

Experiments Aimed at Extending the Applicability of Gas Electron Diffraction Using Real-Time Procedures

Lothar Schäfer and John D. Ewbank

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA

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The current state of real-time data collection in gas electron diffraction and the potential for novel applications is reviewed. In the real-time procedure developed at Arkansas, the diffraction pattern is displayed on a phosphor screen which is optically coupled to a photodiode array. The array can determine on-line, and with integration for a few seconds, up to 1024 independent intensity points along a radial line of the diffraction pattern. Details of ratiometric data analysis are discussed which are typical for the novel procedure. Possible applications of the detection system as an analytical tool in gas chromatography and in studies of photochemical and pyrolytic reactions are described.

Dedicated to Professor Otto Bastiansen on his 70th birthday.

Some twenty years ago, when one of us was introduced to structural studies by gas electron diffraction (GED) in Otto Bastiansen's group, the method involved densitometer traces of photographic plates on ruled paper; intensities were determined manually, point by point, using special rulers; typically many months were needed to analyze the GED data of a molecule. In the mean time, improved techniques of data retrieval, such as digital¹ or multichannel^{2,3} densitometry, have simplified GED investigations, but their basis has essentially remained unchanged: no procedure has yet been developed for GED which is both more accurate and more practical than photographic data collection.

Recent experiments with photodiode arrays (PDA)^{4,5} have brought a sudden turn to this field. For the first time, a method has been implemented which has the chance some day of equalling, or even surpassing, the accuracy of the photographic method, at the same time allowing for real-time measurements, on-line, and without the usual handicaps (such as the rotating sector, the uncertainties of exposure, development, blackness correction and the mechanical manipulations needed for densitometry). It is the

purpose of this paper to review the current state of this novel technique and its promise for future applications.

Description of photodiode array real-time GED

In our instrument,^{4,5} the scattering pattern is displayed on a phosphor screen inside an otherwise conventional diffraction chamber. The visible pattern is focused through a vacuum window onto the surface of a PDA. The PDA can record,

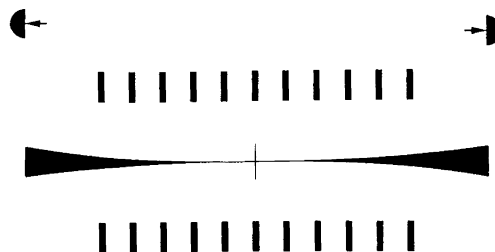


Fig. 1. "Butterfly" slit for recording real-time GED intensities. The bar patterns are used for detector alignment. For more details, see text and Ref. 5.

at a rate of 60 Hz, up to 1024 independent intensity points along a diameter of the pattern. Typically, integration for a few seconds will yield a set of low-noise intensities. Graphical views and analyses of the data during an experiment allow for on-line adjustment of operational conditions.

It is an advantage of the PDA that intensities are recorded without a rotating sector. Intensity curves ranging from about $s = 20$ to 400 nm^{-1} can be obtained in single exposures at an approximately 10 cm scattering distance. A "butterfly" slit⁵ makes this way of recording data possible. A mask covers the bulk of the scattering pattern, except for a slit with an $r^{2.5}$ or r^3 opening which simulates the effects of a sector. A negative image of the slit, which is essential for collecting high-resolution GED data in this way, is shown in Fig. 1. Typical PDA raw data are shown in Fig. 2 (detector images of the scattering of sulfur hexafluoride, SF_6 , and of argon).

At first sight, the graphs of Fig. 2 are rather disappointing. The curve for SF_6 , for example, bears little resemblance to the sinusoidal pattern expected for a molecule. Moreover, all images are visibly discontinuous and asymmetric (the

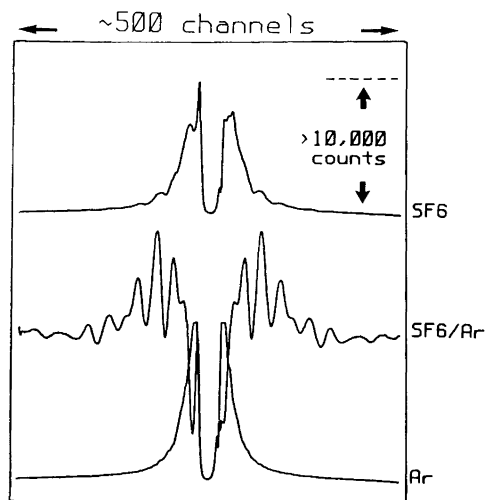


Fig. 2. Unprocessed detector images of some sample diffraction patterns (sulfur hexafluoride, SF_6 , and Argon, Ar), recorded through a butterfly slit with $r^{2.5}$ opening. When the intensity points for SF_6 are divided by those obtained for Ar, the curve (SF_6/Ar) in the middle of the figure results. The center of each image indicates the position of the beam trap (The curves are plotted on different scales).

center of each pattern is at the position of the beam trap, which can be behind a perforation in the center of the phosphor screen, casting a smaller shadow than a frontal device).

When the raw data for SF_6 are divided by those for argon, the information contained in them is suddenly revealed (unsmoothed ratio curve, Fig. 2). In the ratio curve, the discontinuities are eliminated, sinusoidal molecular scattering features emerge, and the pattern is symmetric. When the data are further processed in accordance with standard practice, intensities result which are shown for some standard samples in Fig. 3. Corrections typical for photographic work, such as flat plate ($\cos^3\theta$) and sector corrections, and s^4 terms, are specifically excluded from our data treatment, either because they do not apply or because they are cancelled when the ratio is formed. The model curves in Fig. 3 represent the ratios of total theoretical intensities (data for the molecules divided by data for argon), while the featureless curves, passing through them, represent molecular atomic backgrounds divided by those for argon.

Some characteristic aspects of the ratiometric data analysis procedure

Figs. 2 and 3 illustrate how effective ratiometric procedures are for channel correction in real-time GED. Individual data curves are affected by imperfections of the instrument, such as irregularities in the butterfly slit, inequalities in the PDA channels, graininess of the phosphor surface, etc. When the scattering curve of a molecule is divided by that of an atomic gas, all imperfections which are constant are removed from the data without perturbing the sinusoidal molecular interference waves. The division merely changes the usual zero-lines of intensities to the softly sloping curves (Fig. 3) of the atomic scattering ratios.

When the untreated scattering data for a molecule are divided by those for another, channel correction is achieved as with division by argon data, but some new and potentially valuable features emerge. Fig. 4 shows the radial distribution (RD) curve of CCl_4 which was obtained by Fourier analysis of experimental data whose channel correction was performed with an argon sample containing some nitrogen. That is, in addition to division by argon data, the CCl_4 intensities were

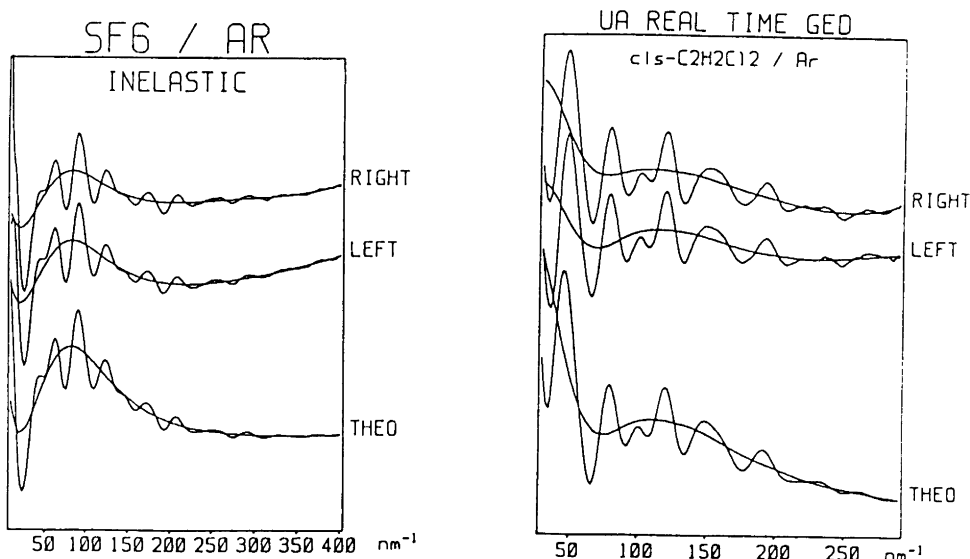


Fig. 3. Experimental (RIGHT and LEFT sides) and theoretical (THEO) total intensity ratios, and corresponding background ratios for SF_6 and C divided by data for Ar. Inclusion of inelastic scattering factors in the theoretical calculations is necessary to generate the characteristic minimum in the SF_6/Ar atomic background at small s . See Ref. 5 and text for more details.

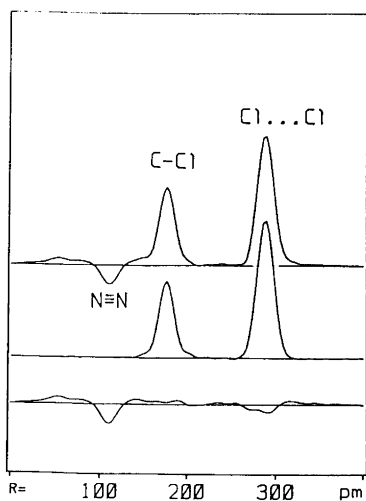


Fig. 4. Top curve: experimental Fourier transform of CCl_4 intensities whose channel correction was executed with an argon sample containing nitrogen gas, N_2 . The negative N_2 peak from the inverse intensities is seen at 110 pm. Middle curve: theoretical RD for CCl_4 (without N_2 contributions). Bottom curve: difference, i.e. experiment minus theory.

also divided by molecular, N_2 contributions. It is seen that the latter generate a negative peak in the Fourier transform at 110 pm, the N_2 bond position. Closer analysis shows that, in general, total intensity ratios are not exactly identical to $M(s)$ differences, but the Fourier transform of a ratio contains essentially the same information as the difference transform.

We have further studied this phenomenon in a number of examples. The SF_6/CO_2 intensity ratio⁵ and its Fourier transform are shown in Figs. 5 and 6. SF_6/CO_2 intensities (Fig. 5) show beat phenomena, not present for SF_6 (Fig. 3). The Fourier transform (Fig. 6) shows negative areas for CO_2 , with the bond distance peak at 116 pm. The $\text{O}\cdots\text{O}$ peak (usually 232 pm⁵) has depleted the $\text{F}\cdots\text{F}(\text{cis})$ peak of SF_6 (221 pm), whose remainder has shifted to 218 pm. The $\text{F}\cdots\text{F}(\text{trans})$ peak at 312 pm is unaffected.

Fourier transform of CO_2/N_2 is shown in Fig. 7. The corresponding data were taken for a mixture of CO_2 (15%) in N_2 , and divided by data recorded for N_2 (pure). Relative surplus of N_2 in the latter engenders negative N_2 contributions in the ratio RD curve, which deplete the $\text{C}=\text{O}$ peak of CO_2 . Since the two interacting peaks are not at the same positions, some fragments remain of N_2

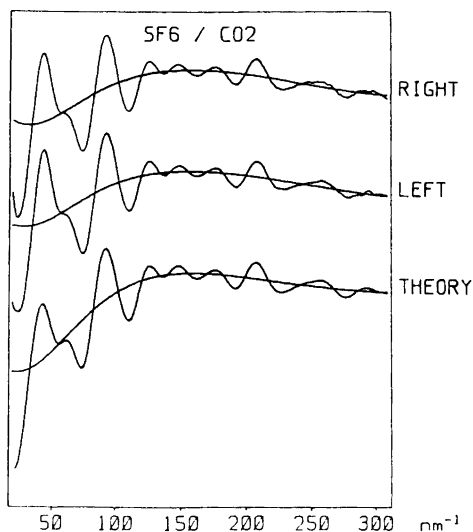


Fig. 5. Experimental (RIGHT and LEFT sides) and theoretical total intensity ratios, and background ratios for SF₆ intensities divided by data obtained for CO₂. For more details, see Ref. 5 and text.

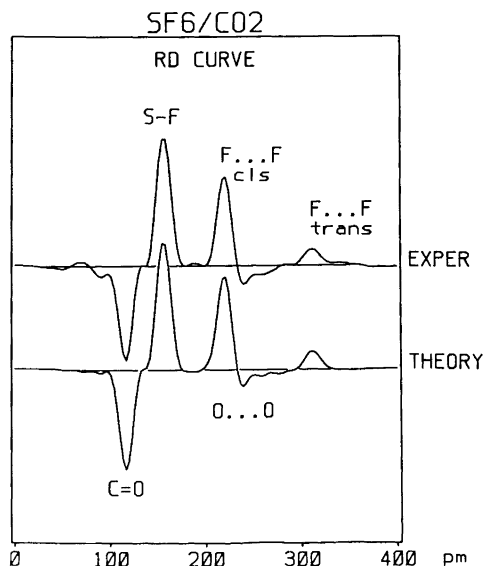


Fig. 6. Fourier transform of molecular intensities of SF₆ which were channel corrected with CO₂ intensities (see Fig. 5 and text). Top: experiment; bottom: theory.

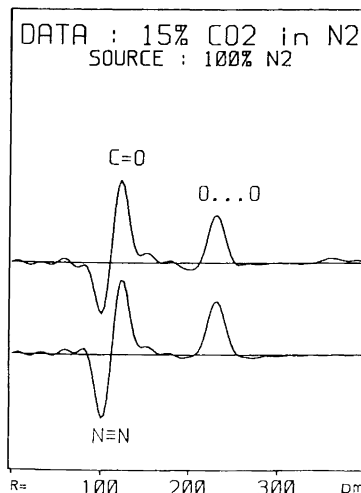


Fig. 7. Fourier transform of CO₂ intensities, channel corrected with data obtained for N₂. Top: experiment; bottom: theory. See text for additional details.

at 100 pm (shifted from 110 pm), and of C=O above 120 pm (shifted from 116 pm). The O...O peak is unaffected.

We think that the option of forming direct molecular intensity ratios represents an interesting aspect of real-time GED. Studies are underway to determine whether ratio analyses offer advantages in data evaluations. It is conceivable that they are useful for enhanced parameter resolution, or in special experiments, for example time-resolved studies, in which subtle changes in intensities are the main point of interest.

Investigations of photochemical and pyrolytic reaction products

Using real-time GED as described above, we have analyzed the data for a number of standard molecules,^{4,5} such as CO₂, CCl₄, C₆H₆, SF₆ and some di-halogenated ethenes.⁶ In each case, bond distances and angles were found in agreement with published values and with a precision comparable to that of photographic GED. In some contrast to this, mean amplitudes of vibration are typically too large compared to literature values. This discrepancy is an imperfection of the current procedure which we believe is caused by the optical component in the detection system. Modifications, using optical fibers, are under investigation.⁷

Regardless of the amplitude problem, the ability to determine accurate distances and angles by a real-time procedure offers interesting possibilities for novel types of experiments which will ultimately extend the domain of applicability that has been characteristic for photographic GED. For example, we expect that the novel procedures will be useful in studying photochemical and pyrolytic reaction products.

Investigations of Photochemical Reactions. One of the promising applications of real-time GED is to time-resolved studies of laser irradiated molecules, in order to determine the structures of transient species, such as excited states and reaction intermediates, and their time-dependent behavior. Pulsed electron beams, needed for pump-and-probe investigations of this kind, are readily generated by photoelectric phenomena.^{8,9} Therefore, a photocathode has been constructed in our laboratory,¹⁰ in which electron pulses, of about 15 ns duration, are generated with excimer laser pulses.

As a preliminary to these studies, we have investigated¹¹ the 193 nm laser-induced interconversion between *cis*-1,2-dichloroethene (C) and *trans*-1,2-dichloroethene (T). This photochemical reaction, involving stable parent and product species, was used to assess the sensitivity of our technique in detecting laser-induced molecular changes.

In these experiments,¹¹ a photolysis cell was installed close to the electron beam, and pure C (or T), flowing into the scattering center, was irradiated with 193 nm, 10 mJ ArF excimer laser pulses. Figs. 8 and 9 show experimental and model RD of irradiated and non-irradiated samples. When the laser was turned on (Fig. 8), the Cl...Cl peak of T, not present in non-irradiated C, emerged at 429 pm in irradiated C. Similarly, the Cl...Cl peak of C (326 pm, Fig. 9), not present in non-irradiated T, was found in irradiated T. In addition, the presence of chloroacetylene and possibly acetylene in the irradiated gases was inferred from the diffraction data, in good agreement with other photochemical studies of these molecules.¹²⁻¹⁵

Changes in intensities, when the laser was turned on, were instantly visible on the monitor of our system while the experiments were in progress, and made it possible to maximize the signals of interest (for example, by varying pulse

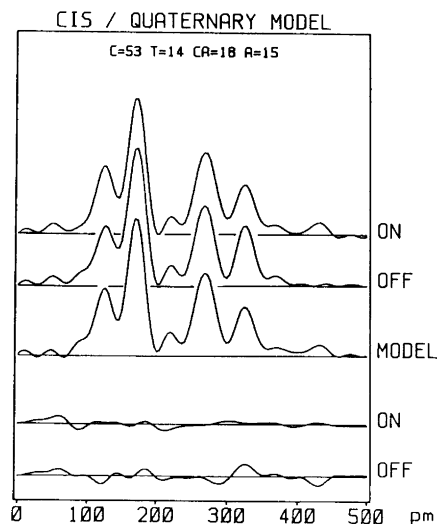


Fig. 8. Experimental radial distribution (RD) curves for irradiated (laser ON) and unirradiated (laser OFF) C. MODEL curve is theoretical RD for a molecular mixture containing 53 % C, 14 % T, 18 % chloroacetylene, and 15 % acetylene. Difference curves are experiment minus theory.

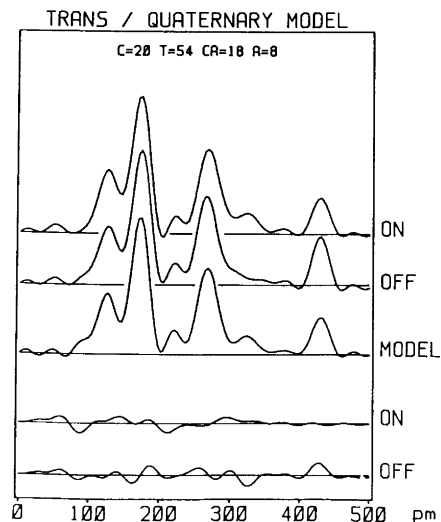


Fig. 9. Experimental radial distribution (RD) curves for irradiated (laser ON) and unirradiated (laser OFF) T. MODEL curve is theoretical RD for a molecular mixture containing 20 % C, 54 % T, 18 % chloroacetylene, and 8 % acetylene. Difference curves are experiment minus theory.

rate and power). Data equivalent to hundreds of photographic plates were recorded within a few hours to obtain consistent results. This is the first time that quantitative GED has been used to monitor a photoreaction.

Studies of Pyrolytic Reactions. During the last decades, the main application of GED has been in studies of ground-state structures of stable molecules, and work on short-lived species is practically non-existent. Andersen^{16,17} pioneered GED investigations of free radicals but his work remained restricted to stable species, similar to that of Bohn and Bauer.¹⁸ Observation of the first short-lived radical, viz. indenyl,¹⁹ was the result of an accidental decomposition which occurred during data recording. In later attempts at systematic investigations of pyrolytic reactions,^{20,21} the results were either not reproducible, or data interpretations were not conclusive.

The essentially off-line nature of photographic GED is the main reason for the lack of success in this attractive field. When transient species are involved, it is particularly important to work under well-defined and reproducible conditions, and to have a means for optimizing a signal of

interest while the experiment is being performed. Both prerequisites are lacking in photographic experiments.

In order to test the utility of real-time GED in this field, we have built^{22,23} a thermal reactor of the kind described by Braun *et al.*²⁴ The system consists of a quartz inlet tube for the diffraction chamber, whose tip is heated by 10.6 μ , 10W, CO₂ laser radiation. By varying laser intensity and focus, the temperature of a narrow zone in the tip of the inlet can be adjusted from room temperature to values above 1500 K (measurement by optical pyrometry). The scattering patterns of flash pyrolysis products of gases flowing through the heated zone are thus recorded before collision-induced secondary reactions occur.

Figs. 10 and 11 show RD curves observed at various temperatures for CF₃I and di-*tert*-butyl peroxide (DTBP), Fig. 12. Additional details of the experiments are described in Refs. 22 and 23.

In the case of CF₃I (Fig. 10), changes observed for different temperatures can be explained by mere variations in amplitudes of vibration. On the other hand, heating of DTBP (Fig. 11) to 800 °C leads to decomposition. The resulting RD curve is similar to that of acetone (quantitative

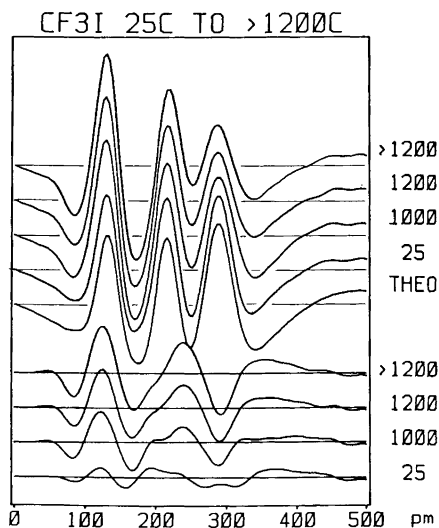


Fig. 10. Experimental RD curves for CF₃I recorded at 25, 1000, 1200 and >1200 °C. Theoretical curve is for the 25 °C experiment. Series of curves in the lower half of the figure are difference curves, i.e. experiment minus theory.

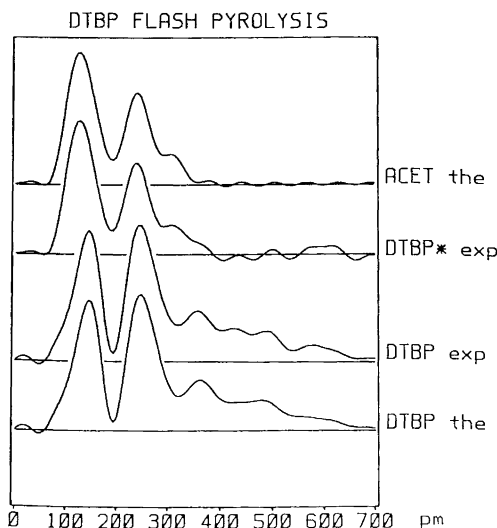


Fig. 11. Experimental and theoretical RD curves for di-*tert*-butyl peroxide (Fig. 12) recorded at room temperature (DTBP) and after flowing through an inlet system heated to >800 °C (DTBP*). The upper curve (ACET) is the experimental RD curve for acetone at room temperature.

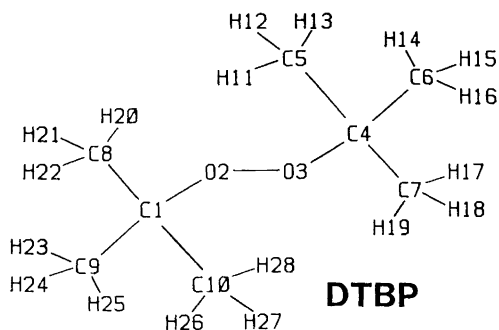


Fig. 12. Di-tert-butyl peroxide.

analysis still pending²²). Thus, while no short-lived species have yet been observed in these experiments, they nevertheless support expectations that identifiable unstable states should be obtainable from suitable parent compounds.

The advantages of the real-time method for investigations of this kind are obvious: since the experimental environment does not have to be disturbed between different sets of exposures, for example to retrieve photographic plates from the vacuum chamber, operational conditions are stable for different experiments and results are reproducible; changes in intensities are instantly discovered when temperature is changed; on-line observations allow for adjusting important operational parameters, such as nozzle temperature, to obtain the best results; finally, in contrast to photographic plates, the aluminized phosphor detector is not sensitive to incandescent light from the heated tip of the inlet.

Real-time GED as a detector in gas chromatography

On-line detection provides some opportunities for applying GED in areas not related to structural chemistry. For example, in GED combined with gas chromatography (GC-GED),^{23,25} the diffraction signal can establish the presence of compounds, at the same time providing molecular fingerprints which are useful for analytical purposes.

When a compound is eluted from the column of a gas chromatograph (GC) connected to the GED inlet,²⁵ total GED detector counts show the same variations as, for example, the thermal conductivity signals of a conventional GC. In Fig. 13,

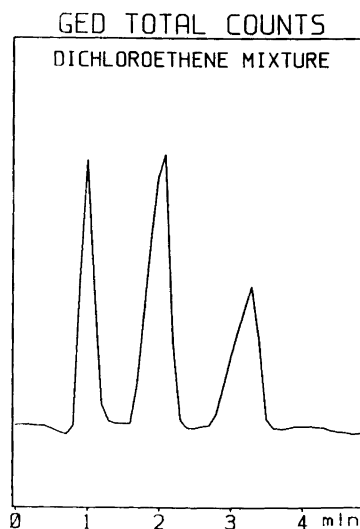


Fig. 13. Plot of variation of GED total counts vs. time during the flow of a 3 μ l sample (equimolar dichloroethene isomer mixture) from a GC column into the diffraction apparatus. For more details, see text and Ref. 25.

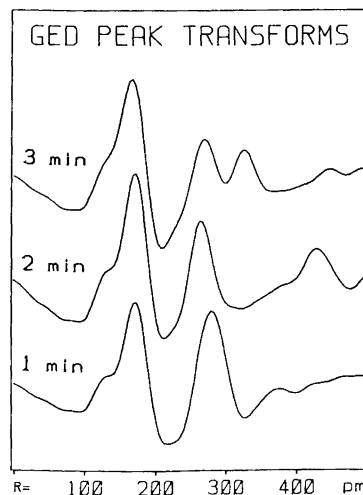


Fig. 14. Fourier transforms of the intensities obtained from the GED total count maxima (observed 1, 2 and 3 min after injecting a dichloroethene isomer mixture into a GC connected with the GED instrument) shown in Fig. 13. The RD curves are those of 1,1-dichloroethene (1 min), T (2 min) and C (3 min). Fourier transforms were performed without inclusion of theoretical points at small s .

time variations of GED total counts are shown which were observed after a nominally equimolar mixture of the dichloroethene isomers was injected into the GC-GED unit. The novel aspect here is that, in addition to signaling the presence of a compound, intensities are observed in each peak which can identify a given component. The Fourier transforms of the peaks of Fig. 13 are shown in Fig. 14.

Due to the small amount of sample injected (1 microliter each), only a limited number of exposures was possible for each experiment (3 to 5, vs. 20 to 40 for high resolution data). In addition the diffraction intensities were recorded in the presence of helium. Thus, the data range was narrow (typically $s = 20$ to 150 nm^{-1}) and the RD curves are of low resolution, sometimes with small artificial maxima resulting from series termination errors. Nevertheless, in Fig. 14, peaks of Fig. 13 are clearly assigned to 1,1-dichloroethene, T and C, respectively. For example, the *cis* and *trans* Cl...Cl peaks at 326 pm (for C) and 429 pm (for T) are clearly resolved in their RD curves. Thus, GED detection has quantified the amount, and identified the nature of the elutants in these GC experiments.²⁵

We think that if the sensitivity of the detector can be increased to measure smaller amounts of weakly scattering molecules, combined GC-GED can be an important tool in chemical analysis. So far, a 50 nanoliter sample of CCl_4 has been the smallest for which we have obtained intensity data and clearly resolved RD.^{23,25} This amount would probably be too small for photographic data recording. We expect that still more sensitive detection is possible for real-time GED.

Apart from the GC experiments, the possibility of obtaining diffraction data in the presence of a carrier gas may be of general interest. It seems that with the aid of a carrier, GED data can be recorded at lower temperatures than without, which may be important for temperature sensitive materials. The peroxide (Fig. 12, b.p. 113°C), for example, was swept through the unheated inlet tube following vaporization in the GC. Without helium and without heating, intensities were much less easily obtained for this molecule.

Conclusion

For investigations of ground-state molecular structures, real-time GED has not yet been developed to the perfection of the photographic method, due to the current amplitude problem. At the same time, since bond distances and angles can be determined accurately, new and exciting types of experiments can already be performed which are not within the reach of conventional GED.

Various possibilities for future improvements come to mind. The use of microchannel plates, fiber optics, or direct counting without a phosphor screen are some of many possible suggestions. Whatever the specific design may be, we have no doubt that multichannel detection will be a powerful tool and an important source of new information in future diffraction studies of structures and chemical reactions.

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