MIXED-HARMONICS Nd LASER PHOTOIONIZATION OF TRYPTOPHAN

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We report on the use of mixed harmonics (265 + 353 nm, or 265 + 529 nm) of an Nd^{3+}-doped glass laser to produce two-photon photochemical reactions. The lifetime of the intermediary state involved in the two-photon process was investigated by splitting the mixed-wavelength laser pulses into double pulses, each of a single wavelength, delayed one with respect to the other by varying periods of time.

This method was applied to determine the pathway of two-photon ionization of tryptophan (Trp) in aqueous solution. Previous studies, reported in the literature, have shown that Trp is photoionized on laser irradiation at 265 nm, as revealed by detection of hydrated electron absorption; the reaction is thought to be partly monophotonic and partly biphotonic. The nature of the intermediary involved in the two-photon process has not been determined.

We have found that the photoionization yield of Trp increases when the mixed 265 and 353 nm harmonics were used for excitation as compared with that obtained with 265 nm irradiation alone, at equal energy of the lower-wavelength irradiation. The same effect was observed using the mixed 265 and 529 nm harmonics. This result directly demonstrates the occurrence of two-photon ionization as light of 353 or 529 nm is not absorbed by ground-state Trp. Possible intermediates in this reaction are the excited singlet state and the triplet state. To determine the pathway of the two-photon process, a double pulse experiment was undertaken with a delay of $\sim$30 ns between a first pulse of 265 nm wavelength and a second of wavelength 353 or 529 nm. The laser pulse duration was in these runs $\sim$10 ns. The delay between the pulses then is long enough to allow the excited singlet state (lifetime $\sim$3ns) to decay between the two pulses while the triplet (lifetime >10 μs) would remain at constant concentration. The Figure shows a typical oscilloscope trace of the double-pulse experiment, representing the variation in light transmission at 650 nm of a Trp solu-

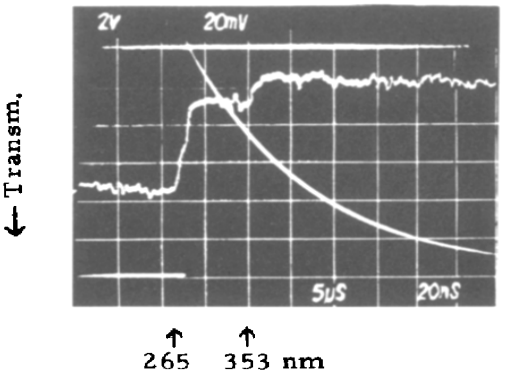

Figure. Oscilloscope trace showing light transmission decrease at 650 nm after two-wavelength double-pulse excitation of Trp (20 ns/div.).

tion due to the formation of hydrated electrons after excitation by a 265 nm pulse followed by one at 353 nm. The decrease in transmission produced by the delayed 353 nm pulse must be due to photoionization of the triplet state populated by the 265 nm pulse. When the same experiment was performed using successive 265 and 529 nm pulses, no increase in absorption was obtained at the arrival of the second pulse, as is expected since the triplet does not absorb at 529 nm. The photoionization produced on mixing the 265 and 529 nm radiation, reported above, thus obviously proceeds by excitation of the excited singlet state at 529 nm.

The pathway of the two-photon ionization produced by excitation at 265 nm alone was studied by varying the laser pulse energy at two different pulse durations: 1.5 and 30 ns fwhm, respectively. Log-log plots of the yield of hydrated electron vs. laser energy gave straight lines with slope 1.6 for the short pulse and 1.3 for the long pulse, confirming the occurrence of partial two-photon ionization. (In this representation, a one-photon reaction should give slope 1.) The higher slope at the shorter pulse duration indicates that at least part of the photoionization proceeds via the excited singlet state absorbing a second photon. A more detailed calculation based on the respective pulse shapes and excited singlet and triplet lifetimes showed that the two-photon ionization of Trp at 265 nm occurs predominantly via the excited singlet state.