from uncertainties in our estimates of the matrix elements used. Even quite large errors due to omitted terms would not alter our general conclusion that two–photon emission does not contribute significantly to the de–excitation rate of the 1S$^0$ level in any ion of the oxygen isoelectronic sequence.

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BIBLIOGRAFIA