the C=C stretch band and also a small downshift of the C–$C_{phenyl}$ stretch in the unrelaxed species. It is found in the present study that these changes are very similar to those observed when the solvent is changed from hexane to acetonitrile. In fact, the difference spectrum in Fig. 1(E) is almost identical to the high-power spectrum in acetonitrile! This new observation suggests the existence of two distinct forms of $S_1$ trans-stilbene in hexane, form A and form B. Form A is the unrelaxed species in hexane which gives rise to the difference spectrum in Fig. 1(E), while the relaxed species form B gives the spectrum in Fig. 1(B). The resemblance of the spectra then leads to the conclusion that a species identical to or very similar to form A exists in acetonitrile. The photoexcitation at 266 nm produces form A in hexane, which relaxes to form B in a picosecond time scale. Therefore, a mixture of forms A and B is observed in the high-power spectrum (effective time resolution ~ 10 ps), whereas only form B is observable in the low-power spectrum ( ~ 100 ps). The spectral changes with increasing the laser power are ascribed to the increasing contributions from form A, which has lower frequencies both for the C=C and C–$C_{phenyl}$ stretches and

thereby causes apparent asymmetric broadenings characteristic to these two bands. In acetonitrile, $S_1$ species similar to form A is produced by the photoexcitation and exists as it is. Therefore, no spectral changes due to optical depletion result.

It is noted finally that the scheme of optical depletion timing is expected to be effective in a variety of pump–probe double pulse experiments including not only Raman but also absorption, fluorescence, and ionization spectroscopy and thus provides us with a practical means to study picosecond phenomena by nanosecond spectroscopic measurements. In fact, a confirmation in fluorescence spectroscopy was recently given for $S_1$ trans-stilbene in a supersonic jet.[3]

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# State-selective detection of CO using a tunable ArF excimer laser

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Several years ago Bokor, Zavelovich, and Rhodes reported on the isotopically selective multiphoton UV photolysis of CO.[1] They used a tunable ArF laser with a large bandwidth (15–30 $cm^{-1}$) to dissociate CO molecules in a multiphoton process. They concluded that C atoms are formed in the metastable 2 $^1D$ state, and are excited further by the same ArF laser to the 3 $^1P$ state. Subsequent $C(3\ ^1P) \rightarrow C(2\ ^1S)$ emission at 247.8 nm was detected. When they tuned the ArF laser over its gain profile a single broad peak centered around the electronic 3 $^1P \leftarrow 2\ ^1D$ transition in the C atom was found, and no further structure was observed.

We will show below that the "single" peak Bokor *et al.* observed, is not due to the power-broadened C atom transition as they suggested,[1] but is just the envelope of the rotational lines in the spin-forbidden $a\ ^3\Pi$, $v' = 2 \leftarrow X\ ^1\Sigma^+$, $v'' = 0$ one-photon transition. Using a tunable ArF excimer laser (Lambda Physik EMG 160 MSC) with a much narrower bandwidth of 0.5 $cm^{-1}$, we were able to resolve single rotational transitions. Rotational states from $J = 6$ till $J = 26$ in the electronic and vibrational ground state of the CO molecule can be probed within the tuning range of this laser. To obtain the spectrum shown in Fig. 1 we irradiated a continuously flowing gas sample at a pressure of typically 10

Torr with the focused 30 mJ output of the narrowband ArF laser. The C-atom emission was collected from a region a few cm away from the focal point. The C-atom fluorescence is the only feature observed in emission under our experimental conditions. The fluorescence was passed through a spectrometer set at 247.8 nm, and imaged onto a PMT. The spectral energy density in the fluorescence detection region was typically 0.2 $GW/cm^2$ $cm^{-1}$, by which the spin-forbidden one-photon transition is still not saturated.[2] Nevertheless it is estimated from known electronic transition strengths[2] that as much as 10% of the molecules in a given quantum state are excited to the $a\ ^3\Pi$, $v' = 2$ state at this laser power. The C-atom fluorescence intensity decreased linearly with CO pressure and pressures as low as 0.1 Torr were detected with the present setup. Much lower pressures can be detected when higher laser powers and improved fluorescence collection optics are used.

Below the experimental spectrum, the simulated $a\ ^3\Pi$, $v' = 2 \leftarrow X\ ^1\Sigma^+$, $v'' = 0$ spectrum is given. The frequencies of the different rotational transitions are taken directly from Ref. 3. The line intensities are calculated under the assumption of a 300 K thermal population distribution in the $X\ ^1\Sigma^+$, $v'' = 0$ state. Hönl–London factors are calculated assuming that the spin-forbidden transition becomes al-
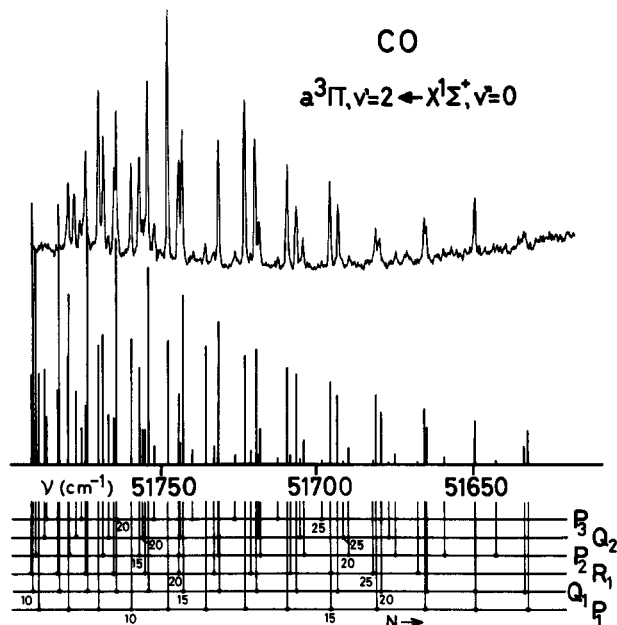
FIG. 1. Observed C($3\,^1P$) → C($2\,^1S$) fluorescence as a function of frequency after three-photon excitation of CO with a tunable ArF excimer laser. The simulated spectrum (lower part) indicates unambiguously that the observed resonances are due to the spin-forbidden $a\,^3\Pi$, $v' = 2 \leftarrow X\,^1\Sigma^+$, $v'' = 0$ one-photon transition of CO. The linewidth of 0.5 cm$^{-1}$ is determined by the laser.

lowed by spin–orbit mixing of the $A\,^1\Pi$ state with the $a\,^3\Pi$ state, as discussed in detail by James.[2] The deviation between observed and calculated line intensities can be completely explained by the variation of the ArF laser power over its gain profile together with the strong power dependence of the C-atom emission. Furthermore, the decrease in laser power when the ArF laser is attenuated by ambient absorption of $O_2(B\,^3\Sigma_u^-$, $v' = 4 \leftarrow X\,^3\Sigma_g^-$, $v'' = 0)$[4] is seen reflected in the CO spectrum.

Although at least three ArF laser photons are needed to reach the C($3\,^1P$) state from which the fluorescence is detected, it is clear from the experimental spectrum that the spectral structure is completely determined by the resonant enhancement in the first one-photon step in the CO molecule. Nevertheless the production of C($3\,^1P$) atoms can proceed via two pathways:

(i) The CO($a\,^3\Pi$, $v' = 2$) molecules absorb *one* additional ArF laser photon and end up in a dissociative continuum with triplet character, via which C($2\,^1D$) and ground state O($^3P$) atoms are produced.[5] The C($2\,^1D$) atoms are excited further to the C($3\,^1P$) state. This latter transition in the C atom is very strong,[6] and will be completely saturated by the small fraction of unlocked, i.e., broad band, ArF laser radiation.

(ii) The CO($a\,^3\Pi$, $v' = 2$) molecules absorb *two* additional ArF laser photons, and C($3\,^1P$) and ground state O($^3P$) atoms are directly produced via a dissociative continuum with triplet character. In this case the accidental coincidence of the C atom transition within the ArF laser gain profile is not important.

To be able to distinguish between these two processes, the power dependence of the C-atom emission was mea-

sured. For process (i) a quadratic power dependence is expected, whereas in process (ii) none of the photon steps will be saturated which results in an expected cubic power dependence. We observed a cubic power dependence (in contrast to earlier work[1,7]) which suggests a three-photon process in the CO molecule [process (ii)].

In a separate experiment, to check if it is possible to determine CO density fields using planar LIF,[8] we illuminated a thin sheet of approximately 2 cm high and 1 mm thick. Fluorescence from separated regions could be easily observed, which makes a two-dimensional mapping of CO concentrations in specific rotational states possible.

The above results demonstrate that CO molecules can be state-selectively detected using a tunable ArF laser. In the gain profile of this laser many well tabulated[3] rotational transitions in the Cameron band system of CO can be induced. Therefore this spectrum is also perfectly suited for wavelength calibration, and to determine the laser linewidth. Preparation of state selected metastable CO is another interesting possibility for the study of state selected chemical reactions. It is also clear that this narrowband laser is much better suited for isotope selected photodissociation of CO than the "broad-band" laser used by Bokor *et al.*[1]

An alternative method to detect CO molecules is to induce the $B\,^1\Sigma^+$, $v' = 0 \leftarrow X\,^1\Sigma^+$, $v'' = 0$ two-photon transition around 230.1 nm and detecting the resulting $B\,^1\Sigma^+$, $v' = 0 \rightarrow A\,^1\Pi$, $v$ ($v = 0-7$) visible fluorescence.[9] We excited this transition using the second Stokes of the tunable ArF laser (Raman shifted in approximately 10 bar $H_2$). The noise free excitation spectrum measured at 10 Torr consisted of many overlapping rotational $Q$ lines falling in the corresponding tuning range. This demonstrates once more that a large number of molecules can be state-selectively excited within the narrow tuning range of the excimer lasers,[4,10-14] which makes these lasers an important tool in, for instance, combustion analysis.

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