

ANALYSIS OF THE PRODUCTS OF PHOTOCHEMISTRY USING TUNABLE DIODE LASERS, WITH APPLICATION TO THE MULTIPHOTON DISSOCIATION OF CHLOROFORM

P. H. BECKWITH, J. J. ORLANDO, J. REID and D. R. SMITH

Departments of Chemistry, Physics and Engineering Physics, McMaster University, Hamilton, Ontario L8S 4M1 (Canada)

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Summary

Tunable diode lasers (TDLs) remain relatively unexploited as a tool in analytical chemistry. We show that TDLs are a sensitive analytical tool for investigating the products of photochemical reactions in the gas phase, and give examples from experiments on the IR photochemistry of chloroform. The sensitivity of the TDL technique is such that we can measure the few parts per million of DCl formed by photolysis of natural abundance CDCl_3 in CHCl_3 .

1. Introduction

For the past decade, lead-salt tunable diode lasers (TDLs) have been widely employed in both pure and applied spectroscopy [1 - 3]. They have, for example, been used extensively for the detection and monitoring of gases in the atmosphere. Schiff *et al.* recently reviewed a variety of TDL systems for measuring trace gases in tropospheric air [3], while Webster and Menzies discuss stratospheric measurements [4]. In the laboratory, TDLs routinely find application in very high resolution measurements of IR spectra [5]. The narrow TDL linewidth allows Doppler-broadened transitions to be measured with negligible instrumental broadening, and enables closely spaced lines from different species to be easily resolved. (TDLs are commercially available covering the wavenumber range $300 - 3000 \text{ cm}^{-1}$, with a given TDL typically being tunable over 100 cm^{-1} . The linewidth is generally less than 0.001 cm^{-1} .) The high power output per unit spectral range and the ability to modulate the TDL wavelength in conjunction with lock-in amplifier signal processing result in very high sensitivity for detection. Indeed, fractional absorptions of $10^{-3} - 10^{-5}$ can routinely be measured in gases. Thus TDLs combine excellent specificity (*i.e.*, the ability to distinguish between different molecules, including different isotopic species of the same molecule) with very high sensitivity, a non-destructive measurement technique and fast

response time. In short, TDLs are ideal instruments for investigating chemical reactions in gases.

It is somewhat surprising that TDLs have rarely been used for this type of measurement; in a recent literature survey of over 500 papers involving TDLs (many articles are listed in ref. 5), only a few papers discussed the use of TDLs to monitor simple chemical reactions [6 - 9]. There may be some reluctance on the part of experimentalists to become dependent on a device which has the reputation of being "tricky" to operate. For example, the single mode *versus* multimode emission and discontinuous tuning behaviour of the TDL require careful attention [2], and until recently TDLs suffered degradation with thermal cycling [1]. However, with modern TDLs, and with experience and care in operation, we feel that the wealth of information available to the analyst using a TDL to probe a chemical reaction more than compensates for any operational difficulties. There is no doubt that for photochemists the ability to carry out chemical and isotopic analysis with high specificity and at low concentrations is very important. High sensitivity analytical techniques allow one to work at low percent photolytic conversion and thus minimize secondary reactions from products. Experiments in laser-induced isotope enrichment can involve very high single-step enrichment factors — values up to 15 000 - 20 000 have been cited for D-H enrichment [10]. In such situations, high sensitivity and selectivity will allow measurements of very low residual levels of a depleted isotope in the reactant. In many applications, it is desirable to obtain data from the system at natural isotopic abundance, which again requires high sensitivity.

To illustrate the advantages of the TDL technique we describe both chemical and isotopic analyses made after IR multiphoton-induced dissociation (IRMPD) of chloroform [11] using a TEA CO₂ laser. The basic concepts of the technique are explained in terms of parameters for DCl and CO detection. (The CO is formed in the photolysis cell as a product of wall reactions.) The detection method is applicable for other irradiation sources such as metal vapour resonance lamps, flash lamps and Nd-YAG or excimer lasers. Indeed the TDL techniques are applicable to chemical and isotopic product analysis of most types of gas phase reaction.

Section 2 describes the experimental apparatus and calibration procedures, and illustrates the high sensitivity that can be attained with harmonic techniques. In Section 3 typical results are described, including the detection of DCl after irradiation of naturally occurring CDCl₃ in CHCl₃.

The importance of wall reactions is also illustrated. The discussion and conclusions are given in Section 4.

2. Experimental apparatus and calibration procedure

Figure 1 is a schematic diagram of the apparatus. The sample is irradiated in a conventional Pyrex or Monel gas cell 10 cm long with the NaCl windows tilted slightly to avoid feedback to either the CO₂ laser or the TDL. The TEA

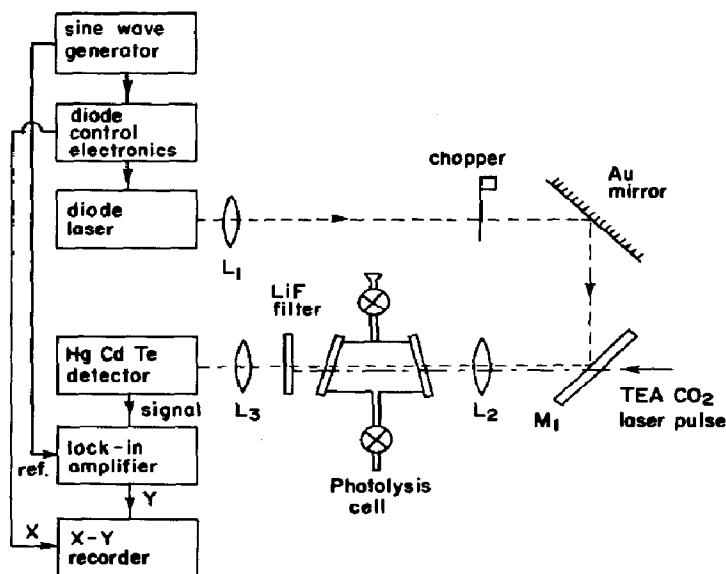


Fig. 1. Schematic diagram of the apparatus. Lens L_1 collimates the output of the TDL, lens L_2 focuses both the TDL and the CO_2 beams into the photolysis cell and lens L_3 focuses the TDL onto the detector. Mirror M_1 transmits about 75% of the TEA CO_2 pulse and reflects about 85% of the TDL radiation. The LiF filter prevents any $11\ \mu\text{m}$ radiation from reaching the detector.

CO_2 laser pulses have energies in the range 0.3 - 2 J and are focused into the gas cell with a BaF_2 lens. The pulses are produced by a Lumonics model K-922S laser, and approximately half the energy is contained in a 100 ns gain-switched spike, with the remainder in the tail of the pulse, which lasts about $1\ \mu\text{s}$. In general, the gas cell was irradiated by several successive pulses and then the TDL was used to monitor product formation.

To demonstrate the application of the TDL as a diagnostic tool, we set out to monitor the formation of DCl after irradiation of $\text{CHCl}_3\text{-CDCl}_3$ mixtures with $11\ \mu\text{m}$ radiation. Herman *et al.* examined the multiphoton dissociation of CDCl_3 in a molecular beam and showed that the dominant dissociation channel (more than 99%) was elimination of DCl [11]. It is noteworthy that although this study was performed with sophisticated mass spectrometer equipment, no direct detection of DCl was carried out. In contrast, DCl is an ideal molecule for TDL detection; it has a strong IR spectrum consisting of isolated lines in the $4.8\ \mu\text{m}$ region. The positions of these lines have been accurately measured [12]. The first part of the experiment consisted of finding suitable conditions of temperature and current for operating the TDL. The TDL beam was directed through a 0.5 m grating spectrometer which was calibrated with an He-Ne laser. With a little care, the TDL operating wavenumber could be determined to $\pm 0.1\ \text{cm}^{-1}$. This accuracy was more than sufficient to identify D^{35}Cl or D^{37}Cl absorption lines when a gas cell containing low pressure DCl was placed in the beam. Several potential operating regions were determined. For each one, the TDL

tuned smoothly through a DCl line with no mode hops and a minimum of laser power in satellite modes. The spectrometer was then removed, and additional scans were taken through a gas cell containing sufficient DCl to be opaque at the line centre. Typical scans are shown in Fig. 2. A chopper and conventional amplitude detection were employed, and the TDL temperature was carefully adjusted to maximize the laser power in the required laser mode. In general more than 90% of the total laser power could be obtained in the mode tuning through the DCl line. The $D^{35}Cl$ line R(7) was finally used for DCl monitoring. Throughout the experimental measurements, periodic checks were made of the DCl optical zero as shown in Fig. 2, and all calculations of absorption coefficients were performed using only the laser power actually in the DCl mode.

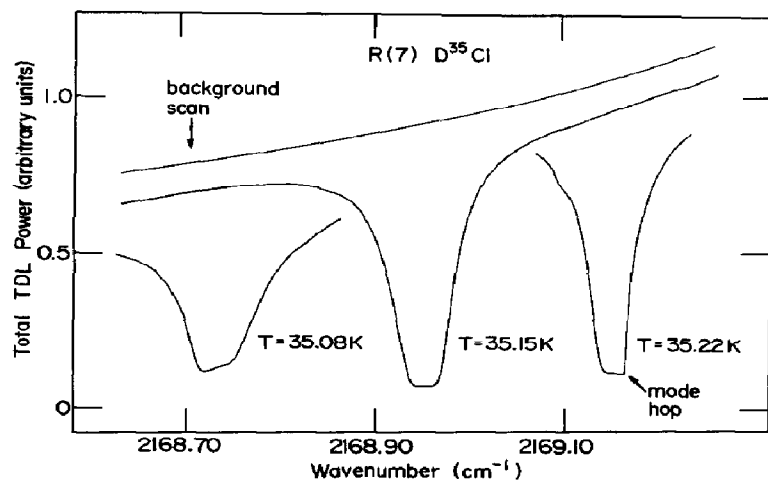


Fig. 2. TDL scans taken during optimization of operating temperature. The laser beam passes through a gas cell containing 3.5 Torr DCl in $CDCl_3$ (50 Torr total pressure) and is scanned in frequency over the R(7) line in $D^{35}Cl$ at 2168.962 cm^{-1} . From the central scan it can be seen that more than 91% of the laser energy is in the mode of interest. The two additional scans illustrate the effect of minor changes in operating temperature.

Figure 3 shows results of TDL scans taken after irradiation of a cell containing pure $CDCl_3$. The measured DCl absorption corresponds to a dissociation of less than 2% of the parent $CDCl_3$ molecules. In addition to absorption at the DCl frequency (2168.962 cm^{-1}), a strong line also appeared near 2169.20 cm^{-1} . This was identified as the R(6) line of CO at 2169.1984 cm^{-1} [13]. By analogy with the wall reaction of $:CF_2$ [14], we believe that the CO is formed by wall reactions of $:CCl_2$ in the cell. CO is easily observed in the scans shown in Fig. 3, even though its concentration in the cell is only 0.3 mol.%. When more intense CO_2 laser pulses were used for irradiation, the formation of DCl and CO was even more dramatic. A single 1.2 J pulse produces substantial absorption (more than 50%) on the R(7) DCl line, even though the "dog-bone" focusing geometry ensures that well below 1% of the gas in the cell is irradiated with intensities above

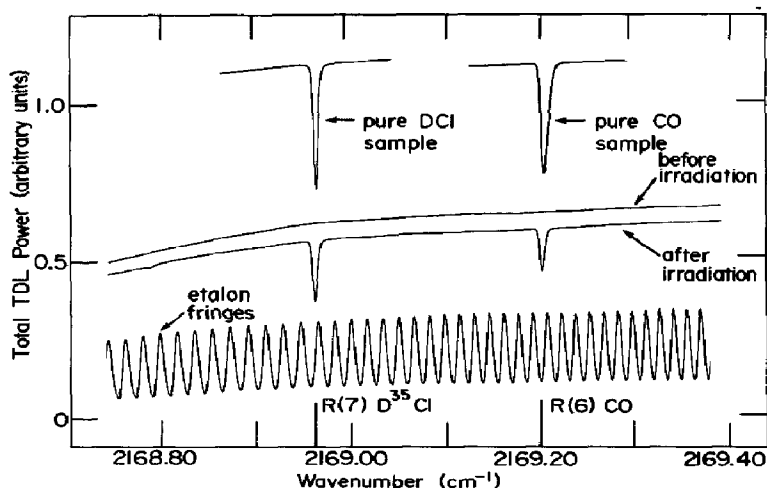


Fig. 3. Typical TDL scans showing the formation of DCl and CO after irradiation of 2 Torr pure CDCl_3 with 80 pulses of 0.4 J energy per pulse. The CO_2 laser transition was 10P(48) (916.76 cm^{-1}). The etalon fringes (separation 0.0163 cm^{-1}) are used to calibrate the wavenumber scale, and additional cells containing pure DCl and CO were used to confirm the line identifications. Also shown at the bottom of the figure are the calculated positions of the R(7) line in DCl (2168.962 cm^{-1}) and the R(6) line in CO ($2169.1984 \text{ cm}^{-1}$) [12, 13].

the dissociation threshold. (In the present series of experiments, sufficient time elapses between irradiation and TDL measurement for the photolysis products to diffuse uniformly throughout the cell volume.)

Although the traces shown in Fig. 3 demonstrate the ease with which DCl formation can be detected after irradiation of pure CDCl_3 , we are more interested in detecting the much lower concentrations of DCl formed when irradiating CHCl_3 - CDCl_3 mixtures. CDCl_3 occurs naturally in CHCl_3 at about one part in 7000, and hence even with complete dissociation DCl would only appear at 140 ppm after irradiation of chloroform at natural isotopic abundance. Fortunately, harmonic detection techniques allow the TDL to monitor DCl at concentrations in the parts per million range. These techniques are fully described in refs. 15 and 16 and are illustrated in Fig. 4. For the scans shown in Fig. 4, the modulation amplitude is optimized to maximize the second harmonic signal. Under such conditions, the ratio of second harmonic signal (peak-to-peak) to direct signal is about 1 [16], and there is no loss in signal in switching to harmonic detection. There is, however, a very substantial reduction in noise [15], and fractional absorptions of about 2×10^{-5} can easily be detected using harmonic techniques. If one considers a single pass through the IR cell, this corresponds to a minimum detectable absorption coefficient of about $2 \times 10^{-6} \text{ cm}^{-1}$, which gives more than sufficient sensitivity for the present experiments.

2.1. Calibration

A further advantage of the TDL technique is that the measurement of an IR absorption coefficient gives an absolute calibration, provided line

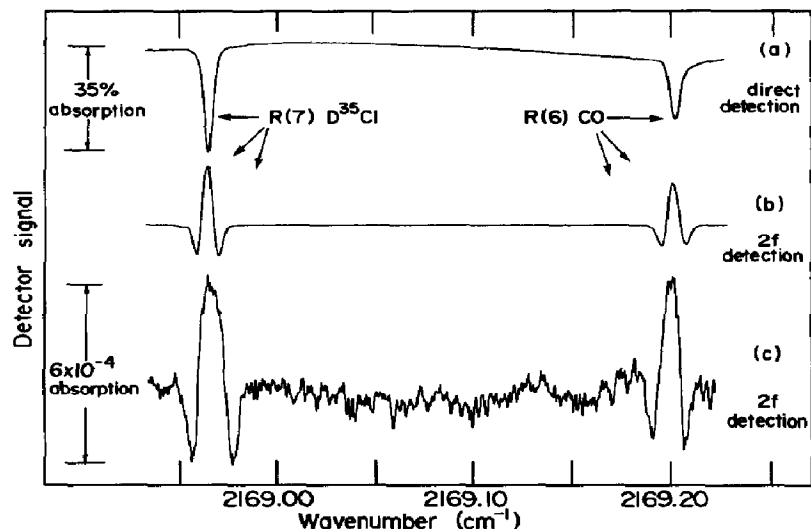


Fig. 4. Second harmonic detection with a TDL. Scan (a) is taken with a chopper and conventional amplitude detection. The DCl absorption is 35% in a path of 10 cm. Scan (b) is taken with the chopper removed and a 2.5 kHz modulation applied to the TDL current. Lock-in amplifier detection is carried out at 5 kHz. Scans (a) and (b) are taken with identical gain settings. For trace (c), amplification is increased by a factor of 1150, and there is only a trace of CO and DCl in 5 Torr CDCl_3 in the cell (noise is not minimized).

strength and linewidth data are available. There is no need to prepare known samples to calibrate the instrument response. This point is illustrated by the experimental calibration plot shown in Fig. 5. A series of CO- CHCl_3 mixtures were prepared on a grease-free vacuum system using a calibrated capacitance manometer to measure pressure. For mixtures containing less than 10 mTorr CO, successive dilutions were employed. We estimated that mixtures could be prepared with a CO concentration known to better than $\pm 5\%$. The TDL was used to scan over a line of CO as shown in the inset of Fig. 5. The area under the absorption line is directly proportional to the number of CO molecules in the path of the TDL beam. The proportionality constant is the line strength S_J of the particular absorption line under investigation. Line strengths have been measured for many of the simple molecules of interest to analytical chemists [17]. For CO, the most recent measurements of band and line strengths are given in ref. 18 and are listed in the U.S. Air Force Geophysics Laboratory (AFGL) line parameters compilation [19].

Experimentally, it is much more convenient to measure the line centre absorption α_0 than the area of the absorption line. α_0 is calculated from

$$I = I_0 \exp(-\alpha_0 L) \quad (1)$$

where I and I_0 are defined in Fig. 5 and L is the length of the cell. The procedure for relating α_0 to S_J and the number of CO molecules in the cell is complicated by the fact that we must generally consider both Doppler and pressure broadening of the absorption line. The Doppler halfwidth at half-

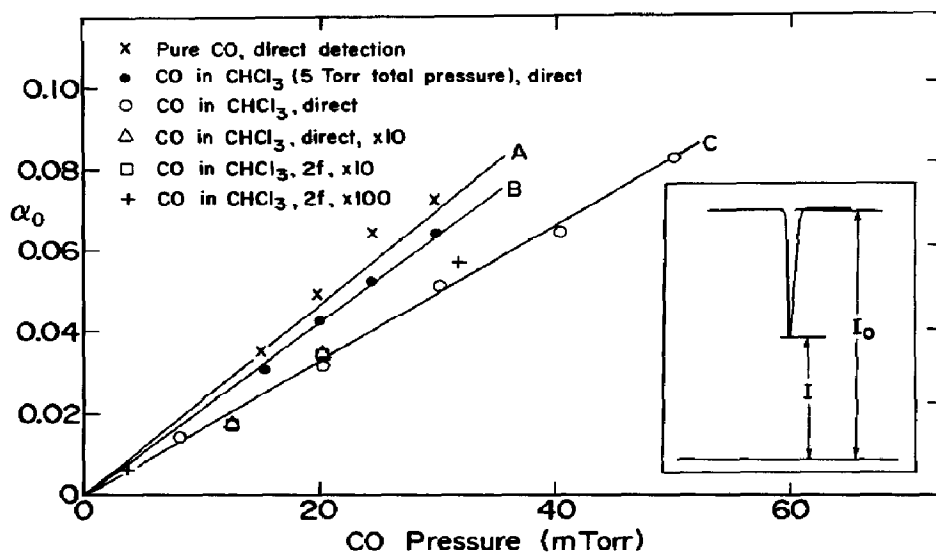


Fig. 5. Calibration plots for CO and CO-CHCl₃ mixtures. The measured absorption coefficients are shown to be linear with CO content for a dynamic range of about four orders of magnitude. The straight line through the pure CO data (line A), from eqn. (3), yields a line strength in agreement with the AFGL value, while line B is consistent with eqn. (5) (using the measured pressure-broadening coefficient of $8.0 \times 10^{-5} \text{ cm}^{-1} \text{ Torr}^{-1}$). Both sets of data were measured on the R(8) transition of CO. The third set of data (line C) was measured on the R(6) transition and illustrates results with both direct and 2f detection. Very dilute mixtures of CO in CHCl₃ are measured with 2f detection and are shown on expanded scales ($\times 10$ or $\times 100$) to demonstrate linearity. The inset defines the parameters used in eqn. (1).

maximum intensity (HWHM) for a molecule of mass M at a temperature T is given by [20]

$$\Delta\nu_D = 3.581 \times 10^{-7} \nu_0 (T/M)^{1/2} \quad (2)$$

where ν_0 is the frequency at the line centre. For CO in the 2170 cm^{-1} region, $\Delta\nu_D = 0.0025 \text{ cm}^{-1}$ at room temperature. Provided pressure broadening is negligible compared with $\Delta\nu_D$, *i.e.* for pressure below 1 Torr,

$$\alpha_0 = \frac{S_J}{\Delta\nu_D} \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{P_{\text{CO}}}{760} \text{ cm}^{-1} \quad (3)$$

where S_J is in units of reciprocal centimetres squared per atmosphere and P_{CO} is the partial pressure of CO in torr. As the gas pressure is raised above 1 Torr, collisional broadening becomes significant. The absorption line shape changes from a gaussian to a Voigt profile and finally becomes lorentzian at high pressure [21]. The pressure-broadened linewidth (HWHM) is given by

$$\Delta\nu_L = \gamma_M P_T \quad (4)$$

where P_T is the total gas pressure in torr and γ_M is the pressure-broadening

parameter for the gas mixture. Typical values of γ_M range from 10^{-4} to $5 \times 10^{-4} \text{ cm}^{-1} \text{ Torr}^{-1}$. In the intermediate pressure region where $\Delta\nu_L \sim \Delta\nu_D$, α_0 is given by

$$\alpha_0 = \frac{S_J}{\pi^{1/2}} \frac{a}{\Delta\nu_L} \left\{ 1 - \text{erf}(a) \right\} \exp(a^2) \frac{P_{\text{CO}}}{760} \text{ cm}^{-1} \quad (5)$$

where

$$a = (\ln 2)^{1/2} \frac{\Delta\nu_L}{\Delta\nu_D} \quad (6)$$

and $\text{erf}(a)$ is the error function [22]. Expressions for α_0 as a function of a have been tabulated by many researchers [23]. At high pressures (typically above 100 Torr) $\Delta\nu_L \gg \Delta\nu_D$, and expression (5) simplifies to

$$\alpha_0 = \frac{S_J}{\pi\Delta\nu_L} \frac{P_{\text{CO}}}{760} \text{ cm}^{-1} \quad (7)$$

Note that for a fixed-composition gas mixture both P_{CO} and $\Delta\nu_L$ are proportional to P_T , and thus α_0 is a constant independent of pressure when collisional broadening is dominant, *i.e.* the analytical sensitivity expressed as a ratio such as parts per million is independent of total pressure. This behaviour can be contrasted with the low pressure behaviour where α_0 is proportional to total pressure (eqn. (3)).

In Fig. 5 plots of α_0 for an isolated absorption line are shown as a function of pressure. The calibration lines A and B illustrate the transition from eqn. (3) to eqn. (5). The measurements for line A are taken in pure CO and, using eqn. (3), yield a line strength of $9.7 \pm 0.8 \text{ cm}^{-2} \text{ atm}^{-1}$ in agreement with the AFGL value of $10.43 \text{ cm}^{-2} \text{ atm}^{-1}$ for R(8). The pressure-broadening coefficient for CO in CHCl_3 was measured to be $(8.0 \pm 0.5) \times 10^{-5} \text{ cm}^{-1} \text{ Torr}^{-1}$, and using this value in eqn. (5) gives good agreement with the data obtained for CO in 5 Torr CHCl_3 (line B). The third set of data in Fig. 5 illustrates that the linearity of calibration is maintained with both direct and second harmonic detection. Direct detection was employed whenever the line centre absorption was more than 5%. Both direct and second harmonic detection were used for line centre absorptions in the range 1% - 5%, and the relative response of the two techniques was determined. (In Fig. 4, for example, the ratio of 2f signal (peak-to-peak) to direct detection is 0.85 and 1.00 for the DCl and CO lines respectively. The slight difference in ratio arises from differences in linewidths and modulation amplitudes for the two lines.) Once this relative response is measured, second harmonic detection alone can be used to determine absorption coefficients when $\alpha_0 L$ lies in the range 10^{-1} - 10^{-5} . The data displayed in Fig. 5 demonstrate that once the line strength and the linewidth are known, low pressure gas mixtures can be calibrated absolutely by simply measuring α_0 . In view of the care taken in CO sample preparation in ref. 18 for the measurements of band strengths, we feel that the measurements displayed in Fig. 5 serve more as a check on our mixture preparation than as a repeat calibration of CO line strengths. However,

it is worth pointing out that the combination of direct and $2f$ detection employed for Fig. 5 gives an absolute linear calibration over four orders of magnitude of CO concentration ($\alpha_0 L$ ranges from 10^{-4} to 1). This dynamic range can easily be extended, if required, by varying L , *i.e.* by using multi-pass cells for low concentrations [15] or a transverse geometry with a short path length for high concentrations.

The calibration procedures for DCl are very similar to those used for CO. We measured the pressure-broadening parameter on the R(7) DCl line for both CHCl_3 and CDCl_3 . Results are shown in Fig. 6. The linewidths were measured by preparing cells containing CDCl_3 (or CHCl_3) with a trace of DCl to give a value of $\alpha_0 L$ in the range 0.2 - 0.5. Careful scans over the DCl line were taken with the TDL, and the tuning rate of the laser was calibrated using a 7.62 cm germanium etalon with a fringe spacing of 0.0163 cm^{-1} (see Fig. 3). The linewidth at half-maximum (*i.e.* the width when $\alpha = (1/2)\alpha_0$) was then measured from the X - Y recorder traces. As a check on the measurement technique, the Doppler width for DCl was determined in a low pressure sample. The measured Doppler width was $2.2 \pm 0.2 \times 10^{-3} \text{ cm}^{-1}$ compared with a calculated value of $2.18 \times 10^{-3} \text{ cm}^{-1}$. This good agreement confirms that the TDL linewidth has a negligible effect on the measured linewidths [24]. From the data shown in Fig. 6, we estimate that the pressure-broadening parameter for DCl collisions with chloroform is $9.7 \times 10^{-5} \text{ cm}^{-1} \text{ Torr}^{-1}$ ($\pm 10\%$). There appears to be no measurable difference between collisions with CHCl_3 and CDCl_3 .

The linewidth measurements shown in Fig. 6 are more than accurate enough to calibrate mixtures of DCl in chloroform. The accuracy of the calibration is limited by the accuracy of the available line strength data. We

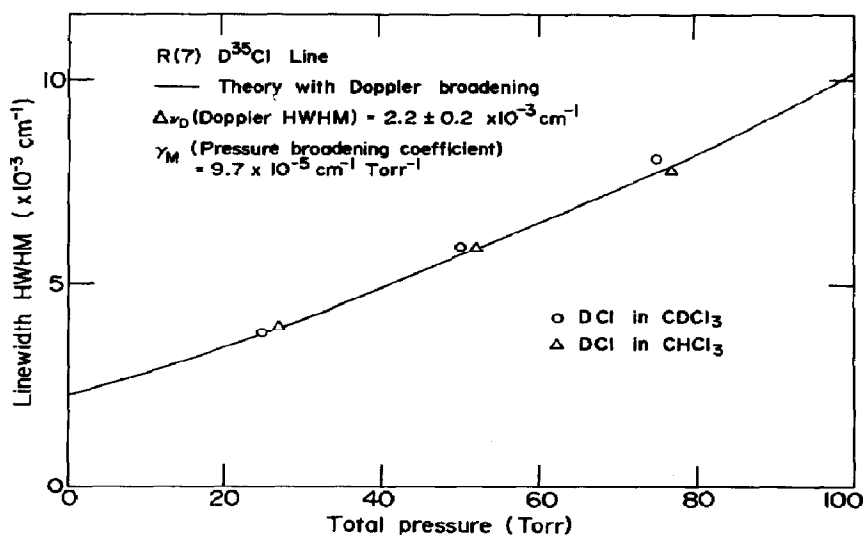


Fig. 6. Measured linewidths for the R(7) line of D^{35}Cl buffered by CHCl_3 or CDCl_3 . The solid line drawn through the data points is the calculated linewidth for $\gamma_m = 9.7 \times 10^{-5} \text{ cm}^{-1} \text{ Torr}^{-1}$ (best-fit value).

have made no attempt to measure experimentally the band strength of the fundamental band of DCl. This type of measurement requires extreme care in preparing samples of a reactive gas such as DCl; the difficulties involved are described in detail in the excellent work of Pine *et al.* [20]. We have chosen to use the band strength of HCl as determined by them and have multiplied it by the ratio 66.6/130 as measured by Benedict *et al.* for the band strength ratio [DCl]/[HCl] [25]. This experimental ratio agrees well with the theoretical value of 0.525 [26]. Consequently, we use a value of $2.60 \text{ cm}^{-2} \text{ atm}^{-1}$ for the line strength of the R(7) DCl line and estimate that this value is accurate to better than 10%.

3. Preliminary results of IR multiphoton-induced dissociation experiments

An initial series of measurements was carried out to check the linearity and reproducibility of the measurement system. A gas cell was filled with 2 Torr pure CDCl_3 and irradiated with 0.5 J pulses of 10P(48) radiation (916.76 cm^{-1}) focused by a BaF_2 lens of focal length 25 cm. The cell was irradiated with 20 pulses and then the DCl concentration was quickly measured. This process was repeated three times for a total of 60 pulses in several different experimental runs. Results confirm that the concentration of DCl increased linearly with the number of pulses. This result is to be expected as the maximum DCl concentration is very low, and the entire measurement process is done quickly (in about 3 min) to prevent any significant loss of DCl to the cell walls.

Further experiments were carried out to monitor the formation of DCl from the photolysis of natural abundance CDCl_3 in CHCl_3 . These experiments required high sensitivity measurements of DCl at the parts per million level. Initially, Pyrex photolysis cells were used, but absorption and isotope exchange at the cell walls resulted in a steady decrease in DCl concentration with time after irradiation. To eliminate these adverse effects a Monel cell was used in which DCl and CO concentrations were stable at parts per million levels.

Figure 7 shows successive second harmonic scans which monitor DCl and CO concentrations before and after irradiation with 10P(38) and 10P(48) CO_2 laser transitions. The irradiated volume was only about 1% of the total cell volume. Note the appearance of DCl after irradiation with 10P(48); the measured DCl concentration corresponds to about 2.5% of the CDCl_3 originally present in natural abundance in the cell. It is extremely significant that DCl only appears after irradiation with 10P(48). In a separate series of measurements on pure CDCl_3 , we determined that under identical conditions 10P(48) irradiation is ten times more effective at producing DCl than 10P(38) irradiation. Thus the appearance of DCl in the upper scan of Fig. 7 can be attributed to the IRMPD of the CDCl_3 in the cell, and not to thermal or shock-induced effects. The increase in CO concentration is probably caused by a reaction between photolytically produced $:\text{CCl}_2$ and

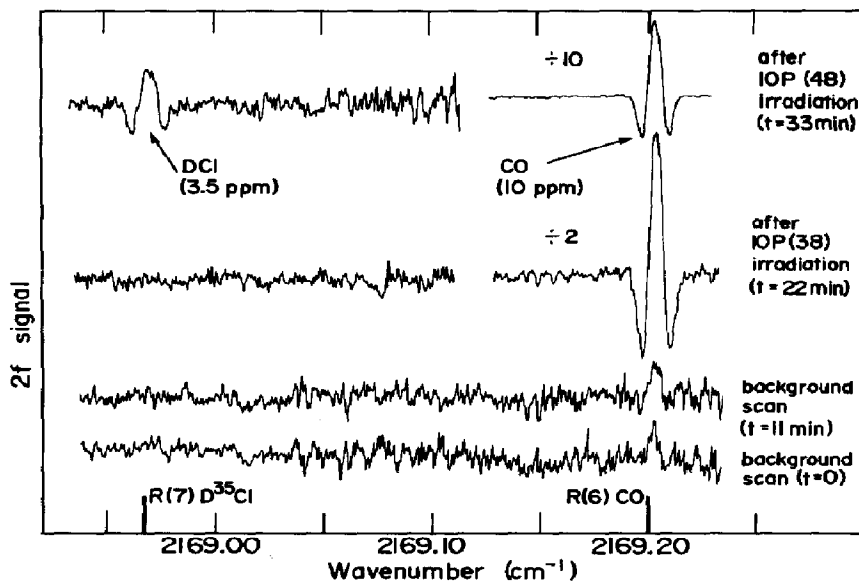


Fig. 7. Successive $2f$ scans taken of a sample of natural chloroform after irradiation with 100 pulses of 10P(38) and 10P(48) radiation (about 0.4 J per pulse). The increase in DCI concentration after irradiation with 10P(48) is attributed to IRMPD of naturally occurring CDCl_3 in the sample. The gas pressure in the cell is 5 Torr. The noise level is equivalent to about 0.8 ppm DCI, or a fractional absorption of 2×10^{-5} in the 10 cm cell.

the cell walls. (In this case, much of the CO derives from the photolysis of CHCl_3 , the dominant species in the cell.)

4. Discussion and conclusions

We describe the first reported measurement of DCI formation from the photolysis of natural abundance CDCl_3 in CHCl_3 . This measurement could not have been made without the high sensitivity of the TDL technique. TDLs allow one to make accurate absolute measurements of trace gas concentrations immediately after photolysis; the technique is very rapid and does not require the removal of a sample of gas from the photolysis cell.

It is instructive to compare our TDL results with other techniques for measuring DCI. (DCI is a favourable case for TDL detection; nevertheless, it is a molecule of primary importance in proposed T from D separation schemes [10].) Fourier Transform IR spectroscopy (FTIR) has many similarities to the TDL technique. However, even the best commercially available FTIR instruments require 16 min to complete a measurement with 0.004 cm^{-1} resolution. For a low pressure DCI gas sample, the minimum detectable absorption is about 0.1% (in ref. 27 results are quoted for the Boman DA-3.002 instrument)—two orders of magnitude worse than with a TDL. In comparing sensitivities with mass spectrometer techniques it must be realized that measurements of DCI^+ ions are almost meaningless after this type of

photolysis experiment, as the DCl^+ ion can originate from either the product DCl or parent CDCl_3 . Isotope exchange on the instrument walls and in the ion source provide additional complexities in interpreting any mass spectrometer measurements. (Our measurements of DCl-HCl exchange in a simple Pyrex cell illustrate the need for rapid *in situ* measurement of DCl formation after photolysis.) A third technique, gas chromatography, is also unsuitable for measurements of DCl after laser photolysis of CDCl_3 [28].

In addition to the unique capability for detecting DCl , the high sensitivity of the TDL to CO provides a unique opportunity to detect CO production after irradiation of small molecules such as CF_2O . Small molecules are difficult to dissociate by IRMPD because of the relatively low density of vibrational states [10]. CF_2O is such a molecule [29]; however, we have easily detected CO formation in preliminary experiments on CO_2 laser photolysis of 5 Torr CF_2O [30].

Clearly, the use of a TDL provides the analytical chemist with a powerful technique for investigating gas phase reactions. We feel that TDLs will become much more widely used in this type of application and that TDL measurements will prove invaluable in determining the mechanism of photochemical reactions.

Acknowledgments

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