Infrared diode laser probing of methane in excimer laser photolysis of pyruvic acid

SISIR K SARKAR, JAI P MITTAL[1]* and GEORGE W FLYNN[2]

[1] Bhabha Atomic Research Centre, Bombay 400085, India
[2] Department of Chemistry, Columbia University, New York 10027, USA

Abstract. The photodissociation of pyruvic acid at 193 nm has been studied and one of the photoproducts, methane, was detected using an infrared diode laser absorption probe technique. Using second-derivative absorption spectroscopy at $1346 \cdot 326\,cm^{-1}$ $[R^{(-)}(7)$ transition in v_4 band], the progress of the reaction was monitored. The quantum yield of formation of methane $= 0 \cdot 09 \pm 0 \cdot 01$ and was further corroborated by a simple measurement of pressure changes following the photolysis. The secondary photolysis of the photoproduct acetaldehyde via the established route was found to be negligible. This result may help to account for the energetics of the photodissociation process by a $6 \cdot 4\,eV$ excimer laser photon. The possibility of using this technique to examine the nascent methane molecule in real-time domain to gain better insight of the dissociation dynamics is also indicated.

Keywords. Diode laser; absorption spectroscopy; photodissociation.

1. Introduction

The traditional way of studying a chemical reaction relies on monitoring the changes in concentration of reactive species. The result of such analysis can be used to infer the details of the processes. Vibrational spectroscopy, in particular infrared spectroscopy, provides reliable fingerprints of specific molecular identity. Therefore, high resolution IR spectroscopy in conjunction with kinetic studies, has afforded remarkable insight into reaction dynamics. Conventional IR spectroscopy is rather poor in sensitivity, primarily because of weak light sources. Similarly emission in IR is also weak and thus IR fluorescence is not very promising, specially in terms of spectral resolution required to obtain state-specific information. However, a revolutionary change has been brought about after the introduction of the IR laser, specially the diode laser with its high resolution ($0 \cdot 003\,cm^{-1}$) and tunability (3–$30\,\mu m$). In IR laser absorption spectroscopy, one can conveniently measure a fractional absorption of 10^{-3} with a typical $1\,mW$ diode laser and cooled IR detectors. Therefore, in recent times, the diode laser probe has been used widely in a variety of interesting processes such as photodissociation, inelastic scattering, bimolecular and surface chemical reactions (Chu *et al* 1984; Wood *et al* 1984; O'Neill *et al* 1986).

Using this technique (O'Neill *et al* 1987), the photodissociation dynamics of pyruvic acid $CH_3COCOOH$ (hereafter denoted as PA) has previously been investigated by monitoring the nascent vibrational population distribution in CO_2 photoproduct (Chu *et al* 1984; Wood *et al* 1984; O'Neill *et al* 1986). These and other previous photochemical studies (Leermakers and Versley 1963; Versley and Leermakers 1964; Arnett *et al* 1973; Rosenfeld and Weiner 1983) indicated that the route for 193 nm

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*For correspondence

excimer laser photolysis of PA is

$$CH_3COCOOH + h\nu \ (193\,nm) \longrightarrow CH_3CHO + CO_2 \ (mn^1 p, J). \tag{1}$$

However, with the very low yield ($\cong 3\%$) of excited CO_2 produced, the energetics of the process could not be satisfactorily accounted for. Therefore, various possibilities have been proposed to account for the 'missing' energy. One of these is the multiple bond breakage in PA by highly energetic 193 nm (6·4 eV) photons to produce more than two fragments i.e., CO_2, CO, CH_4 etc. Although formation of CO and CH_4 in small quantities (1–2%) has been reported during low intensity photolysis at 366 nm (Versley and Leermakers 1964), a photoproduct analysis has not been made at 193 nm.

In the present investigation, we have studied the other possible route of photo-dissociation of PA by looking at the formation of methane using the diode laser absorption technique. The quantum yield of methane formation was determined which was further corroborated by the measurement of pressure changes in the system following photolysis.

2. Experimental

Typically 0·4 Torr of PA in a 30 cm long cell was photolysed with a 30 mJ pulse delivered from an ArF excimer laser (Lambda Physik EMG 101). The formation of CH_4 was probed after photolysing for a preset number of excimer laser pulses.

The laser diode ($1300-1350\,cm^{-1}$) which spans the ν_4 absorption band of methane was contained in a Laser Analytics liquid helium-cooled closed cycle refrigerator. The laser beam after collimation ($f/2$ ZnSe lens) passed through the cell containing either the photolysed sample or methane (typically 0·1 Torr) for reference calibration. The laser light was detected after passing through a 0·5 m monochromator (to select a single laser mode and coarse wavelength setting) with a liquid nitrogen-cooled HgCdTe detector/preamplifier system (response time: 1 μs).

The diode laser frequency was coarse set by the temperature of the diode and the frequency scan over the previously assigned CH_4 absorption features was accomplished by ramping the diode current. The absorption lines were recorded and analysed by phase sensitive detection. In the second derivative mode, the laser frequency was modulated (1 kHz) by applying a low amplitude saw-tooth wave function to the diode current and the absorption signal was measured with a lock-in-amplifier set for detection at twice the modulation frequency.

The pyruvic acid (Aldrich, 98% purity) was further purified by repeated fractional distillation and final purity was checked with NMR spectroscopy. Methane (Matheson, 99·5% purity) used for calibration was thoroughly degassed by multiple freeze-pump-thaw cycles at 77 K. The pressures were measured with a capacitance manometer (MKS Baratron).

3. Calibration procedure

Methane, a tetrahedral molecule (T_d), has four fundamental vibrational modes of which two triply degenerate ν_3 and ν_4 modes are infrared active. The present diode

probed the v_4 mode whose centre originates at 1306 cm^{-1}. The rovibrational spectra of methane is quite rich and complex due to appreciable coriolis splitting among closely spaced mode v_2 (e) at 1526 cm^{-1} and v_4 (f_2) at 1306 cm^{-1} and symmetry properties of rotational levels in T_d point group. The first step in the detection of methane was the mapping of the diode laser tuning characteristics, i.e. assignments of various laser modes as a function of temperature and current range. This is conveniently accomplished by identifying characteristic absorption features of CH$_4$ contained in the cell. The frequency scale was determined using methane absorption line positions taken from the work of Botineau (1972).

A computer program LINESEAR, developed to aid in assigning diode modes by fitting the observed line positions to the tabulated spectra of various gases (AFCRL 1973) was used. To assign a diode mode, the observed diode spectra under full modulation amplitude was recorded in single mode condition. A Ge etalon (1″ thick, FSR:0·0475 cm^{-1}) was used to measure the relative frequency spacings between several lines within a mode (usually 3–5 lines were sufficient). With the help of a set of etalon fringe counts, the approximate frequency range set by the monochromator and absorption coefficients, the program searches the database for a specific pattern of lines and plots them on a plotter. With the help of this program, we characterised several modes of the diode by employing 0·1–1·0 Torr of methane in 30 cm cells. Figure 1 showed a typical mode at 1306 cm^{-1} which spans several $Q^{(0)}$ lines near the band centre, which can be compared with the upper trace from the work of Restelli and Cappellani (1979).

Various detection schemes were employed in the diode laser absorption technique. For relatively large absorptions ($\geqslant 5\%$), the most usual method was to chop the laser beam mechanically and to detect synchronously using a lock-in-amplifier, while scanning the laser through absorption features. For smaller fractional absorption, greater detection sensitivity was achieved by rapid current modulation of the diode as it scans slowly through the absorption line and synchronous detection at the fundamental (first derivative) or at first harmonic (second derivative) of the modulation frequency. These techniques had the advantage that the absorption signal was seen as a variation from an essentially zero level base line. However, the calibration and analysis of signals which were less direct is described below.

The intensity of diode laser transmitted through a gas at a pressure 'p' and pathlength 'l' is given by Beer's law,

$$I(v) = I_0(v)\exp[-\alpha(v)pl], \tag{2}$$

where $I_0(v)$ and $\alpha(v)$ are the incident intensity and the absorption coefficient of the gas at laser frequency v. In derivative spectroscopy (Olson *et al* 1980; Reid and Labrie 1981; Weitkamp 1984), the frequency v of the diode laser is scanned or modulated and the quantity d^n/dv^n[I/I_0] rather than [I/I_0] is measured. For second derivative spectroscopy ($n = 2$), it can be shown from (2) that

$$\mathrm{d}^2 I(v)/\mathrm{d}v^2 = I_0(v)lp[lp\{\mathrm{d}\alpha(v)/\mathrm{d}v\}^2 - \mathrm{d}^2\alpha(v)/\mathrm{d}v^2], \tag{3}$$

assuming modulation amplitude to be small enough to keep I_0 practically independent of frequency v. Now the absorption coefficient can be expressed as

$$\alpha(v) = Sf(v), \tag{4}$$
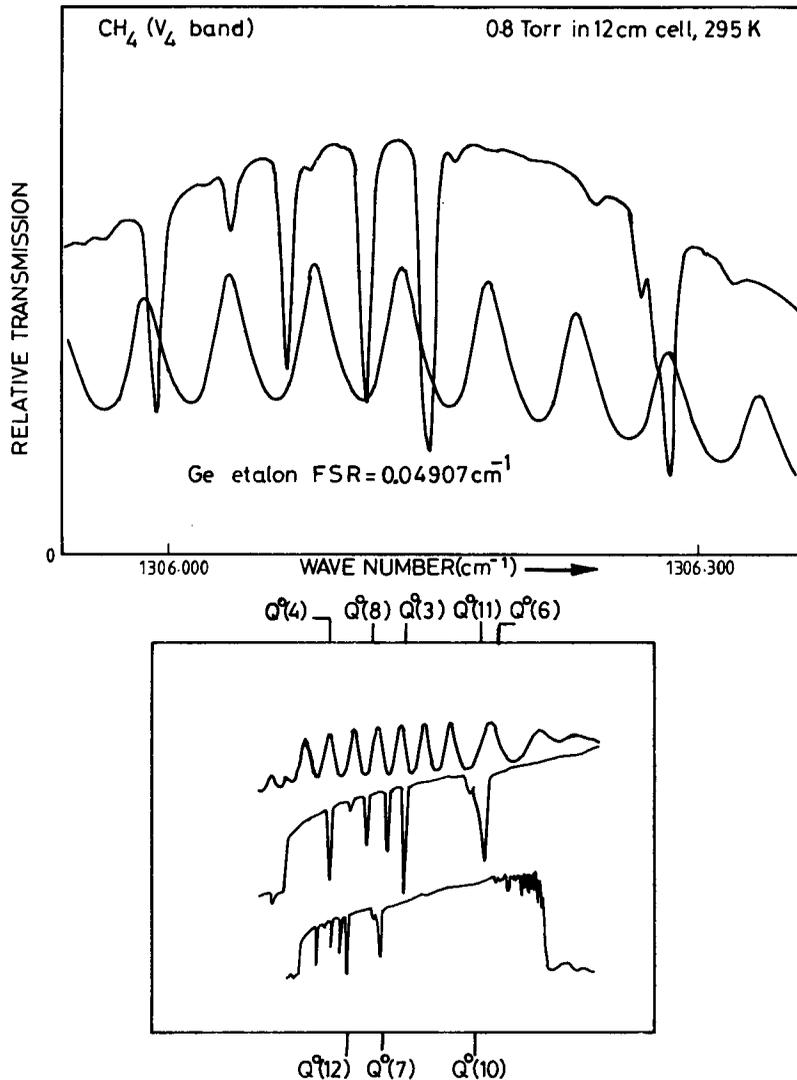
Figure 1. Typical single mode of the diode laser ($T = 80\,\text{K}, I = 0.562\,\text{A}$) scanning the band-centre at $1306\,\text{cm}^{-1}$. Several $Q^{(0)}$ lines are indicated (0.1 Torr CH_4, $30\,\text{cm}$ cell). This can be compared with the upper figure taken from Restelli and Cappellani (1979).

where S is the line strength which is constant for the purpose of such analysis. The line shape function $f(v)$ which is gaussian for doppler broadened absorption

$$f(v) = A \exp[-(v - v_0)/v_D]^2 \tag{5}$$

where A is a constant, v_0 is the line centre frequency and v_D is doppler width (HWHM). This assumption is justified for pressures below 1 Torr at ambient temperature. Substituting for $f(v)$ in (4) and differentiating and setting $v = v_0$, the second derivative signal at the centre of the absorption peak is obtained as

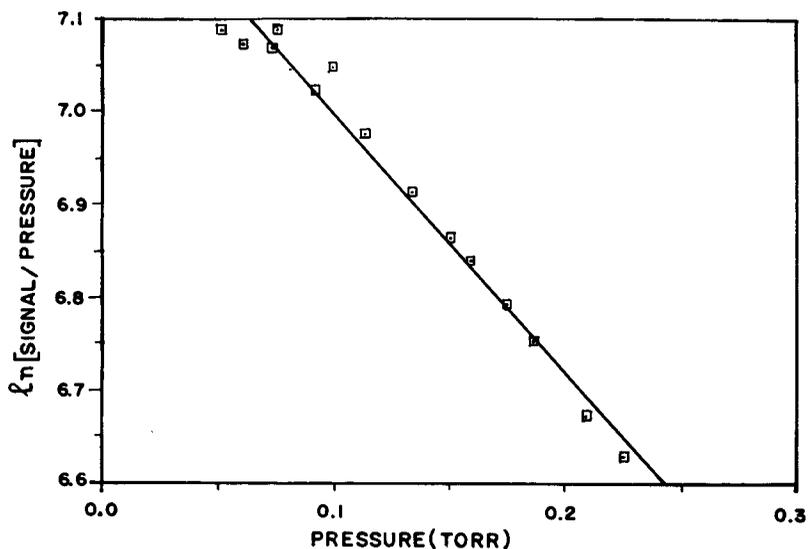$$d^2 I(v)/dv^2 = [2I_0 \alpha(v_0) pl/v_D] \exp[-\alpha(v_0) pl]. \tag{6}$$

Figure 2. Calibration curve for methane using second-derivative spectroscopy. The signal is measured from negative to positive excursion. The solid line is least-square fit to the data.

Rearranging (6), a convenient form for data analysis can be achieved

$$\ln[\{d^2 I(v)/dv^2\}/p] = -\alpha(v_0)pl + \ln[2I_0\alpha(v_0)l/v_D]. \tag{7}$$

Therefore by measuring the second derivative signal amplitudes at various pressures of the gas one could easily determine $\alpha(v_0)$ and a calibration curve could be obtained for determining the unknown concentration of the sample.

Figure 2 shows a calibration run for CH_4 using $R^{(-)}(7)$ transition at $1346 \cdot 326 \, cm^{-1}$ which gave an absorption coefficient value of $9 \cdot 2 \times 10^{-2} \, cm^{-1} \, Torr^{-1}$ consistent with the reported literature value (Botineau 1972). The only precaution to be taken was adjustment of the modulation amplitude so as to avoid line broadening. During the second derivative measurement, standard etalon fringes were recorded simultaneously which ensured that the recorded line width was doppler-limited. We have also verified the possibility of line broadening of CH_4 in an actual photolytic run in presence of PA ($0 \cdot 4$ Torr), which showed no such effect within experimental accuracy.

4. Results and discussions

Under static conditions, typically $0 \cdot 4$ Torr of PA was photolysed and the formation of methane could be quickly observed by looking at its spectrum around $1346 \cdot 326 \, cm^{-1}$ region. Figure 3 shows a typical digital oscilloscope trace for methane transition under full modulation amplitude ($\cong 2 \, cm^{-1}$ scan). The middle trace is for methane produced after 400 pulses which can be compared with standard spectra at 1 and $0 \cdot 1$ Torr pressures (top and bottom traces). Incidentally, a rise in pressure was noticed in the cell during irradiation as monitored by a capacitance manometer. Such rise in pressure was expected if PA photodissociated into several fragments.
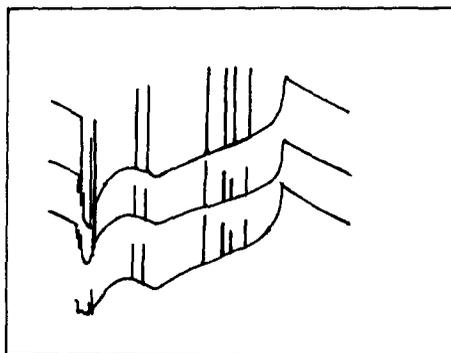
Figure 3. Digital oscilloscope recordings for methane transitions around $1346 \cdot 326 \text{ cm}^{-1}$ under full modulation amplitude ($\sim 2 \text{ cm}^{-1}$ scan). Top and bottom traces are for $1 \cdot 0$ and $0 \cdot 1$ Torr CH_4 respectively. Middle trace is for CH_4 produced in photolysis of pyruvic acid with 400 excimer laser pulses.

Probe freq.: 1346.326 cm^{-1}

Transition: $R^-(7)/v=0 \rightarrow 1 (v_4)$

CH_4 (Reference):

CH_4 (Product):

10 Pulses

CH_4 (Product):

50 Pulses

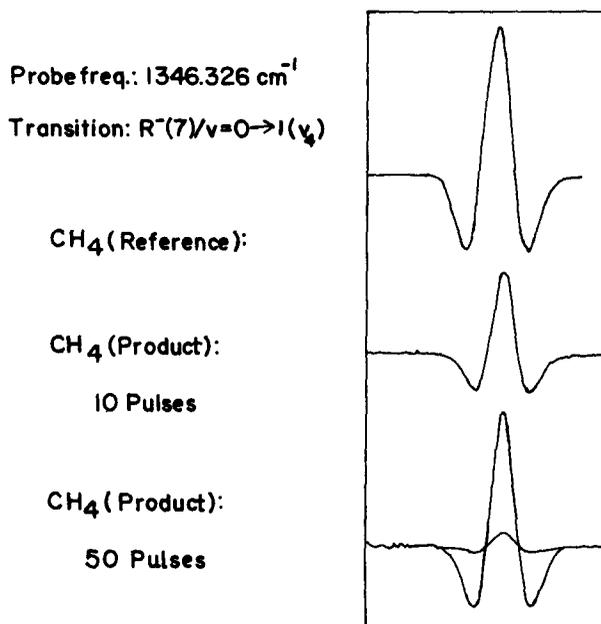**Figure 4.** Growth of typical second derivative signal for CH_4 with continuing photolysis of pyruvic acid.

After establishing that methane was indeed produced in 193 nm photolysis of PA, the quantitative estimate was carried out using second-derivative spectroscopy with the calibrated set up. PA was photolysed for a preset number of pulses and methane signals were recorded each time. With the present set-up, methane could be conveniently measured even after 5 pulses. With continuing photolysis, the signal was found to increase indicating the progress of photolysis (figure 4). Parametric studies on the amounts of methane formed with the number of laser pulses indicated that after about 100 pulses the rate gradually decreased (figure 5). This was not unexpected
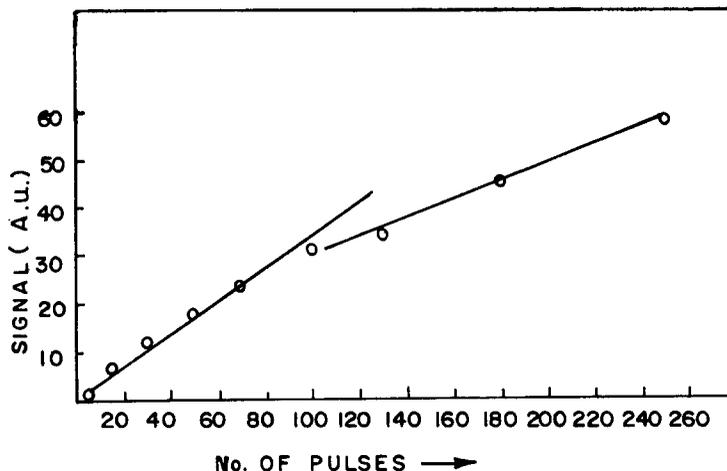
Figure 5. Growth of methane signal with number of excimer laser pulses. In the beginning the signal grows at a faster rate but eventually slows down after about 100 pulses.

in a static cell as accumulation of photoproducts may retard the progress of photolysis. Therefore, the quantitative estimate of methane formation was carried out in the initial linear regime of figure 5. Using the known absorption coefficient of PA $(0.05\,cm^{-1}\,Torr^{-1})$ at 193 nm (Chu *et al* 1984; Wood *et al* 1984; O'Neill *et al* 1986), the quantum yield of methane formation was 0.09 ± 0.01.

After each set of irradiations with laser pulses, the pressure build-up in the cell was also recorded. Though simplisitic in approach, such pressure measurements could be used to determine the kinetics of the process. Assume that PA dissociated via a second channel, along with (1),

$$CH_3COCOOH + h\nu(193\,nm) \longrightarrow CH_4 + CO + CO_2 \qquad (8)$$

The relative contributions are x for the above and $(1 - x)$ for (1) respectively. Using material balance, the final pressure $P_f(n)$ after 'n' pulses can be given by.

$$P_f(n) = P_i + n(1 + x)\Delta P, \qquad (9)$$

where P_i' is initial pressure of PA and ΔP is the equivalent pressure of PA dissociated

Table 1. Changes in pressure during the excimer laser photolysis of PA.

Number of laser pulses (n)	$[P_f(n) - P_i]$ (mTorr)	x^a
5	15	0.098
15	46	0.120
30	90.5	0.105
50	149	0.090
70	208	0.088

[a] Initial PA pressure: 0.42 Torr; ΔP was measured and was 2.73 mTorr per pulse

per pulse. Assuming a quantum yield of unity for PA dissociation, ΔP was measured and equalled 0·65%. From the measurement of final pressures as a function of laser pulses (cf. table 1), an average value for x was determined to be 0·1 which agreed well with the direct quantum yield measurement.

Experiments were also carried out to check the possibility of secondary decomposition of acetaldehyde produced via (1) to yield methane. Photolysing neat acetaldehyde under similar conditions in the present set-up, we could not detect any methane. However, we had difficulty in measurement due to the interference of ν_7 band of acetaldehyde in the probing frequency range.

5. Conclusion

The present investigation demonstrated that 193 nm photolysis of PA proceeds through two different dissociation channels having different fragmentation mechanisms. In one of the routes, methane was detected and estimated using the diode laser absorption technique. Using second-derivative spectroscopy, such photoproducts can conveniently be estimated and in the present case, CH_4 was found to form with a quantum yield of at least 10%. This result was corroborated by the measurement of increase in pressure during photclysis. This result would help to account for the 'missing' energy of the photodissociation process. By increasing the sensitivity of the present set-up, it would be possible to examine the state-specific information on nascent CH_4 and CO molecules in a real-time domain (O'Neil *et al* 1987), which would afford better insight into dissociation dynamics.

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