Relative fine-structure intensities in two-photon excitation

David R. Crosley and William K. Bischel
Molecular Physics Department, SRI International, Menlo Park, California 94025
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Relative intensities for different fine-structure components of the two-photon transitions $2p\,^3P \rightarrow 3p\,^3P$ in oxygen and $2p^3\,^4S^o \rightarrow 2p^2 3p\,^4D^o$ in nitrogen had been measured and found to agree well with calculations involving a single virtual intermediate level. They are in direct conflict, however, with a two-photon selection rule $\Delta J \neq 1$ derived in an earlier but erroneous purely theoretical treatment of these transitions. Five other experiments are also briefly examined, with the conclusion that relative fine-structure intensities in two-photon transitions are well understood as straightforward extensions of angular momentum coupling in single-photon cases, in accordance with allowed $\Delta J = 0, \pm 1$, and ± 2 transitions.

Experiments performed previously in a low-pressure flow discharge constituted the first demonstration and study of two-photon excitation of fluorescence in oxygen and nitrogen atoms.[1,2] In the method, two laser photons in the ultraviolet (near 226 nm for O and 211 nm for N) elevate the atom to the first excited state of the same symmetry as the ground state, which then emits a near-infrared photon (O, 845 nm; N, 869 nm) in a transition to a lower lying level. The actual sequences are $2p\,^3P \rightarrow 3p\,^3P \rightarrow 3s\,^3S$ for O and $2p^3\,^4S^o \rightarrow 2p^2 3p\,^4D^o \rightarrow 2p^2 3s\,^4P$ for N. The method permits the selective excitation of states inaccessible with single-photon excitation for purposes such as lifetime and collisional rate measurements as in Refs. 1 and 2. It also can be used for diagnostics purposes to detect the atomic species under conditions where the vacuum ultraviolet nature of the lowest energy transition renders single-photon laser-induced fluorescence impossible. The technique has now been used to detect O in tokamak plasmas[3] and atmospheric pressure flames,[4] and was proposed for remote sensing of O atoms from spacecraft.[5]

One part of the experimental studies[1,2] comprised measurement and calculation of relative intensities for different fine-structure components of the two-photon transitions. The three ^3P_J ground-state components for O were well separated but the upper state components were split by amounts comparable to the combined laser and Doppler linewidths, so the measured intensities were sums over the upper-state J's. In the case of N, there is one ground-state level but four fully resolved upper-state components. The calculations[2] were performed by describing the states in a standard *LSJ* coupling scheme, and assuming that a single virtual intermediate state (of ^3S symmetry for O and ^4P for N) dominates the two-photon transition probability. Excellent agreement[2] was achieved between experimental and calculated intensities.

Prior to the experiments there appeared two theoretical papers, describing calculations of absolute two-photon absorption coefficients and relative fine-structure intensities for O (Ref. 6) and for O and N.[7] In the latter paper[7] new selection rules for two-photon transitions were derived, so that $\Delta J = 0, \pm 2$ only, and $\Delta J = 0$ when $\Delta L = 0$. These results are in direct conflict with the observation[1,2] of $J = \frac{3}{2} \rightarrow \frac{1}{2}, \frac{5}{2}$ transitions in N and the relative experimental intensities in the case of O.

It is the purpose of this Comment to point out this discrepancy and that the expression for the two-photon absorption cross section in Ref. 7 is erroneously written. Derived correctly, the $\Delta J \neq \pm 1$ restriction and the $\Delta L = 0 \rightarrow \Delta J = 0$ rule disappear, and the results are in agreement with the calculations (and thus the experiments) of Ref. 2.

In the case of $N(^4S \rightarrow {}^4D)$ the only possible intermediate is ^4P. In $O(^3P \rightarrow {}^3P)$, however, there could be contributions from ^3P and ^3D intermediates in addition to the ^3S state assumed in the simple calculations.[2] The ^3S can only involve $m_L = 0$ excitation from ground ^3P with a cross section β_0 whereas ^3P and ^3D intermediates can also include $m_L = \pm 1$ cross sections β_1 as well. Pindzola[6] explicitly calculated the relative contributions, arriving at ratios $\epsilon = (\beta_1/\beta_0)^{1/2}$ between 0.15 and 0.22 depending on the form of the wave function and radiative interaction. In the case of a $^3P_{J''} \rightarrow {}^3P_{J'}$ transition, the relative $J'' \rightarrow J'$ intensities are sensitive to the value of ϵ (see Table II of Ref. 2) but the sum over J' corresponding to the experimental measurements is independent of ϵ. However, in a study of the analogous $3p^3P \rightarrow 4p^3P$ two-photon transition in *S*, Brewer, van Veen, and Bersohn[8] were able to separate individual $J'' \rightarrow J'$ components and found a best fit value to their results of $\epsilon = 0.24 \pm 0.06$.

On the other hand, Goldsmith[9] has made ionization measurements of O in flames, using the same two-photon pumping to $3p^3P$ followed by single-photon ionization from the upper state. He too resolved only the lower state fine structure but observes ratios from $^3P_2{:}^3P_1{:}^3P_0$ of 1.6:1.3:1 in contrast to values of 6:3:1 expected using the calculated relative intensities[2] and the relative state populations in the flame at 1500 K. Goldsmith's laser intensities together with the two-photon cross section[1,2] appear two orders of magnitude below saturation values, using the quenching rate constant measured for N_2 (Ref. 1 and 2) as a likely lower value. We do not know the reason for the discrepancy.

Three other experiments also bear on the question of relative fine-structure transitions in two-photon excitation. Eight separate $J'' \rightarrow J'$ components of the $^3P_{J''} \rightarrow {}^3D_{J'}$ two-photon transition in carbon at 287 nm have been resolved;[10] excellent agreement exists between measured and calculated intensities. Two extensive sets of measurements of rotational line strengths in two-photon excitation of $^2\Sigma^+ - {}^2\Pi$ transitions of diatomic molecules have also been compared with calculated values. For both NO (Ref. 11) and OH (Ref. 12) the calculated and measured values agreed to

within experimental scatter. We can conclude overall that the angular momentum aspects of two-photon excitation are well understood as extensions of standard single-photon treatments, including $\Delta J = 0, \pm 1$, and ± 2 as allowed transitions.

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