Off-Resonant $E2$ Transition Observed in Two-Photon Absorption in Xe I

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In xenon, the $5p^5\,5d[K=\frac{5}{2}]_{J=3}$ and $5p^5\,5d[K=\frac{7}{2}]_{J=3}$ atomic states have been excited by two-photon absorption from the ground state. It is shown that the two-photon absorption proceeds via off-resonant $E1$-$E2$ and $E2$-$E1$ transitions. Satisfactory agreement is found between experimental and estimated two-photon absorption rates for these processes.

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Two-photon absorption[1-4] is a well-established technique in atomic spectroscopy. Usually, the excitation proceeds via resonant or off-resonant dipole-dipole transitions. It was discussed by several authors (see, e.g., Refs. 5 and 6), however, that in multiphoton spectroscopy the dipole approximation might not be sufficient and higher multipole contributions, i.e., $E2$, need to be considered. Because of the small transition probability, processes such as $E1$-$E2$ were thought to be observable only when the laser radiation is resonant or nearly resonant within a few wave numbers with the atomic quadrupole transition. In this Letter we report a two-photon absorption in Xe I, which involves quadrupole transitions off-resonant by more than 26 000 cm^{-1}. For such vast mismatch, this is the first time the influence of off-resonant electric quadrupole transitions has been verified experimentally. Previously, only resonant or nearly resonant quadrupole transitions were observed in nonlinear atomic spectroscopy. Lambropoulos *et al.*[7] succeeded to photoionize sodium by three-photon $E1$-$E2$-$E1$ absorption. In order to discriminate against the $E1$-$E1$-$E1$ background, the laser was tuned to resonance with the sodium $3p$-$5p$ or $3p$-$4f$ transitions. Recently, stimulated Raman scattering was detected in potassium[8] when the pump laser was adjusted to match the $4s$-$3d$ transition within 5 cm^{-1}. In resonantly enhanced multiphoton ionization of Xe, Aron and Johnson[9] found evidence for a parity forbidden three-photon transition, but no conclusive explanation was offered. Furthermore, resonant quadrupole transitions have been employed for sum-frequency generation in atomic vapors.[10,11]

Starting from the $5p^6\,{}^1S_0$ ground state we have excited the atomic states $5p^5 5d[K=\frac{5}{2}]_{J=3}$ and $5p^5 5d[K=\frac{7}{2}]_{J=3}$ of xenon (Fig. 1). The output of a dye-laser amplifier, pumped by a nitrogen laser, was frequency doubled to yield 200 W of linearly polarized radiation, tunable between 240 and 250 nm with a bandwidth of $\Delta\nu_L \approx 15$ GHz. The laser beam was focussed ($I_0 \sim 5$ MW/cm^2) into a gas cell filled with 30 Torr xenon. Excitation spectra were recorded by monitoring the fluorescence perpendicular to the laser beam after each pulse (duration 4 nsec) with the aid of a solar-blind photomultiplier, sensitive between 110 and 190 nm. The deexcitation of the $5d$, $J=3$ states is expected to proceed via $6p$ and $6s$ and possibly $5d$, $J=1$ atomic states, with the resulting vacuum-ultraviolet fluorescence falling into the spectral window of our detector. In case of excimer formation at 30 Torr, the decay[12] would contribute to the first or second continuum at 140 and 170 nm, respectively, and hence be registered. Furthermore, at this pressure we neglect any anisotropy of the fluorescence radiation from a possible alignment of the $5d$ states by linearly polarized laser light. Consequently, the fluorescence is a measure of the two-photon absorption rates. Single-photon counting was used to achieve the high sensitivity necessary to detect weak atomic transitions. Typical excitation spectra are shown in Fig. 2. In this way, we obtain for the transitions

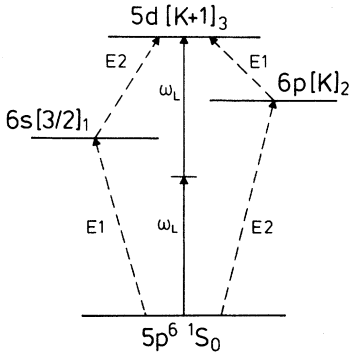

FIG. 1. Principal excitation scheme for two-photon absorption in Xe I, with $\Delta J = 3$ and $K = \frac{5}{2}$ and $\frac{5}{2}$. The detunings are about 27 000 cm^{-1} and 38 000 cm^{-1} for the $5p^5\,6s$ and $5p^5\,6p$ intermediate states, respectively.

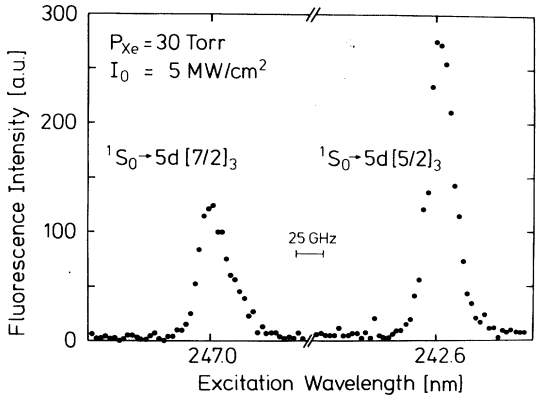

FIG. 2. Excitation spectra of dipole-forbidden two-photon transitions in XeI.

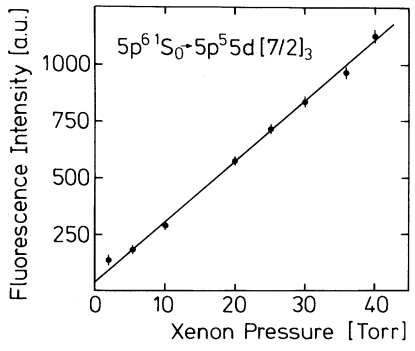

FIG. 3. Pressure dependence of the observed fluorescence intensity after two-photon absorption in xenon at 247.0 nm.

to the $5p^2 5d[K=\frac{5}{2}]_{J=3}$ and $5p^2 5d[K=\frac{7}{2}]_{J=3}$ states experimental two-photon absorption rates of 0.03 and 0.02 $\sec^{-1}$, respectively. Because of uncertainties in the estimated power density, solid angle, and detector efficiency, these rates might be in error by at most a factor of 3.

To prove that the excitation spectra in Fig. 2 correspond to atomic two-photon absorption we have measured the dependence of the fluorescence intensity on pressure and power density. The linear variation with pressure, illustrated in Fig. 3, presents clear evidence for an atomic transition. In addition, a log-log plot of the fluorescence intensity versus power density results in a straight line with a slope of 2.0 ± 0.1, excluding the occurrence of higher multiphoton processes. For a two-photon excitation, the changes in parity and angular momentum ($\Delta J = 3$) of the levels involved are inconsistent with a dipole-dipole transition (including $E1$-$M1$). Hence, we conclude that the absorption proceeds via $E1$-$E2$ and $E2$-$E1$ transitions (cf., Fig. 1). Generally, the cross section for such processes are considerably smaller than for dipole-allowed two-photon absorption. Indeed, the signals at 242.6 and 247.0 nm (see Fig. 2) are weaker by about four orders of magnitude compared to the fluorescence intensity observed after exciting $J=0$ and 2 levels of the $5p^5 6p$ configuration by dipole-allowed two-photon transitions.[13] For the proposed $E1$-$E2$ and $E2$-$E1$ processes, the $5p^5 6s[K=\frac{3}{2}]_{J=1}$ and $5p^5 6p[K=\frac{3}{2},\frac{5}{2}]_{J=2}$ are the lowest excited states to act as intermediate levels, respectively. Therefore, the electric quadrupole transition is, in both cases, off resonant by more than 26 000 cm^{-1}.

Further support for this interpretation is derived from the agreement between the experimental transition rates and theoretical estimates. The electric dipole and quadrupole interaction between the xenon atoms and the laser radiation can be written as

$$\mathcal{H} = -\tfrac{1}{2} ezE_0(\omega_L)\exp(-i\omega_L t) - \tfrac{1}{4} iezxk_L E_0(\omega_L)\exp(-i\omega_L t) + \text{c.c.} \tag{1}$$

The quantization axis is taken to be parallel to the electric field vector of the linearly polarized laser radiation propagating along the x axis. If we assume a Gaussian distribution for the spectral power density $I(\omega)$ [full width at half maximum (FWHM) = $\Delta\omega_L$], and take into account that the bandwidth of the laser is much larger than the Doppler width ($\Delta\omega_L \gg \Delta\omega_D$), second-order perturbation theory yields, for the two-photon absorption rate at resonance,[1,4]

$$W(5p^6\,^1S_0;\ 5p^5 5d[K]_J) = Ck_L^2 M, \tag{2}$$

where

$$C = 16\pi^2 e^4 I_0^2 (2\pi \ln 2)^{1/2}/\hbar^4 c^2 \Delta\omega_L$$

and

$$M = \sum_{m_J=\pm 1} \left| \sum_a \frac{\langle 5p^5 5d[K]_J\, m_J | zx | a\rangle\langle a | z | 5p^6\,^1S_0\rangle}{\omega_a - \omega_L} + \sum_{a'} \frac{\langle 5p^5 5d[K]_J\, m_J | z | a'\rangle\langle a' | zx | 5p^6\,^1S_0\rangle}{\omega_{a'} - \omega_L} \right|^2 . \tag{3}$$

The first and second term in Eq. (3) represent $E1$-$E2$ and $E2$-$E1$ processes, respectively, as illustrated in Fig. 1. Since the operator zx changes the magnetic quantum numbers by ± 1, only the Zeeman levels $m_J = \pm 1$ of the $5d$ states will be populated. Although the summation over a and a' includes all excited states, we shall restrict ourselves to the lowest ones with the same $^2P_{3/2}$ core as the final state. This approximation is expected to reproduce only the correct order of magnitude, because the detuning of the $6s$ and $6p$ states is not significantly smaller than the detuning of higher lying levels. Also, we shall calculate the contributions due to $E1$-$E2$ and $E2$-$E1$ processes separately and neglect interference terms.

In the following, the excitation of the $5p^5 5d[K=\frac{5}{2}]_{J=3}$ state will be discussed explicitly. For the dipole matrix elements experimental or theoretical oscillator strengths are used. The quadrupole matrix elements are unknown and estimates are either obtained from Coulomb approximation results[14] or derived from experimental dipole-allowed two-photon absorption rates.[13,15]

For the $E1$-$E2$ route we obtain from Eqs. (2) and (3)

$$W(E1\text{-}E2) = 3\times 10^{-4} f_{\mathrm{abs}}(5p^6\,{}^1S_0; 5p^5 6s[K=\tfrac{3}{2}]_{J=1}) \left|\langle 5p^5 6s[K=\tfrac{3}{2}]_{J=1} \| r^2 C^{(2)} \| 5p^5 5d[K=\tfrac{5}{2}]_{J=3}\rangle\right|^2 a_0^{-4}\ \mathrm{sec}^{-1}. \quad (4)$$

The dipole oscillator strength ($f_{\mathrm{abs}} = 0.28$) is taken from the measured lifetime of the $5p^5 6s[K=\frac{3}{2}]_{J=1}$ state.[16] By assuming jl coupling and using the Coulomb approximation[14] we calculate the absolute value of the quadrupole matrix element in Eq. (4) to be $43a_0^2/\sqrt{5}$. In this way we find for the absorption rate $W(E1\text{-}E2) = 0.03\ \mathrm{sec}^{-1}$.

There are two levels ($[K=\frac{3}{2}]_{J=2}$ and $[K=\frac{5}{2}]_{J=2}$) of the $5p^5 6p$ configuration which need to be considered as intermediate states for the $E2$-$E1$ route. However, the two corresponding dipole transitions to the final state differ in their calculated oscillator strengths by a factor of 10.[17] Therefore, only the contribution from the $5p^5 6p[K=\frac{3}{2}]_{J=2}$ state has to be taken into account (see Fig. 1). Hence the $E2$-$E1$ transition rate can be approximated by

$$W(E2\text{-}E1) = 94\times 10^{-4} f_{\mathrm{abs}}(5p^5 6p[K=\tfrac{3}{2}]_{J=2};\ 5p^5 5d[K=\tfrac{5}{2}]_{J=3}) \times \left|\langle 5p^5 6p[K=\tfrac{3}{2}]_{J=2} \| r^2 C^{(2)} \| 5p^6\,{}^1S_0\rangle\right|^2 a_0^{-4}\ \mathrm{sec}^{-1}. \quad (5)$$

The calculated oscillator strength is $f_{\mathrm{abs}} = 0.232$.[17] In contrast to the $E1$-$E2$ case, the Coulomb approximation is inadequate for calculating the quadrupole matrix element. Instead, we use the procedure suggested in Ref. 15 to derive a value for this matrix element from the experimentally observed dipole-allowed two-photon transition rate to the $5p^5 6p[K=\frac{3}{2}]_{J=2}$ state. Defining an average detuning frequency $\bar{\omega} - \omega_L$, the usual expression[1,4] for the $E1$-$E1$ two-photon absorption rate is found to be proportional to the quadrupole matrix element in Eq. (5). We chose for $\bar{\omega}$ a value halfway between the ionization energy and the $6s$ state. From the $E1$-$E1$ absorption rate of $3.5\times 10^3\ \mathrm{sec}^{-1}$, observed in a different experiment[13] by using a laser power density $I_0 = 1.8\ \mathrm{MW/cm^2}$ and a bandwidth $\Delta\nu_L \simeq 2.8$ GHz, we obtain for the absolute value of the reduced quadrupole matrix element in Eq. (5) $(3\pm 1)a_0^2$. The uncertainty reflects the somewhat arbitrary choice of $\bar{\omega}$. In the jl coupling scheme, this result corresponds to a one-electron integral $|\langle 5p \| r^2 \| 6p\rangle| \simeq 8a_0^2$. This value compares favorably with $\langle 5p \| r^2 \| 5p\rangle = 6.45\times a_0^2$ reported in Ref. 18 and supports our procedure for evaluating Eq. (5). With the value of $3\times a_0^2$, we obtain for the $E2$-$E1$ transition rate $0.02\ \mathrm{sec}^{-1}$.

As a result, the experimental two-photon absorption rate agrees surprisingly well with the estimates for the $E1$-$E2$ and $E2$-$E1$ transition rates and strongly supports our explanation given for the excitation of the $5p^5 5d[K=\frac{5}{2}]_{J=3}$ state. The close numerical agreement should not be taken too literally, if one takes consideration of the uncertainty in the experimental result, and the approximations made for estimating the transition rates. Also, interference terms between both routes might be important [cf., Eq. (3)] since the numerical estimates for $W(E1\text{-}E2)$ and $W(E2\text{-}E1)$ are of the same size.

The same considerations as for the $5p^5 5d[K=\frac{5}{2}]_{J=3}$ apply to the excitation of the $5p^5 5d[K=\frac{7}{2}]_{J=3}$ state. Here, the estimated rates $W(E1\text{-}E2) = 0.14\ \mathrm{sec}^{-1}$ and $W(E2\text{-}E1) = 0.05\ \mathrm{sec}^{-1}$ are both larger than the experimental rate of $0.02\ \mathrm{sec}^{-1}$, possibly indicating the influence of interference effects and contributions from higher intermediate states.

In conclusion, we have demonstrated the importance of largely off-resonant electric quadrupole transitions in multiphoton absorption proc-

esses. Such transitions can be exploited to excite those atomic states directly from the ground state which cannot be reached by dipole-allowed two-photon absorption. In comparison, a dipole-allowed three-photon absorption has the disadvantage of induced Stark effects and competing higher multiphoton processes caused by the larger laser-power densities required.

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Critical Slowing Down of the Soret-Driven Convective Instability in a Two-Component Liquid Layer Heated from Below

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A critical slowing down is shown of the time relaxation in the Soret-driven instability after a perturbation, described by $\tau = \tau_0 \epsilon^{-1}$, $\epsilon = (N_{Ra} - N_{Ra}{}^{crit})/N_{Ra}{}^{crit}$, and τ_0 is calculated exactly, i.e., with no extra assumptions other than a Boussinesquian and Newtonian fluid; τ_0 is correlated to all the parameters of this problem such as the Prandtl number, the Schmidt number, the Soret coefficient, and the solute Rayleigh number.

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There exists a large amount of literature on the influence of the thermal diffusion (Soret) effect on the stability of a horizontal liquid layer heated from below. We would like to single out two recent papers[1-2] particularly relevant to the present Letter. Degiorgio[1] in his study of the dynamics of convective instabilities in a horizontal liquid layer assumes that the Rayleigh-Bénard instability (RBI) and the Soret-driven instability (SDI) may be treated simultaneously, because the Schmidt number $N_{Sc} = \nu/D$ (ν is the kinematic viscosity and D is the isothermal diffusion coefficient) is much greater than the Prandtl number $N_{Pr} = \nu/K$ (K is the thermal diffusivity), implying that the lifetime of concentration fluctuations is also much greater than the lifetime of temperature fluctua-

