

INFRARED DETECTION OF REACTIVE SPECIES PRODUCED THROUGH FLASH PHOTOLYSIS

G. C. PIMENTEL

Chemistry Department, University of California, Berkeley, California, U.S.A.

The spectroscopic study of transient species using flash photolysis has been most fruitful during the last decade. Infrared spectroscopy has not, however, played its full partnership role with u.v. visible spectroscopy because of the absence of suitable rapid-scan or photographic techniques. While the matrix isolation method opened the infrared study of free radicals, gas phase methods were still needed.

Rapid-scan infrared spectroscopy was finally realized with the successful operation of an instrument constructed by Herr^{1,2}. This spectrometer has been in operation now for two years and has been applied to the detection of transient species, including free radicals, both in absorption and emission. New developments are appearing, both in the Berkeley laboratories and, more recently, at Mellon Institute through the work of Hand and Hexter^{3,4}. It is timely to assess the results now attained and the prospects for the future.

ABSORPTION SPECTRA OF TRANSIENT SPECIES

After two years of experimentation, three transient species have been detected in the Berkeley laboratories, CF_2^3 , ClOOH^3 , and CF_3^5 . Measured effective half-times were, respectively, 2.5 msec, 50–70 μsec , and 60 μsec . The mere detection of these highly reactive species is, we feel, a significant milestone. Nevertheless, it is appropriate to ask what other significance can be attributed to the studies, both to illustrate their potentialities and to seek the limitations that remain. Fortunately these three molecules furnish interesting examples in both regards.

The flash photolysis detection of CF_2 followed its matrix detection by Milligan *et al.*⁶ and the gas phase study fulfilled the desired intent. Although Milligan and his coworkers were able to observe two C—F stretching frequencies (at 1222 and 1102 cm^{-1}), the spectra provided little clue as to the proper assignment, a general characteristic of matrix spectra. The band contour of the gas phase absorption observed by Herr and Pimentel (at 1113 cm^{-1}) identified this absorption (and the matrix absorption at 1102 cm^{-1}) as ν_3 . This complementary relationship between matrix and gas phase methods will probably be common, particularly in the earliest applications of the rapid-scan instruments. The gas phase frequencies and rotational structure furnish an alluring goal, even after the matrix work has pointed the way.

The transient molecule of chloroformic acid, though not a free radical, demonstrates vividly the value of infrared methods in flash photolysis experiments. Infrared detection of this molecule as an intermediate species in the chlorine–formic acid reaction immediately corroborated the reaction

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mechanism proposed earlier by West and Rollefson⁷ and provided an avenue for quantitative kinetic studies. This pentatomic, unsymmetrical molecule was readily recognized in the infrared spectrum by the characteristic C—Cl stretching frequency, though the molecule had never been detected earlier by any spectroscopic technique. It is plain that recognition of the species by electronic spectroscopy would be very uncertain.

The detection of CF_3 by Carlson and Pimentel⁵, recently corroborated by Hand and Hexter⁴, presented a more difficult problem in identification. At the time of its detection (at $1259 \pm 6 \text{ cm}^{-1}$) none of the ground state frequencies of CF_3 were known and the problem resolved to proof of the identity of the transient absorber. As resolution, flash technique, and hence, photometry accuracy were improved, it became possible to verify the identity by measurement of the second order reaction rate constant. While, in this case, the rate constant was used as a means of verifying the identity of the absorber, the study demonstrates the rapid-scan capability for measurements of reaction rate constants for free radicals†.

EMISSION SPECTRA OF TRANSIENT SPECIES

Quite as interesting as the absorption spectra have been the attempts to observe infrared fluorescence following flash photolysis and using the rapid-scan spectrometer. Kasper designed a multiple reflection Raman cell which permitted light collection from a path up to 40 m in length. A quartz cylinder extending through the cell accommodated a metre-long flash tube⁹. The light emitted during and immediately after photolysis was focussed into the rapid-scan spectrometer.

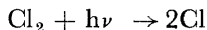
Kasper examined two types of systems, the $\text{H}_2\text{—Cl}_2$ flash-initiated explosion and the photolysis of halogenated methanes of the type CF_3X . In the case of the $\text{H}_2\text{—Cl}_2$ explosion, the intent was to observe the intensity and time-history of the HCl emission implied by the infrared fluorescence observed by Polanyi using flow conditions¹⁰. The CF_3X photolyses were expected to give CF_3 vibrationally excited in the out-of-plane or "umbrella" mode. In either experiment, positive results would indicate energy distribution during bond rupture and also the rate of collision-induced energy exchange processes.

The hydrogen-chlorine experiment was at first bedevilled by shock waves in the multiple reflection cell. Only when these were identified with their rather slow build-up and long period ($\sim 1.4 \text{ msec}$) was it possible to recognize that stimulated emission was occurring in the pulsed form characteristic of laser action. Variation of the intensity with the number of traversals confirmed the presence of stimulated emission, since the apparent mirror reflectivity exceeded unity. Using the rapid-scan spectrometer as a mono-

† It was gratifying that the report by Carlson and Pimentel at the 1965 Columbus Symposium on Molecular Spectroscopy evoked from Milligan and Jacox the announcement that they had detected CF_3 in matrix isolation experiments. Their experiments corroborated the CF_3 absorption at 1259 cm^{-1} and added the second C—F stretching absorption that establishes the non-planar structure of CF_3 . With the aid of their second frequency it was possible for Carlson to detect it in the gas phase, using hexafluoroacetone instead of CF_3I as a parent molecule to avoid parent-molecule interference. We thank Milligan and Jacox for permission to quote their private communication of these results here⁸.

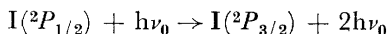
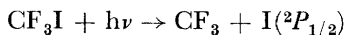
chromator, the emission was found to be almost wholly in one of the $1 \rightarrow 0$ P -branch transitions, $P(8)$, $P(9)$, $P(10)$, or $P(11)$.

Thus was discovered the first chemical laser. In this laser, the excitation of the population-inverted state results from the intrinsic energy distribution of an exothermic chemical reaction. The flash serves only to initiate the explosion chain.



Subsequent experiments were conducted in conventional laser geometry (a 60 cm confocal cavity) and the results have been interpreted in terms of the implied vibrational energy distribution¹¹. More experiments are under way and it seems likely that collision-induced energy transfer can be so investigated.

The photolysis of CF_3I provided equally novel results despite the fact that infrared emission was not observed from CF_3 . Instead, near-infrared emission was observed, again in pulsed form and with extremely high intensity. Frequency measurements identified the emission with the ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition of atomic iodine. Once again, population inversion was obtained, sufficient to provide laser action either in the multiple reflection cell or in the conventional laser geometry¹².



$$\bar{\nu}_0 = 7603 \text{ cm}^{-1}$$

It is gratifying that this photodissociation laser, again the first of its kind, has opened a variety of interesting chemical questions. For example, quenching of the laser emission can occur and this has been associated with temperature rise during photolysis¹³. A variety of normal alkyl and perfluoroalkyl iodides have been shown to give the iodine laser action¹³. On the other hand, neither isopropyl iodide nor iodine gives stimulated emission. The significance of the latter results is now under further study and it seems that these substances act as quenchers, probably because of preferential or rapid reaction with ${}^2P_{1/2}$ excited iodine atoms. This inference highlights one of the most unique aspects of this laser system: it provides a means of distinguishing the chemistries of ${}^2P_{1/2}$ and ${}^2P_{3/2}$ iodine atoms.

PROSPECTS FOR THE FUTURE

With some reassurance provided by these successes, we can investigate the limitations of present instruments and the prospects for improvement. *Table 1* lists six experimental variables which presently limit rapid-scan methods: scan rate, flash noise duration, resolution, scan repetition interval, data recording, and concentration of transient species. The second column shows the present performance of the Berkeley instrument, the third column

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lists the performance of the Mellon Institute instrument (as described by Hand at this meeting⁴) and the last column indicates the performance that is likely within the next three years. The six variables are discussed in turn below.

Table 1. Limiting variables in rapid-scan i.r. spectrometers

<i>Limiting variables</i>	<i>Berkeley instrument</i>	<i>Mellon Institute instrument</i>	<i>Reasonable and needed goals</i>
Scan rate ($\text{cm}^{-1}/10 \mu\text{sec}$)	100	2500	1000
Flash-noise duration (after flash peak) (μsec)	30-40	100-150	10
Resolution (cm^{-1})	3-5	18-20	1-3
Scan repetition interval (μsec)	3.5×10^3	500	300
Data recording	Oscilloscope, photo	Oscilloscope, photo	Magnetic tape, digitalized data
Concentration of transient species			
Flash energy (J)	2000-4000	2000-4000	2000-10,000
Flash duration ($1/e$) (μsec)	20-40	—†	2-20

† Not known to writer.

Scan rate

Experience has shown that the $100 \mu\text{sec}$ scan time of the Berkeley instrument is not yet a severe limitation because of the flash noise duration. By careful synchronization, it is possible to scan through a selected 100 cm^{-1} region about $40 \mu\text{sec}$ after the flash peak and flash noise prevents a closer approach at any scan rate. There is reason to expect that flash noise duration can be reduced to $10 \mu\text{sec}$, however, and then the $100 \mu\text{sec}$ scan rate will provide an undesirable limitation. The means for removing this limitation is, however, already at hand. *Figure 1* shows three of the various scan methods

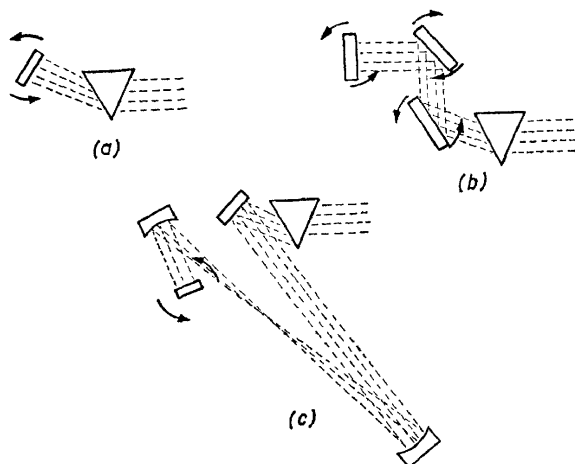


Figure 1. Three scan methods now in use. (a) Rotating, single Littrow mirror; (b) rotating, multiple Littrow mirror⁹; (c) telescope⁴

that are now in use in rapid-scan spectrometers. *Figure 1(a)* is simply a rotating Littrow mirror, such as described by Herr and Pimentel. Three-inch glass mirrors, high tensile strength aluminium mirrors, and replica gratings on glass have been rotated at 100 to 200 rev/sec. Material strengths probably limit such Littrow scanning to 500 rev/sec and scan rates to near $1000 \text{ cm}^{-1}/30 \text{ } \mu\text{sec}$. *Figure 1(b)* shows a synchronized multiple Littrow system now used by Terenin, Dmitrievsky and Shakhverdov¹⁴ in a visible u.v. rapid-scan spectrometer. Scan times of 30–40 μsec are thus obtained with less demanding mirror rotation speeds. This is particularly important as a means of avoiding an excessive rotation speed of a replica grating. *Figure 1(c)* shows the telescope optical design used at present by Hexter and Hand⁴. The telescope permits rotation of a smaller mirror to rates over 5000 rev/sec. These workers have already achieved scan rates of $2500 \text{ cm}^{-1}/10 \text{ } \mu\text{sec}$ with spectral widths in the range 20–30 cm^{-1} .

Flash noise duration

The extreme sensitivity of the semiconductor detectors results in disturbing signals during and following a high energy (kilojoule) photolysis flash. The flash noise duration presently obstructs reducing the time delay between flash peak and scan more than does the scan rate in both the Berkeley and the Mellon instruments. There are several measures that help, some of them obvious, such as use of shielding (both electrical and magnetic) and geographical separation of the flash apparatus and the detector. Acoustic shielding seems to help as well, as provided, for example, by a rigid wall. This susceptibility to acoustic sensitivity is aggravated if the detector double dewar is not provided with spacers to prevent shock-induced movement of the detector. Grounding is extremely important. Heavy ground leads are desirable and the detector dewar needs a ground system electrically separated from that of the flash power supply.

Resolution

In all respects the usefulness of any infrared spectrometer declines significantly as spectral slit width increases from about 1 cm^{-1} up to about 30 cm^{-1} . At the upper limit, gas phase band contours are lost, and sensitivity drops severely. As usual, increased detector sensitivity and source intensity are needed. The former is available, at the cost of scan range and flexibility, through the use of cold filters¹⁵. High source intensity has been obtained at the Berkeley laboratories through the adaptation, by Miss J. J. Moore, of a large carbon arc of the type used in commercial theatres. At d.c. currents of 180 A and voltages near 60 V, the positive crater of such an arc approximates a solar spectrum. Of course fluctuations of light intensity from the crater, a chronic carbon arc difficulty, are not even noticed during a 100 μsec scan.

Further gain may be available from flash sources, used as a "spectral flash" just as in conventional flash spectroscopy. Such flash sources are being developed by Hexter and Hand.

The plasma jet is a possible high temperature source that proves to be ineffective. With the cooperation and help of the Forrest Electronics Corporation, Dr. K. C. Herr and Miss J. J. Moore measured the infrared emission of a plasma jet in the 3–15 μ region. Several powdered

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refractories were fed into the flame, but despite visible emissions characteristic of temperatures as high as 50,000°K, the infrared continuum never exceeded 1000°K.

It seems that the combination of grating dispersion, cold filters, and either the carbon arc or flash source will permit use of spectral slit widths in the range 1–3 cm^{-1} .

Scan repetition interval

Kinetic studies of transient species are more powerful if scans can be repeated at intervals comparable to the scan time. This proves to be rather difficult since the scan usually involves only a few degrees of Littrow rotation (perhaps 6 degrees) whereas a 180 degree rotation is needed for a repeat scan using a two-sided Littrow. Thus the repeat interval is about 30 times as long as the scan time. To shorten, then, the scan repetition interval, it is necessary to shorten correspondingly the scan time, as has been accomplished by Hexter and Hand.

Data recording

Photography of an oscilloscope trace has a number of disadvantages. Repetitious scans can be recorded with a faster displacement of successive traces but only a few spectra can be so recorded on a single picture. A particular scan range must be selected in advance and spectral information outside that range is lost.

For the 100 μsec scan time, magnetic recording is possible. Magnetic recorders with band width near 2 Mc which have been developed for television use are quite suitable. They permit the recording of many successive scans, followed by whatever type of retrieval desired. The most obvious retrieval is to display and photograph the successive spectral records on an oscilloscope, choosing scale expansions to suit the spectral analogue signal *a posteriori*.

If scan times are shortened to 10 μsec , magnetic recording is no longer readily available. Furthermore, the information rate challenges present-day digitalization schemes. Nevertheless, fast digitalization techniques, not in use but already foreshadowed, seem to contain the answer to data recording in the rapid-scan infrared field.

Concentration of transient species

The greatest limitation of infrared methods in flash photolysis is connected with the concentration of transient species. This is a problem shared with visible-ultraviolet methods but much enhanced in i.r. studies by the relatively low absorption coefficients of vibrational transitions. Multiple path cells are a great help—10m path-lengths are readily obtained with commercial cells. Beyond this, the principal remaining variables are connected with the intensity of the photolysis flash. Unfortunately, both higher energies and shorter flashes are needed, these presenting conflicting requirements. For fixed charging voltage, energy is raised by increasing the capacity of the condenser bank, which lengthens the flash and the flash noise duration. Hence it is desirable to use high voltage, low capacitance flashes, despite the attendant triggering difficulties. Circuit inductance must be kept as low as

possible. Flash tube construction must be perfected to avoid flash tube destruction.

These same needs have been faced for several years by laboratories conducting conventional flash photolysis work. Their experience seems to indicate that 2000 J flashes can be shortened to $1/e$ times as short as 2 μ sec, with corresponding gains at still higher energies.

CONCLUSION

If the performance given in the last column of *Table 1* is realized, as seems likely, the progress of infrared detection of transient species should be extremely fruitful during the next few years. Already the initial investigations have provided some exciting precedents: the first infrared detection of gaseous free radicals, CF_3 and CF_2 ; the first infrared detection of a reaction intermediate, $ClCOOH$; the first infrared measurement of a free radical reaction rate constant; the first photodissociation laser and the first chemical laser. We can only expect that these examples will be richly multiplied as instruments are improved, at Berkeley, at Mellon Institute, and at other laboratories entering the field.

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