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TIME-RESOLVED IR SPECTRAL PHOTOGRAPHY*

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Summary

The non-linear optics basis and experimental realization of time-resolved IR spectral photography (TRISP), a new technique of nanosecond time-resolved IR absorption spectroscopy, are described. TRISP has been applied to the study of transients. It was used to study the time evolution of the rotational temperature of HCl during CO_2-laser-induced explosions of HN_3–HCl mixtures. In a recent experiment *tert*-butyl radicals were formed by ruby laser photolysis of $(CH_3)_3CNO$. TRISP was used to obtain the gas phase IR spectrum of the radicals in the 3 μm region. By following the decay of this transient IR absorption, the rate coefficients for the combination and disproportionation reactions between *tert*-butyl radicals were deduced.

1. Introduction

Time-resolved spectroscopy techniques are used extensively to probe the dynamics of chemical reactions to provide information regarding the distribution of energy among internal states of reaction products and to obtain the structures and energy levels of transient chemical intermediates. Vibrational spectroscopy in particular is an indispensable technique for "fingerprinting" molecular structures. Furthermore, unlike techniques of electronic spectroscopy, IR or Raman techniques allow the determination of vibrational and rotational populations of product molecules with only a knowledge of ground state properties. It is highly desirable, therefore, to be able to record transient broad-band IR absorption spectra.

At IBM we have developed a non-linear optical technique for taking single-shot time-resolved IR absorption spectra (time-resolved IR spectral photography (TRISP)) [1]. Spectral regions of the order of 1000 cm^{-1} can be covered at each shot with a spectral resolution better than 0.5 cm^{-1} and a time resolution of about 10 ns. TRISP has already been applied to a study of the transient rotational temperatures of exploding HN_3–HCl mixtures [1].

Here we first describe the optical principles on which TRISP is based (for experimental details see ref. 1). Then we present an application of TRISP to the

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study of chemical transients. *Tert*-butyl radicals were produced by ruby laser photolysis of $(CH_3)_3CNO$. The transient $(CH_3)_3C\cdot$ gas phase spectrum in the range near 3 μm was observed and the decay was utilized to deduce bimolecular reaction rates.

2. The basis of time-resolved IR spectral photography

TRISP is accomplished by (1) generating a short pulse of collimated broad-band IR radiation, (2) passing the IR radiation through a sample so that the emerging beam has its spectral envelope modulated by the sample absorption and (3) up-converting the IR radiation to give a visible light pulse whose spectral envelope is proportional to the IR spectral envelope. The up-converted spectrum is recorded photographically or through the use of an optical multichannel analyzer.

The non-linear optical processes involved are shown in Fig. 1. Figure 1(a) is a schematic level diagram for rubidium atoms, with the stimulated electronic Raman scattering (SERS) process responsible for the IR generation indicated by the arrows. When the SERS threshold is exceeded, broad-band visible continuum light ν_C from a broad-band dye laser is absorbed and simultaneously broad-band IR (Stokes) radiation ν_{IR} is emitted. For each visible frequency there is produced a corresponding IR frequency shifted by $\Delta\nu_R$, the frequency associated with the 5s–6s transition. Thus, the broad-band visible spectrum is transformed to an IR spectrum with essentially the same spectral bandwidth.

The up-conversion process is shown in Fig. 1(b). In this process a narrow-band laser (with frequency ν_L) drives the SERS in a second rubidium vapor cell, generating a narrow-band Stokes IR beam (with frequency ν_S). This stimulated scattering process produces an electronic oscillation of the atoms at frequency $\Delta\nu_R = \nu_L - \nu_S$. The incoming IR continuum, imprinted with the sample absorptions, is scattered by this electronic oscillation and for each IR frequency ν_{IR} an

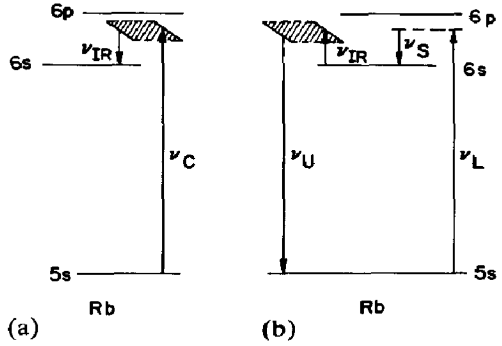

Fig. 1. Level diagrams for the SERS IR generation and four-wave parametric up-conversion processes in rubidium vapor: (a) Raman cell; (b) up-conversion cell; ν_C and ν_{IR}, broad-band visible and IR continua; ν_L and ν_S, broad-band visible laser and its Raman Stokes IR beam; ν_U, up-converted visible beam.

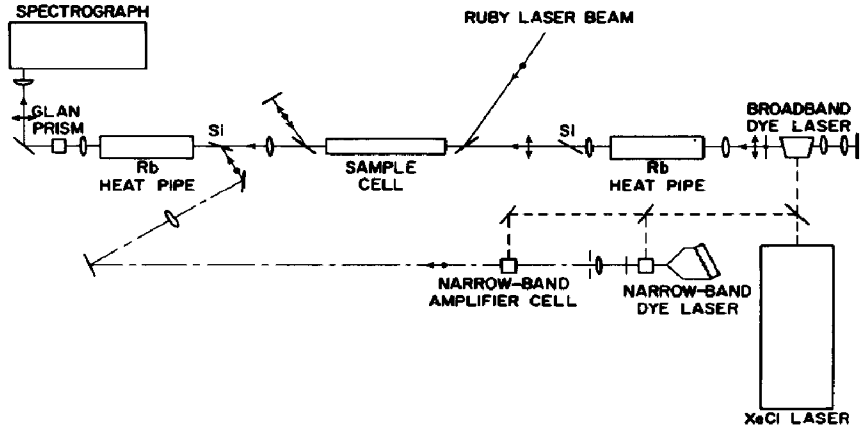

Fig. 2. The experimental set-up.

up-converted frequency $\nu_U = \Delta\nu_R + \nu_{IR}$ appears. The intensity at ν_U is proportional to the intensity at ν_{IR}, *i.e.* the up-converted spectrum is linearly proportional to the IR spectrum. The actual experimental arrangement for the study of *tert*-butyl radicals is shown in Fig. 2.

3. Time-resolved IR spectral photography study of *tert*-butyl radicals

The vibrational spectroscopy of matrix-isolated free radicals has long been a very active research area [2 - 4]. However, gas phase IR spectroscopy of radicals has the obvious advantages of giving spectra free of matrix perturbations, permitting the observation of rotational structure (if it is resolvable) and, of more importance, allowing the time-resolved study of collisional processes, *e.g.* bimolecular reactions involving these reactive species.

Among the hydrocarbon radicals, the *tert*-butyl radical has received considerable attention. The IR spectrum of matrix-isolated *tert*-butyl radicals has recently been obtained [5]. In the region near 3 μm this spectrum is dominated by a single intense band at 2825 cm^{-1}, which has been shown [5] to be a characteristic feature for a weak β CH bond *trans* to the unpaired electron. The bimolecular reactions of the *tert*-butyl radicals, namely (a) the combination reaction in which the dimer of the radical is formed according to $R\cdot + R\cdot \rightarrow R_2$ and (b) disproportionation in which a hydrogen atom is transferred from one radical to the other, giving a saturated molecule RH and an olefin R(–H), *i.e.* $R\cdot + R\cdot \rightarrow RH + R(-H)$, have been a subject of study for the past 20 years [6 - 10]. Most of the methods applied to obtain the combination rate constant k_c were indirect and the range of the deduced rate constants spans more than three orders of magnitude.

In our study we produced high densities (approximately 10^{17} cm^{-3}) of *tert*-butyl radicals by irradiation of monomeric 2-methyl-2-nitrosopropane gas

$(CH_3)_3CNO$ with a Q-switched ruby laser (694 nm; power, approximately 1 J cm^{-2}) with a pulse duration of about 25 ns.

3.1. The IR spectrum of the tert-butyl radical

In Fig. 3(a) we show the optical thickness αl in the region near 3 μm for 975 Torr cm (p = 15 Torr; l = 65 cm) of $(CH_3)_3CNO$. The main peak occurs at about 2980 cm^{-1}, with lesser peaks at about 2945, 2880 and 3090 cm^{-1}.

The prompt appearance of a prominent new component in the IR spectrum after the ruby photolysis pulse is seen in Fig. 3(b). For Fig. 3(b) the TRISP probe was set to occur at the peak of the ruby pulse. The new component has its main peak at 2833 ± 4 cm^{-1} and there is a hint in Fig. 3(b) of a much weaker side band at about 2750 cm^{-1}. The new peak at 2833 cm^{-1} was observed to decay immediately, and after a few microseconds (Fig. 3(c)) it had completely gone.

All these features of the observed transient spectrum (its frequency, its prompt appearance and its rapid decay) can only be accounted for by assuming that it represents, indeed, the *tert*-butyl radical.

3.2. Decay kinetics of the tert-butyl radicals

By varying the time delay between the ruby and TRISP probe pulses and measuring the resulting optical thickness at 2833 cm^{-1}, the decay of the transient spectrum was followed. Such a decay curve is shown in Fig. 4. The data were fitted to a bimolecular decay law, *i.e.* $dn/dt = -2k_r n^2$ where n is the free-radical concentration. The initial radical concentration $n_0(x)$ is not uniform along the axis of the sample cell (the sample is not optically thin). Taking this into account, the following expression for the optical thickness can be derived [11]:

$$\alpha_{\text{eff}} l = \frac{\sigma_r}{\sigma_p}\frac{1}{1+\tau}\ln\left\{\frac{1+S(1+\tau)}{1+S(1+\tau)\exp(-\alpha_p l)}\right\} \qquad (1)$$

where σ_r is the radical absorption cross section, σ_p is the parent absorption coefficient ($\alpha_p = n_p\sigma_p$), τ is a scaled time equal to $2n_p k_r t$ and $S = \exp(\varphi_0\sigma_p) - 1$ (φ_0 is the laser fluence at the cell entrance window).

The optical thickness data of Fig. 4 were fitted to eqn. (1) by using carefully measured values of φ_0 and σ_p and adjusting σ_r and k_r to achieve a least-squares best fit. Thus the values $\sigma_r = 3.95 \times 10^{-19}$ cm^2 and $k_r = 3.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} ($10^{10.26}$ l mol^{-1} s^{-1}) were obtained. The value $k_r = 10^{10.26}$ l mol^{-1} s^{-1} represents the sum of combination (k_c) and disproportionation (k_d) rate coefficients. To determine the relative rates of these two reaction pathways, a gas chromatography–mass spectrometry analysis of the products generated by the ruby photolysis was performed [11]. From the ratio of isobutane (or isobutene) to 2,2,3,3-tetramethylbutane, the ratio k_d/k_c was found to be 2.9 ± 0.2. This ratio is similar to other recently published values. We therefore conclude that the combination and disproportionation rate coefficients are $k_c = 10^{9.67 \pm 0.05}$ l mol^{-1} s^{-1} and $k_d = 10^{10.13 \pm 0.05}$ l mol^{-1} s^{-1}.Our results indicate that the value of k_c is much higher than that deduced in some of the earlier studies [7, 8] and is closer to the most recent k_c value ($10^{9.3}$ l mol^{-1} s^{-1}) deduced by the more direct technique of molecular modulation spectroscopy [10].

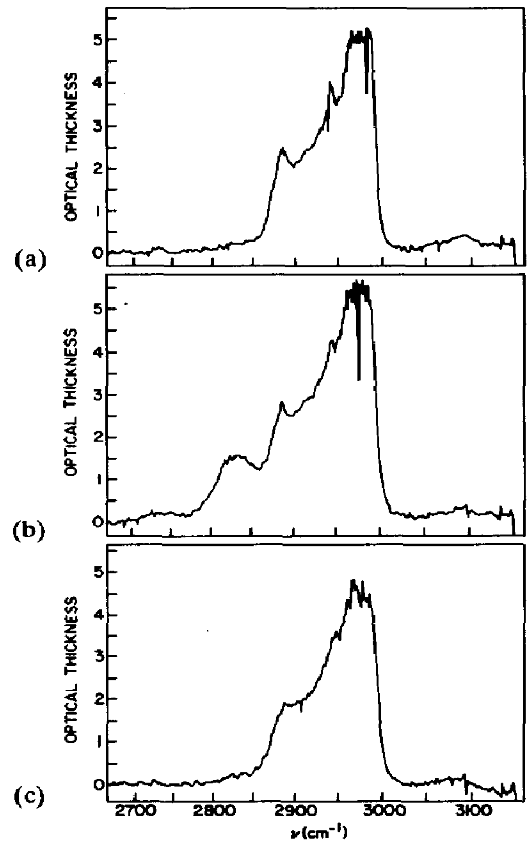

Fig. 3. Optical thickness *vs.* wavenumber for 975 Torr cm (p = 15 Torr; l = 65 cm) of $(CH_3)_3CNO$: (a) before the ruby pulse; (b) at the peak of the ruby pulse; (c) 4.8 μs after the ruby pulse. The very sharp negative spikes are electronic artifacts in the OMA.

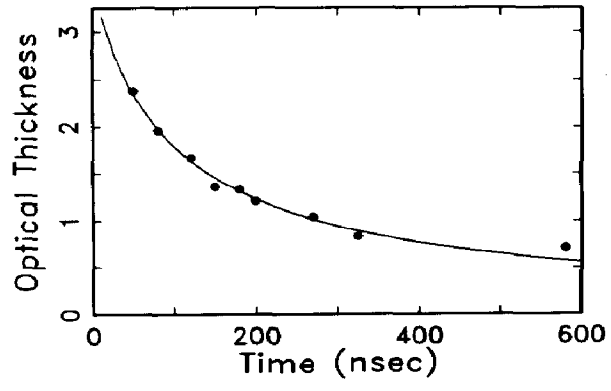

Fig. 4. The measured decay of the *tert*-butyl radical population at a parent pressure of 30 Torr. The optical thickness at 2833 cm^{-1} is plotted vertically. Time is measured from the peak of the ruby photolysis pulse. The curves are best fits of the data points to eqn. (1).

4. Future directions

We are currently working to extend the spectral range of TRISP eventually to cover the entire fingerprint region of the IR. To achieve this we have increased the power of our XeCl pump laser and have switched to UV dyes in the broadband dye laser. In this way we have already observed SERS and up-conversion in the 5.7 - 8.5 μm region. We are particularly interested in the 9 and 10 μm regions which are of great importance in the field of CO_2-laser-induced multiphoton vibrational photochemistry. We hope that TRISP will provide valuable information regarding the photophysical processes (*e.g.* rotational hole burning and rotational redistribution, red shifting of vibrational absorption etc.) occurring during the vibrational up-pumping process. In addition, we plan to continue the work we have just started on the spectra and reaction kinetics of reactive species.

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