

Single-frequency laser measurements of two-photon cross sections and Doppler-free spectra for atomic oxygen

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Absolute bound-bound atomic two-photon cross sections have been measured using a single-frequency laser for the first time, eliminating the usual uncertainties about unresolved temporal fluctuations. For the $3p\ ^3P_{J'} \leftarrow 2p\ ^3P_2$ transition in atomic oxygen at 226 nm the integrated cross section is $\sum_{J'} \sigma_0^{(2)}(J' \leftarrow 2) = 1.87 \pm 0.60 \times 10^{-35} \text{ cm}^4$. Doppler-free spectra have been used to measure relative fine-structure cross sections and energy spacings. Absolute and relative two-photon cross sections agree well with perturbation theory, validating this approach.

The measurement of absolute two-photon absorption cross sections requires a thorough characterization of the radiation field. Because two-photon transition rates are proportional to the instantaneous square of the light intensity, unresolved temporal fluctuations can be a source of considerable uncertainty.^{1,2} With two exceptions^{3,4} absolute two-photon cross-section measurements have been carried out using pulsed, multimode laser systems subject to unresolvable temporal fluctuations. A single-frequency laser (one whose bandwidth and temporal profile are related by the uncertainty principle) has no such fluctuations. In this Rapid Communication we report the first absolute measurement of a bound-bound atomic two-photon cross section with a single-frequency laser, and compare it with *ab initio* calculation.⁵ Comparison with earlier experimental results⁶ yields a quantitative value of the second-order intensity correlation function for a tunable, multimode ultraviolet laser system. The first Doppler-free spectra of atomic oxygen have been obtained, allowing comparison with theoretical relative fine-structure cross sections,⁵ leading to precise relative energy measurements in the $3p\ ^3P$ electronic state, and extending Doppler-free spectroscopy⁷ to shorter wavelengths (226 nm) than ever before.

The experimental procedure used to determine absolute two-photon cross sections for the $3p\ ^3P_{J'} \leftarrow 2p\ ^3P_{J''}$ transition has been described in detail elsewhere.⁶ Oxygen atoms are generated in a microwave discharge in pure O₂ at a total pressure of 0.5 Torr, with concentrations determined by titration with NO₂.⁸ Tunable laser radiation near 226 nm is used for the two-photon excitation. Fluorescence at 845 nm from the $3p\ ^3P_{J'} \rightarrow 3s\ ^3S_1^o$ transition (with the fine-structure components unresolved, collection axis perpendicular to the propagation direction of the laser), is used to determine the number of excited atoms after absolute calibration of the fluorescence collection system at this wavelength.⁹ The laser is linearly polarized in the vertical direction (perpendicular to the direction of fluorescence detection). Temporal and spatial profiles of the laser are measured in a gently focused geometry, and rate equations are used to extract the two-photon cross section. In all experiments reported here the peak laser intensity is less than 2 MW/cm², well below the

value at which photoionization by a third 226-nm photon can cause significant excited-state depletion. (The excited-state photoionization cross section is $5 \times 10^{-19} \text{ cm}^2$.)⁶ Because the excited-state photoionization cross-section measurement is unaffected by unresolved temporal fluctuations, it is not repeated in this work.

The laser source¹⁰ is built around a neodymium-doped yttrium-aluminum garnet (Nd:YAG) laser (Moletron MY34) whose oscillator cavity has been converted to a negative-branch self-filtering unstable resonator (SFUR).¹¹ A diode-pumped Nd:YAG laser (Lightwave Electronics) provides single-frequency continuous-wave (cw) radiation that is used to injection-lock the SFUR laser cavity. The 1.064- μm radiation is then passed through a single amplifier and frequency doubled in a potassium dihydrogen phosphate (KDP) crystal, producing 150 mJ at 532 nm in a 10-ns pulse. The second harmonic radiation is used to pulse amplify a cw-ring dye laser (Coherent 699-29, pumped by a Spectra-Physics SP171 ion laser) in a pulsed dye amplifier (Quanta-Ray PDA), to produce tunable radiation around 574 nm. This radiation is frequency doubled and mixed in another KDP crystal with residual 1.064- μm radiation to provide a narrow-band source of 226-nm photons. The 226-nm pulses have an energy of up to 500 μJ , a pulse length full width at half maximum (FWHM) of ≈ 4.5 ns, a linewidth of ≈ 105 -MHz FWHM, and a shot-to-shot frequency jitter of ± 25 MHz in the ultraviolet. Spatial filtering and reflection losses reduce the energy reaching the fluorescence cell to less than 100 μJ . Doppler-free spectra are obtained by reflecting the beam off a normal-incidence mirror located 18 cm from the center of the cell. Because the beam is nearly collimated and relatively large (≈ 1 mm) in diameter, good spatial overlap of the counterpropagating beams is easy to obtain. Relative cross sections and energy splittings for the fine-structure components are derived from the Doppler-free spectra. Absolute cross sections are obtained in the normal single-pass configuration, using the $3p\ ^3P_{2,1,0} \leftarrow 2p\ ^3P_2$ transition.⁶ The fluorescence signal changes by less than 3% when a magnetic field of ≈ 10 G is applied to scramble the magnetic sublevels in approximately 20% of a radiative lifetime;^{12,13} this confirms the absence of significant anisotropy in the spatial distribution

of the fluorescence. Fluorescence lifetimes of the three upper-state fine-structure levels agree to within the experimental precision of 5%, ruling out any state-dependent quenching process.

Figure 1 shows three typical Doppler-free spectra, corresponding to the three fine-structure levels in the $2p^3P$ ground electronic state. The area under the Doppler-free peaks is 1.5 ± 0.2 times the Doppler-limited area, close to the ideal value⁷ of 2.0. (The deviation from the ideal reflects the imperfect temporal and spatial overlap of the counterpropagating beams.) After subtraction of the Doppler-limited background, peak areas are used to obtain relative fine-structure cross sections. Splittings are measured by a least-squares fit of the peaks to Gaussian line shapes.

The widths of the Doppler-free peaks can be used to estimate the laser linewidth. Because the Fourier transform of the laser temporal profile is nearly Gaussian, the width of a Doppler-free atomic transition, in units of the two-photon frequency (i.e., the atomic frequency) is expected to be $\sqrt{2}$ times larger than the uv laser linewidth if the laser is transform limited and has no frequency jitter.¹⁴ The shot-to-shot frequency jitter of ± 25 MHz in the uv (Ref. 10) will increase the peak width (in units of the two-photon frequency) by roughly 100 MHz. The homogeneous linewidth predicted from direct lifetime measurements⁶ is only 6 MHz, making a negligible contribution to the observed linewidth. Because the observed peak widths are typically ~ 250 -MHz FWHM, the single-shot laser linewidth appears to be within 12% of the 95-MHz Fourier limit. Thus, we are confident that the laser can be regarded as a coherent field with no unresolved intensity fluctuations.

Absolute cross sections are derived from integrated areas in the single-pass configuration. They are combined with the experimental relative fine-structure cross sections

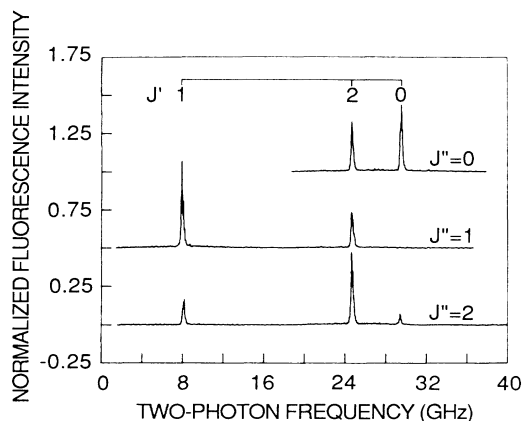


FIG. 1. Doppler-free spectra for the $3p^3P_{J'} \leftarrow 2p^3P_{J''}$ two-photon transitions in atomic oxygen. The level of two-photon excitation is monitored using fluorescence from the $3p^3P_{J'} \rightarrow 3s^3S^{\circ}\tilde{\eta}$ transition at 845 nm, normalized to the square of the laser intensity. Doppler-limited absorption forms a broad pedestal underneath each peak. Each spectrum has the same integrated area. The middle and top spectra are displaced from the bottom one by 0.5 and 1.0 vertical units, respectively.

to produce the numbers in Table I. Theoretical values from the best available *ab initio* calculation⁵ are shown for comparison. For a given J'' , the upper-state fine-structure levels can be summed over to yield this value:

$$\sum_{J'} \sigma_0^{(2)}(J' \leftarrow 2) = 1.87 \pm 0.60 \times 10^{-35} \text{ cm}^4. \quad (1)$$

The corresponding theoretical number is $1.32 \pm 0.2 \times 10^{-35} \text{ cm}^4$. As discussed previously,⁶ the $\pm 30\%$ uncertainty limits on the experimental number represent the estimated accuracy of the measurement, after considering all calibration factors. The experimental precision is much better, $\pm 10\%$. Experiment and theory agree within their combined uncertainties.

The relative fine-structure cross sections are a sensitive test of the quality of the atomic wave functions used in the perturbation theory calculations. The agreement between theory and experiment is excellent.

Because the usual experimental uncertainties about photon statistics have been removed, and because high-quality atomic wave functions have been used in the calculations, the numbers in Table I subject the standard perturbation theory description of two-photon absorption to its most rigorous test to date. This description is clearly very accurate at the intensities used in our experiment. Absolute two-photon cross-section measurements with a single-frequency laser have also been carried out for two-photon absorption in nitric oxide molecules⁴ and for two-photon ionization of cesium atoms;³ neither measurement was accompanied by a comparison with *ab initio* calculation.

Table II gives observed fine-structure splittings, along with a comparison with previous work.¹⁵ The agreement is very good. The literature values, based on a combination of calculation and emission wavelength measurements,¹⁶ are comparable to ours in precision.

TABLE I. Experimental and theoretical (in parentheses, from Ref. 5) integrated two-photon cross sections for the $3p^3P_{J'} \leftarrow 2p^3P_{J''}$ transition in atomic oxygen.

J''	J'	$\sigma_0^{(2)}(J' \leftarrow J'')$	
		Absolute (10^{-36} cm^4) ^a	Relative ^b
2	2	13.2 (9.42)	0.706 ± 0.077 (0.714)
2	1	3.63 (2.61)	0.194 ± 0.043 (0.198)
2	0	1.87 (1.16)	0.100 ± 0.040 (0.088)
1	2	6.98 (4.34)	0.373 ± 0.067 (0.329)
1	1	11.7 (8.86)	0.627 ± 0.067 (0.671)
1	0	0 (0)	0 (0)
0	2	9.01 (5.79)	0.482 ± 0.045 (0.439)
0	1	0 (0)	0 (0)
0	0	9.69 (7.41)	0.518 ± 0.045 (0.561)

^aThese numbers must be multiplied by a line-shape factor $g(\omega - \omega_{J'})$ to get the effective cross section at any given two-photon radial frequency, ω . If the line-shape function is a 300-K Doppler profile $g(0) = 1.81 \times 10^{-11} \text{ sec}$.

^bExperimental error limits are $\pm 1\sigma$, where σ is the sample standard deviation.

TABLE II. Fine-structure splittings in the O ($3p^3P$) electronic state.

Splitting $\Delta\nu(J') = \nu(J'=2) - \nu(J')$	This work (cm^{-1}) ^a	Previous work (cm^{-1}) ^b
$J'=1$	0.555 ± 0.006	0.560
$J'=0$	-0.159 ± 0.004	-0.156

^aError limits are $\pm 2\sigma$.

^bReference 15.

In our previous work⁶ the quantity measured was the product $\sum_{J'} \sigma_0^{(2)}(J' \leftarrow 2) G^{(2)}$, where $G^{(2)}$ is the second-order intensity correlation function of the laser field at time zero.¹⁷ The ratio of the earlier number, $2.66 \times 10^{-35} \text{ cm}^4$, to the number in Eq. (1) yields the value $G^{(2)} = 1.4 \pm 0.2$ for the laser system used in Ref. 6. (Because most systematic errors cancel, this ratio is known to high precision.) This represents the first measurement of $G^{(2)}$ for tunable ultraviolet radiation produced by stimulated Raman scattering. The pump source⁶ was a multimode, doubled dye laser. If the N modes in a multimode laser have random phases, $G^{(2)}$ will be $[2 - (1/N)]$, while in the mode-locked case (fixed phases) it equals $(\frac{1}{3})[2N + (1/N)]$.¹⁸ The visible dye laser used in Ref. 6 had $N \approx 10$. However, we are unable to separate the effect of the dye laser oscillation from that of the subsequent frequency conversion steps in producing the final value of $G^{(2)}$. Thus, neither of the simple formulas above is applicable to our experimental situation. In a separate paper¹⁹ we give values of $G^{(2)}$ for several different 226-nm laser systems, and examine the effect of nonlinear frequency conversion processes on this parameter.

The development of reliable single-frequency Nd:YAG laser systems, crucial to the success of this experiment, has allowed Doppler-free spectroscopy to be extended further into the ultraviolet than before. Prior to this experiment, the shortest wavelength used in a Doppler-free experiment was 243 nm.²⁰⁻²² Because the phase matching limit for the KDP crystal used for frequency mixing in our

experiment is 217 nm, other techniques such as anti-Stokes stimulated Raman scattering (SRS) must be used to obtain narrow-band radiation at shorter wavelengths. Unfortunately, SRS of a pulsed single-frequency laser leads to an anti-Stokes linewidth significantly greater than the Fourier limit.²³

The absolute two-photon cross section measured here, along with the excited-state photoionization cross section,⁶ can be used to estimate sensitivity limits for O ($3P$) detection. We assume a laser system similar to ours (narrow band, 5 ns long, 1 mm in diameter, collimated, with a pulse energy of 500 μJ) and a low pressure at which quenching of the $3p^3P$ excited state is insignificant. The fluorescence and ion collection systems are also assumed similar [$f/0.7$ collection lens, 25% filter transmission, 10% photomultiplier tube (PMT) quantum efficiency for fluorescence, several cm collection length, and unit collection efficiency for ions]. In a single-pass configuration, a PMT signal of one photoelectron per laser pulse can be obtained with an O-atom density of $\approx 10^{10} \text{ cm}^{-3}$, while one ion per pulse will be collected at a density of $\approx 10^8 \text{ cm}^{-3}$. In the Doppler-free case the sensitivity will be approximately 100 times higher. Focusing a laser with the assumed characteristics will increase the fluorescence signal by an additional factor of ≈ 50 , with the optimum focal length determined by the competition between fluorescence and excited-state photoionization.

We have carried out the first absolute measurement of a bound-bound atomic two-photon cross section using a single-frequency laser, and have obtained good agreement with *ab initio* calculation. In doing so, we have shown that a single-frequency laser source can lead to significant improvements in the accuracy of quantitative nonlinear optical experiments. Uncertainties about photon statistics, which have plagued this area of research from the beginning,^{1,2} can now be eliminated.

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