PICOSECOND CARS AS A PROBE OF THE MULTIPHOTON PHOTOFRAGMENTATION OF BENZENE

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Picosecond laser pulses have been used to photofragment benzene and to detect the C_2 fragment by a CARS probe technique The C_2 fragment, generated by a UV multiphoton excitation process, is found to appear extremely rapidly, i e , within the laser excitation pulse width, <25 ps

1. Introduction

In addition to transient electronic absorption and emission methods, the use of non-linear Raman scattering [1—3], and in particular coherent anti-Stokes Raman scattering (CARS) [4—8], is becoming increasingly important in the investigation of molecular phenomena In the present work we have used picosecond CARS to study time-dependent phenomena and specifically to observe short-lived chemical species and excited-state molecules. A principal objective of this work is to investigate the species produced in the initial steps of laser-induced UV photofragmentation of molecules. We were aided in this study by the successful work of others in applying CARS to the observation of transient species generated in the photolysis of benzene on the nanosecond time scale [9].

In the CARS technique [4—7] input light at the frequencies ω_1 and ω_2 are coupled by their interactions with the molecules present in the system to produce a new frequency, ω_3. The beam at ω_3, called the anti-Stokes light, is energetically related to the input light at ω_1 and ω_2 by $\omega_3 = 2\omega_1 - \omega_2 = \omega_1 + (\omega_1 - \omega_2)$. A large signal is obtained at ω_3 when the frequency mismatch $\Delta = \omega_1 - \omega_2$ corresponds to a Raman active transition of the system [†]. To observe

the Raman resonances of the molecular species, one of the input frequencies is tuned across the spectral range of interest while the other input frequency is held fixed. One approach to achieving tunability is to use dye lasers. We have employed a different method, namely optical parametric generation and amplification, to achieve picosecond pulses which are continuously tunable across the visible spectrum from 420 to 730 nm. With this tunability we have initiated studies using picosecond CARS to probe the excited states and fragments resulting from the UV (266.0 nm) photolysis of gas-phase benzene.

2. Experimental

The experimental apparatus, shown schematically in fig. 1, is based on a passively mode-locked Nd YAG laser. A single pulse, fwhm $\leqslant$ 25 ps, from the mode-locked pulse train is twice frequency doubled to generate pulses at 532.0 nm and 266 0 nm. These collinear green and ultraviolet pulses pass through an optical parametric amplifier, OPA, that consists of two temperature-tuned ADP crystals [10]. Acting as the pump pulse, the 266.0 nm pulse is split into two tunable visible pulses in the range of 420—730 nm.

The CARS experiment is performed using the red OPA pulse as the Stokes pulse, ω_2, and the 532.0 nm pulse as ω_1. All other pulses are blocked by a filter. To ensure that the probe and excitation pulses overlap

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[†] Strong signals at ω_3 can also result from one- and two-photon electronic resonances not associated with vibrational Raman resonances
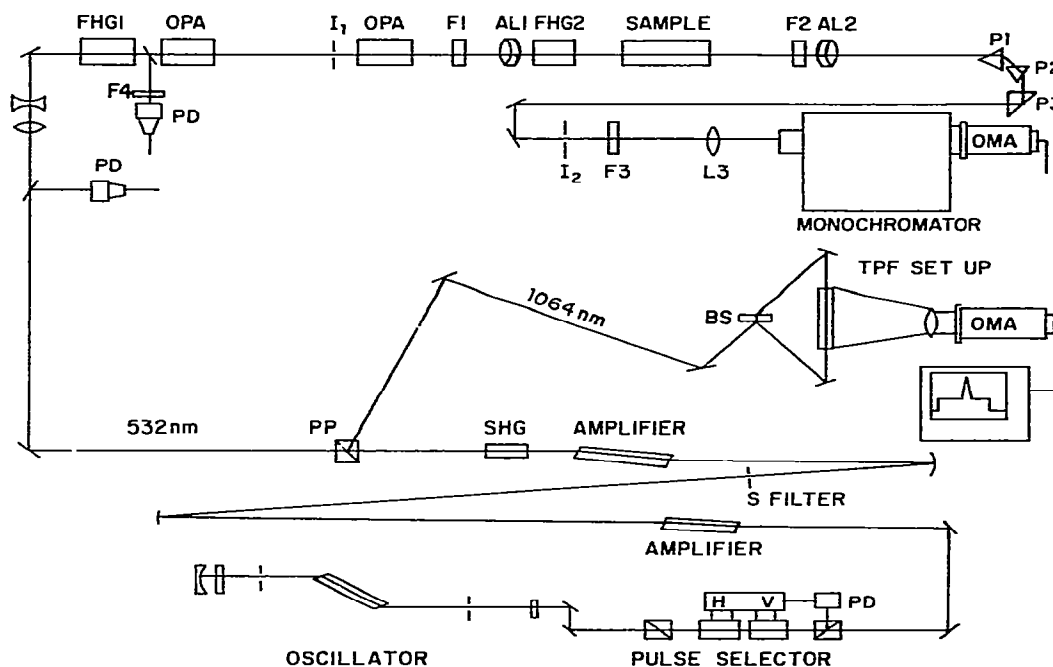
Fig. 1. Picosecond CARS and photolysis apparatus consisting of a mode-locked Nd-YAG laser system with second harmonic (SHG), fourth harmonic (FHG1, FHG2), and optical parametric amplifier (OPA) components. Other components include filters (1—F4), achromatic lenses (AL1, AL2), and two-photon fluorescence (TPF) apparatus.

in space and time, we use a second ADP crystal immediately before the sample to generate the 266.0 nm excitation pulse. The pulses are focused with a 0.5 m achromatic lens into a 20 cm suprasil gas cell filled with benzene vapor at 80 Torr. The pulse energies entering the sample cell are <0.2 mJ at 532.0 nm, ≈5 μJ in the Stokes pulse (OPA), and ≈40 μJ at 266.0 nm. The generated anti-Stokes pulse is collimated, dispersed, and focused into a $\frac{1}{4}$ m Jarrell—Ash monochromator with multichannel detector. The signals obtained are rated as strong, medium, weak, or no signal on the basis of an average over many laser shots to minimize the effects of energy fluctuations in the excitation and probe beams.

3. Results and discussion

In the absence of the 266.0 nm excitation pulse, a strong CARS signal at ω_3 was obtained on tuning the energy mismatch, $\omega_1 - \omega_2$, of the probe beams to 3070 cm^{-1}. This signal is due to the ν_1 totally symmetric C—H stretch of benzene in its ground electronic state. No CARS signals were obtained on tuning $\omega_1 - \omega_2$ from 2800 cm^{-1} to 3070 cm^{-1}; a region which becomes Raman active on photolysis, as we shall discuss later. For a similar reason an energy shift of 3130 cm^{-1} was also probed and no CARS signal was detected. This latter energy corresponds to a vibrational resonance in the first excited singlet state of benzene. The absence of CARS signals at these various energies, with the 266.0 nm excitation blocked, indicates that the probe beams at ω_1 and ω_2 are not strong enough to excite or fragment ground-state benzene by a multiphoton absorption process. It is also to be noted that the cross section for one-photon absorption by ground-state benzene is very small at 266 0 nm since this wavelength is on the low-energy tail of the $A_{1g} \to B_{2u}$ absorption and furthermore does not even coincide with hot-band absorption.

In the presence of the 266.0 nm photolysis pulse, we have carried out CARS experiments at more than ten separate anti-Stokes shifts in the energy range from 2800 cm^{-1} to 3130 cm^{-1}. In all of these experiments

Table 1

Picosecond CARS signals from a gas-phase benzene sample at 25°C, in the presence and absence of a UV photolysis pulse

Anti-Stokes shift (cm⁻¹) $\Delta = \omega_1 - \omega_2$	Relative signal strength [a]	
	with photolysis pulse (266.0 nm)	no photolysis pulse
2800–2850	vw	ns
2854	w	ns
2868	m	ns
2875	m	ns
2888	m	ns
2967	s	ns
3007	s	ns
3014	m	ns
3070	w	m
3130	w	ns

[a] s = strong, m = medium, w = weak, vw = very weak, ns = no signal.

the excitation and probe pulses overlapped both in time and space. A general characteristic of our results was the appearance of the strongest CARS signals in the region of 2870–3015 cm⁻¹ with a fairly rapid decline on the low- and high-energy sides, table 1. An example of the CARS data obtained from only one firing of the laser is shown in fig. 2. The two signals shown are the anti-Stokes signal, ω_3 = 459.5 nm corresponding to a shift of 2967 cm⁻¹, and a mercury source reference signal at 435.8 nm. All of the signals observed in these experiments are attributed to a CARS process rather than processes such as fluorescence from excited-state benzene, fluorescence from excited-state fragments, or stimulated Raman scattering. In support of this we note that the signals obtained in the presence of the 266.0 nm pulse required both the 532.0 nm and Stokes pulses, if one of the probe pulses was absent, no signal was obtained. The possibility of the signals being due to a fluorescence arising from a combination of the 266.0 nm and ω_1 and ω_2 pulses is un-
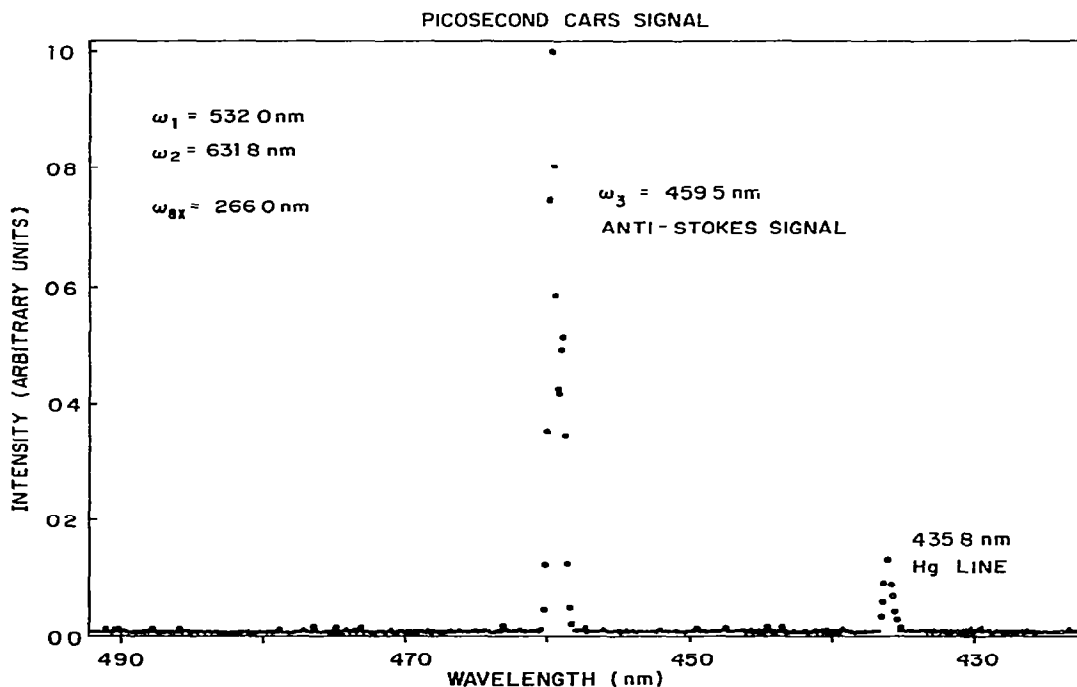
PICOSECOND CARS SIGNAL

Fig. 2. A picosecond CARS signal at $\omega_1 - \omega_2$ = 2967 cm⁻¹ resulting from a single firing of the laser photolysis and probe pulses into benzene at 80 Torr.

likely, since the observed signals appeared only at ω_3 = $2\omega_1 - \omega_2$ and at no other frequencies. This can be seen in fig. 2. This absence of signals at frequencies other than the CARS signal, ω_3, was found to be the case for all values of ω_2 employed.

Although a CARS signal was observed at the energy position (3130 cm^{-1}) which corresponds to the ν_1 carbon—hydrogen stretch in the excited $^1B_{2u}$ state of benzene, it is to be noted that it was weak, table 1. We therefore find no evidence for a large excited benzene population.

To interpret the CARS signals observed, let us consider the effects of the laser radiation on the gas-phase molecules comprising our system. It has been shown that the intense fields of nanosecond and picosecond lasers induce by a multiphoton absorption an extensive ionization and fragmentation of gas-phase molecules [9,11—15]. The particular-ion fragments of benzene photolysis extending from C_1^- to $C_6H_6^+$ have been identified using mass spectrometry [11,12]. The generation of excited neutral fragments in the photolysis of benzene and other organic molecules has been established by fluorescence measurements [9,13,14]. Of particular importance is the C_2 fragment, in its ground and excited states, which has been shown to be largely responsible for the nanosecond CARS signals in the 2800—3100 cm^{-1} energy region [9]. The picosecond experiments, carried out under similar excitation and probe conditions (the same excitation and probe wavelengths) as the nanosecond experiments, yielded CARS signals in the same energy region (2800—3100 cm^{-1}) having similar relative strengths. We therefore conclude that the same fragments are responsible for the signals observed in both experiments. The present work thus demonstrates that small fragments, in particular C_2, are produced within the excitation pulse width (25 ps). Further work is necessary to determine the full kinetic curve for the formation of C_2.

What then is the pathway, or pathways, for production of C_2 in 25 ps? A possible first step, which has been shown to be important in the production of ion fragments, is the two-photon ionization of benzene yielding the $C_6H_6^+$ fragment [12]. This ion in turn absorbs light and dissociates to yield the observed smaller ion fragments. It is possible that the C_2 fragment is also produced from the $C_6H_6^+$ precursor; the most direct pathway being,

$$C_6H_6^+ + nh\nu \rightarrow C_4H_6^+ + C_2^* \,,$$
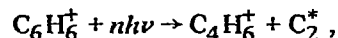
where C_2^* is the vibrationally and electronically excited C_2 fragment. We can speculate that a more likely pathway based on the observed abundance of $C_4H_4^+$ [11, 12], C_2H_2 [9], and the absence of the butadiene ion, $C_4H_6^+$ [11,12], is

$$C_6H_6^+ + mh\nu \rightarrow C_4H_4^+ + C_2H_2 \,,$$

$$C_2H_2 + m'h\nu \rightarrow C_2^* + H_2 \,.$$
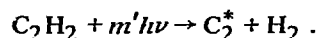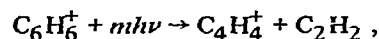
There is, of course, a direct pathway which is the sum of the two reactions above.

A mechanism for the production of neutral fragments, which is independent of the ion pathways, is a multiphoton excitation of benzene directly to a dissociative state. The competition between this mechanism and the two-photon ionization mechanism is determined by the relative rates of these two processes from the common two-photon excited level, i.e. rate of electron ejection versus the pumping rate to dissociative levels of neutral benzene. Even at the high laser intensities used in these experiments (≈ 5 GW/cm^2), the 10^{12} s^{-1} pumping rate estimated from a strong transition is not competitive with the electron ejection rate. We therefore expect that the neutral fragments are generated in these picosecond experiments from ionic precursors, e.g. $C_6H_6^+$, rather than from high dissociative levels of neutral benzene.

4. Summary

In this work we have successfully used CARS to observe molecular fragmentation on the picosecond time scale. For gas-phase benzene photofragmentation, the CARS signals, attributed to C_2, appear within the 25 ps duration of the excitation process. Currently work is underway to determine the product distribution and their ultrafast formation rates.

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