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TIME-RESOLVED STUDIES OF MOLECULAR PROCESSES INVOLVING
TRANSIENT SPECIES B. (U) ARKANSAS UNIV FAYETTEVILLE
DEPT OF CHEMISTRY AND BIOCHEMISTRY. 14 JUN 86

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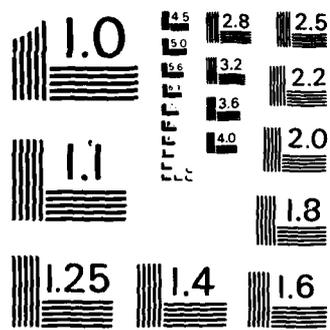
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University of Arkansas

ONR Contract End-of-the-Grant-Year Report 1985/86

1. Contract Information

1.a. Title: "Time-Resolved Studies of Molecular Processes Involving Transient Species by Synchronously-Pulsed Optical Excitation and Diagnostic Electron Scattering"

1.b. ONR Contract Number: N00014-85-K-0757

1.c. ONR Work Unit Number: NR 092-804/4-12-85 (430)

1.d. Principal Investigators:

Dr. John D. Ewbank

Dr. David L. Monts

Dr. David W. Paul

Dr. Lothar Schafer

1.e. ONR Scientific Officer:

Dr. Richard S. Miller

Code N00014

1.f. Period Covered: June 15, 1985 to June 14, 1986

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2. Research Description

2.a. Description of Research

We are constructing a Time-Resolved Electron Diffractometer (TRED) to study the structures of short-lived, energetic molecular states and the dynamics of primary dissociation processes found in molecules of energetic materials.

The experiments in preparation make use of the technology and techniques developed on our real-time data acquisition Gas Electron Diffractometer (GED), which is currently the only one of its kind. In this instrument, a 40 keV, continuous, focused electron beam is crossed at right angles by a gaseous molecular beam, and the electron scattering pattern generated is converted to an optical image by a phosphor screen; this image is then transferred by a lens onto a 1024 element photodiode array (PDA). The channels of the PDA detect the angular dependence and intensity profile of the electron scattering along a radial line of the circularly symmetric pattern. This new procedure effectively replaces conventional photographic GED techniques. On-line optimization of GED experimental conditions and ratiometric data analysis are essential for studying short-lived energetic species and for performing time-resolved investigations.

The TRED experiments will be performed by focusing the 193 nm output of a pulsed excimer laser (pulse duration 10-20 nanoseconds) onto the cold photocathode of a high voltage electron gun, where electron pulses will be generated by field-assisted photoelectric emission. These pulses will be scattered off the gas-phase molecules in an effusive molecular beam after some fraction of the beam population has been excited by a pulse from an excimer-pumped dye laser. Electron diffraction intensities will be recorded using our real-time GED technology. By synchronizing the dye laser excitation pulse and the diagnostic electron pulse, scattering data can be obtained from molecules which all have the same age relative to the time of excitation. Thus, both time-resolved and time-unresolved observations of excited molecular states and of transient reaction products should be possible.

The TRED pump-and-probe experiments represent a new approach to structural studies of reactive systems and of the dynamics of dissociation processes of energetic molecules. These investigations can be expected to enhance our understanding of chemical reactivity in a fundamental way. The results can be of crucial importance, for example, in the design of energetic materials.

2.b. Significant Results of the First Grant Year

2.b.1. Design and Construction of TRED Apparatus

A considerable portion of our time during the past year was devoted to designing the space charge-limited photocathode and the associated detection scheme needed for the TRED experiments. Assembly of the TRED system has begun and soon we will be testing the performance of our first photocathode design.

Substantial effort was also exerted on the optical aspects of the TRED unit. An excimer laser-pumped dye laser has been installed. The optical system for delivery and containment of the 193 nm laser light simultaneously from two directions onto the photocathode has been designed and acquisition of components completed. The performance of the present excimer laser has been characterized as part of the design work for the optical system. The process of purchasing the required second excimer with DoD-URIP funds has been initiated.

2.b.2. Improvement of Angular Detection Range

The first published description of the real-time GED unit appeared in the fall of 1984 [Rev. Sci. Instrum. 55(1984) 1598].

At that time the instrument had begun to generate useful data, but the accessible data range was somewhat limited. During the last year, this deficiency has been further diminished. That is, the accessible scattering range is now similar to that achieved in conventional photographic GED studies. Descriptions of these improvements have recently been published [see section 2.f, reference 1 (i.e., 2.f:1); see also 2.d:1; reprints attached]. Preliminary results indicate that an additional extension of the detection range to twice that in our Initial Rev. Sci. Instrum. report may be possible [see Figure 2.1:1].

2.b.3. Characterization of Multi-component Systems

During a structural study of the cis- and trans-dichloroethenes [preprint attached], observation of a negative N_2 peak due to an air leak in the sample line [see Figure 2.1:2, and also ref. 2.f:1] inspired us to investigate the minimum amount of "impurity" that might be observed. We obtained a calibrated gas mixture of 15.0% CO_2 in N_2 . This mixture was chosen because the $N\equiv N$ bond distance in N_2 is similar to the $C=O$ internuclear distance of CO_2 , and thus the CO_2 "simulates" a minority species, such as an excited electronic state or a dissociation product. The scattering pattern of the mixture was compared to the scattering pattern of the pure N_2 , thus enhancing

differences. The 15% CO₂ component was readily detected, and the Fourier transformed data are shown in Figure 2.1:3. Attempts to detect 0.100% vinyl chloride in N₂ have not yet been conclusive, but we feel that further improvements in instrumentation may lead to success. These results were so encouraging that we submitted a proposal to the National Science Foundation to use the real-time GED as a detector for gas chromatography [2.k:2].

Figure 2.1:4 shows the Fourier transformed data for the two isomers of 1,2-dichloroethene, as well as the transform of their ratio. These curves indicate the subtleties of internal structure which may be available under actual TRED conditions, when the ratiometry of data sets is fully utilized. In the example, bond length changes of a few picometers are readily detected. It must be emphasized that these conclusions are preliminary, since TRED conditions should often result in a more complicated, multi-component mixture of species that must be analyzed.

2.b.4. Pyrolytic and Photolytic Investigations of Transient Species

A collaboration has been formed with Dr. Walter Braun of the National Bureau of Standards to use the present real-time GED

to study transient species generated by laser-induced flash pyrolysis. In Braun's technique [Chem. Phys. Letters 113 (1985) 407 and ibid., 118(1985) 229], the gas of interest is passed through a quartz tube whose exit is drawn out to a small orifice. A cw CO₂ laser is focused down the tube so that the quartz only absorbs light near the orifice. Gas-phase molecules in that vicinity can be heated to temperatures exceeding 1000 K, and consequently undergo thermolysis. Since their transit time through the heated orifice is short (typically 20 microseconds), secondary reactions are severely limited. These pyrolytic GED experiments should aid our efforts to interpret TRED results, since they allow us to use a continuous electron beam GED unit with known performance to refine the data analysis techniques necessary to characterize transient species. Dr. Walter Faust has obtained the loan of the laser necessary to perform these experiments, and we are currently nearing completion of its rejuvenation. Dr. Braun has fabricated several quartz cells for use on this project.

Also using the present GED unit to develop techniques required for TRED, we are currently attempting to observe transient photodissociation products formed by focusing the 193 nm, pulsed excimer laser beam through the window of a modified sample inlet mounted inside the present real-time GED unit. It is hoped that the entrained volume of this photolysis cell will

provide a quasi-continuous population of transient species for probing by the continuous electron beam.

2.b.5. Detector Sensitivity for Diffracted Electrons

Another project devoted to the essential techniques required for optimum TRED performance involves improvement of the sensitivity of the data collection system. Calculations based on reasonable estimates of the detection parameters yield a sensitivity of 10^{-3} counts per diffracted electron for the existing detector system [2.k:1]. This estimate for the sensitivity is relatively small, mainly because the light collection efficiency of the transfer lens is only 0.5%, which we cannot expect to improve significantly. Lateral light propagation in the glass support of the phosphor also contributes to the diffuse background that is characteristic for our instrument, and leads to phosphor screen "cross-talk" that has been recently described [2.f:1]. We predict that optical inefficiencies can be virtually eliminated by fiber optic coupling of the phosphor screen to the PDA. The sensitivity for the resultant system can be expected to be much greater than 0.1 counts per diffracted electron, approaching single electron counting. This improvement could be an important factor in the TRED studies to be carried out in the coming months. From the promise of these calculations,

a proposal for a fiber optic PDA detection system for the TRED apparatus was generated and submitted [2.k:1].

A phosphor-coated fiber optic vacuum view port for the present real-time GED unit was designed in anticipation of ultimately fiber optically coupling the TRED PDA and to test our understanding of lateral light propagation. This was constructed using funds specifically allocated for this purpose. The device has only just arrived and has yet to be tested. We currently believe that the existing detection system will be sufficient for the initial TRED experiments, but for ultimate sensitivity with weak signals, the fiber optic coupled detector will be essential.

2.b.6. Studies of Ground State Systems

During the first grant year, the structures of several molecules which are candidates for TRED experiments have been calculated. These ab initio gradient results can be combined with GED data in the MOCED [Molecular Orbital Constrained Electron Diffraction] technique, which was pioneered by the Arkansas group [for a review, see 2.g:1]. Molecules studied to date are nitromethane, nitrosomethane, and methyl nitrite; soon to be included are dimethyl nitramine and dimethyl nitrosamine. All calculations provide a conformational energy and structural

map at both the 421-G and the 531-G** gradient level. Although the ground states of some of the above molecules have been studied previously by conventional GED, the results are somewhat dated; additionally, the power of MOCED to accurately resolve subtleties of structure has only more recently been demonstrated [J. Mol. Struct. 100(1983) 51].

2.b.7. Postdoctoral Search

We have conducted a postdoctoral search to fill the position funded by this grant. The successful candidate is Dr. Khamis Siam, a recent graduate of this Department. Dr. Siam has expertise in electron diffraction and quantum chemical methods for the calculation of molecular structures. He will provide the additional manpower power necessary for the assembly and testing of the TRED unit in a timely fashion. His duties will also include quantum chemical calculations on candidate molecules. He voluntarily performed the calculations described in section 2.b.6 even before his appointment began.

2.c. Plans for Future Research

Testing and characterization of the photocathode performance

will begin in the coming months. Successful TRED detection of transient species present in low concentration requires extensive characterization and optimization of the laser-induced photo-emissive beam. This process is currently expected to require substantial effort during the next year and will be performed by producing scattering patterns of stable systems, including solid state powder or foil samples.

Specific experiments on laser-initiated flash pyrolysis will include studies of CF_3I , CCl_3Br , CH_3I , and cyclopropane. Experiments on laser-induced photolysis using the present real-time GED will attempt to observe the CS radical produced by the photolysis of CS_2 at 193 nm.

Testing of the phosphor-coated fiber optic view port will also be performed this year. Further, attempts will be made to improve the detector sensitivity by fiber optically coupling the phosphor signal to a PDA.

2.d. Grant Related Presentations:

1. John D. Ewbank, Lothar Schafer, and David W. Paul, "Recent Improvements in Real Time Gas Electron Diffraction", Eleventh Austin Symposium on Molecular Structure, University of Texas, Austin, Texas, March 3-5, 1986, paper WM2.

2. Seminars presented by Lothar Schafer at University of Ulm (W. Germany), University of Tübingen (W. Germany), University of Antwerp (Belgium), and University of Bologna (Italy), May/June, 1986; and Louisiana Tech University, Louisiana State University at Shreveport, Northeast Louisiana University, Centenary College, and East Texas Baptist University, March, 1986.
3. Seminar entitled "Recent Advances in Real-Time Electron Diffraction" presented by David Paul at Texas Woman's University, April, 1986.

2.e. Technical Reports: none.

2.f. Grant Related Publications:

1. J.D. Ewbank, L. Schafer, D.W. Paul, D.L. Monts, and W.L. Faust, "Improvements in Real-Time Data Acquisition for Gas Electron Diffraction", Rev. Sci. Instrum. 57(1986) 967. [Reprint attached.]
2. D.W. Paul, J.D. Ewbank, and L. Schafer, Invited Description of the University of Arkansas Real-Time Electron Diffraction Unit (IR-100 award publication), Res. Dev. 27(10)(1985) 64. [Reprint attached.]
3. L. Schafer, J.D. Ewbank, K. Siam, D.W. Paul, and D.L. Monts, "Molecular Structures of cis- and trans-1,2-Dichloroethene: A Real-Time Gas Electron Diffraction and ab initio Study", J. Mol. Struct. (accepted for publication). [Preprint attached.]

2.g. Other Publications:

1. L. Schafer, "Concerted Use of Electron Diffraction and Quantum Chemical Calculations" in Stereochemical Applications of Gas-Phase Electron Diffraction (I. Hargittai, editor) (VCH Publishers, 1986).
2. K. Siam, J.D. Ewbank, and L. Schafer, "Comparison of the

- Electron Diffraction and ab initio Structures of Neopentane and Di-tert-butyl Methane", J. Mol. Struct. 137(1986) 155.
3. L. Schafer, J.D. Ewbank, C. Van Alsenoy, V.J. Klimkowski and K. Siam, "Predictions of Relative Structural Trends from Standard Geometry Functions", J. Mol. Struct. (accepted for publication).
 4. L. Schafer, K. Siam, J.D. Ewbank, and E. Osawa, "Simple Procedure for Quantitative Prediction of the C-C Framework Bond Distances and Angles in n-Hydrocarbons", J. Mol. Struct. (submitted).
 5. C. Van Alsenoy, K. Siam, J.D. Ewbank, and L. Schafer, "Ab initio Studies of Structural Features Not Easily Amenable to Experiment. 49. Conformational Analysis and Molecular Structures of Ethylenediamine and Aminoethanol", J. Mol. Struct. 136(1986) 77.
 6. K. Siam, C. Van Alsenoy, J.D. Ewbank, N.L. Allinger, and L. Schafer, "Ab initio Studies of Structural Features Not Easily Amenable to Experiment. 50. Standard Geometry Functions for Ethanol, Ethylamine, Propanol and Propylamine", J. Mol. Struct. (submitted).
 7. C. Van Alsenoy, K. Siam, J.D. Ewbank, and L. Schafer, "Ab initio Studies of Structural Features Not Easily Amenable to Experiment. 51. Conformational Analysis and Molecular Structures of Methoxyacetic Acid", J. Mol. Struct. (accepted for publication).
 8. B. Brown, D.W. Paul, W.R. Heineman and T.H. Ridgway, "Purification of Supporting Electrolyte by a Moderate Current Pre-Electrolysis Potentiostat", Analytical Instrumentation, 15, (1986), 63-76.
 9. J.C. Lowrey, T.M. Scott, and D.W. Paul, "Development of an Electroanalytical Method to Monitor Reactions on a Lithium Surface", J. Electrochem. Soc. (accepted for publication).
 10. D.G. Grande and D.W. Paul, "A Data Collection and Analysis System for Frequency and Electrochemical Data", Analytical Instrumentation (accepted for publication).

2.h. Honors, Awards:

Our present real-time electron diffraction unit has received a 1985 IR-100 award. It was selected by Research and Development magazine as one of the 100 most important technological advances of the year. (Material describing the award is attached.)

2.i. Current Participants:

Department of Chemistry and Biochemistry, University of Arkansas:

Dr. John D. Ewbank, Senior Research Associate; Dr. David L. Monts, Assistant Professor; Dr. David W. Paul, Associate Professor; Dr. Lothar Schafer, Professor; Dr. Khamis Slam, post doctoral fellow.

Department of the Navy, Naval Research Laboratory:

Dr. Walter L. Faust, code 6540.

Center for Chemical Physics, National Bureau of Standards:

Dr. Walter Braun.

2.j. Other Sponsored Research:

1. L. Schafer, "Construction of a Real-Time Gas Electron Diffraction System and Structural Studies by Joint Experimental and ab initio Calculations", US/NSF/ ARKANSAS/EPSCOR, 10/1/83 to 3/31/86, \$91,341.
2. L. Schafer and D.L. Monts, "Picosecond Time-Resolved Electron Diffraction Studies of Unimolecular Decomposition", DoD-URIP, 8/1/84 to 8/31/86, \$257,000.
3. D.L. Monts and L. Schafer, "Time-Resolved Studies of Transient Molecular Species by Synchronously Pulsed Optical Excitation and Diagnostic Electron Scattering", ACS-PRF, 7/1/86 to 8/31/88, \$35,000.
4. D.L. Monts, "Investigation of the Use of Heavy Bridging Atoms as Energy Flow Blockers for Laser-Selective Chemistry", Arkansas Science and Technology Authority, 5/15/86 to 5/14/87, \$14,898.
5. D. Paul, "Refinement of a Transferase Analyzer", NIH-BRSG, 11/15/85 - 10/31/86, \$4,200.
6. D. Paul, "A Fundamental Study of the Reaction Between Organic Halides and Lithium Metal", Research Corporation, 11/1/82 - undefined, \$9,300.
7. D. Paul, "Determination of Transferases Using a Piezoelectric Crystal", NIH-BRP, 7/15/84 - 7/14/85, \$14,956.
8. D. Paul, "Investigation of Electrodeposited Films Using a Piezoelectric Crystal", DOE Used Equipment grant, 6/1/86, \$1,067.

2.k. Proposals Submitted:

1. D.W. Paul, D.L. Monts, J.D. Ewbank, and L. Schafer, "Optimum Detector for Time-Resolved Electron Diffraction Studies of Energetic States and the Dynamics of Primary Dissociation Processes of Energetic Materials", DoD-URIP, \$177,000 (Declined).
2. L. Schafer, J.D. Ewbank, D.W. Paul, and D.L. Monts, "Research Toward the Application of Real-Time Gas Electron Diffraction as a Detector for Gas Chromatography", NSF, \$115,504 (Pending).

Figure 2.2:1. Experimental (right and left sides) and theoretical total intensity ratios for SF₆ divided by Ar. These extended data represent an included scattering angle for simultaneous detection of about 45°.

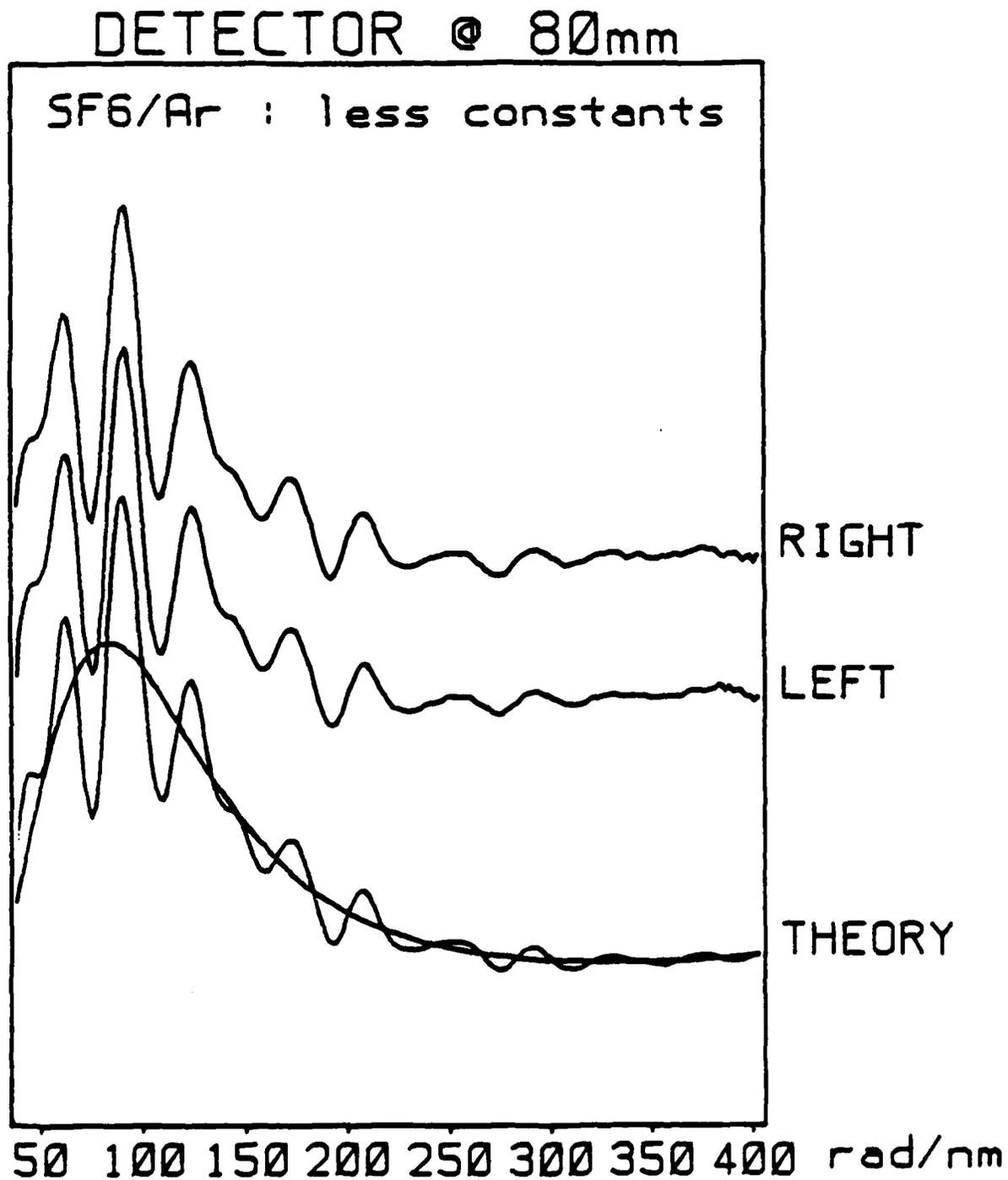


Figure 2.2:2. Experimental (top) and theoretical (middle) Fourier transformed data and the differences (bottom), experiment minus theory, for CCl_4 . The experimental data are contaminated with N_2 ; the negative N_2 peak is seen at about 110 μm .

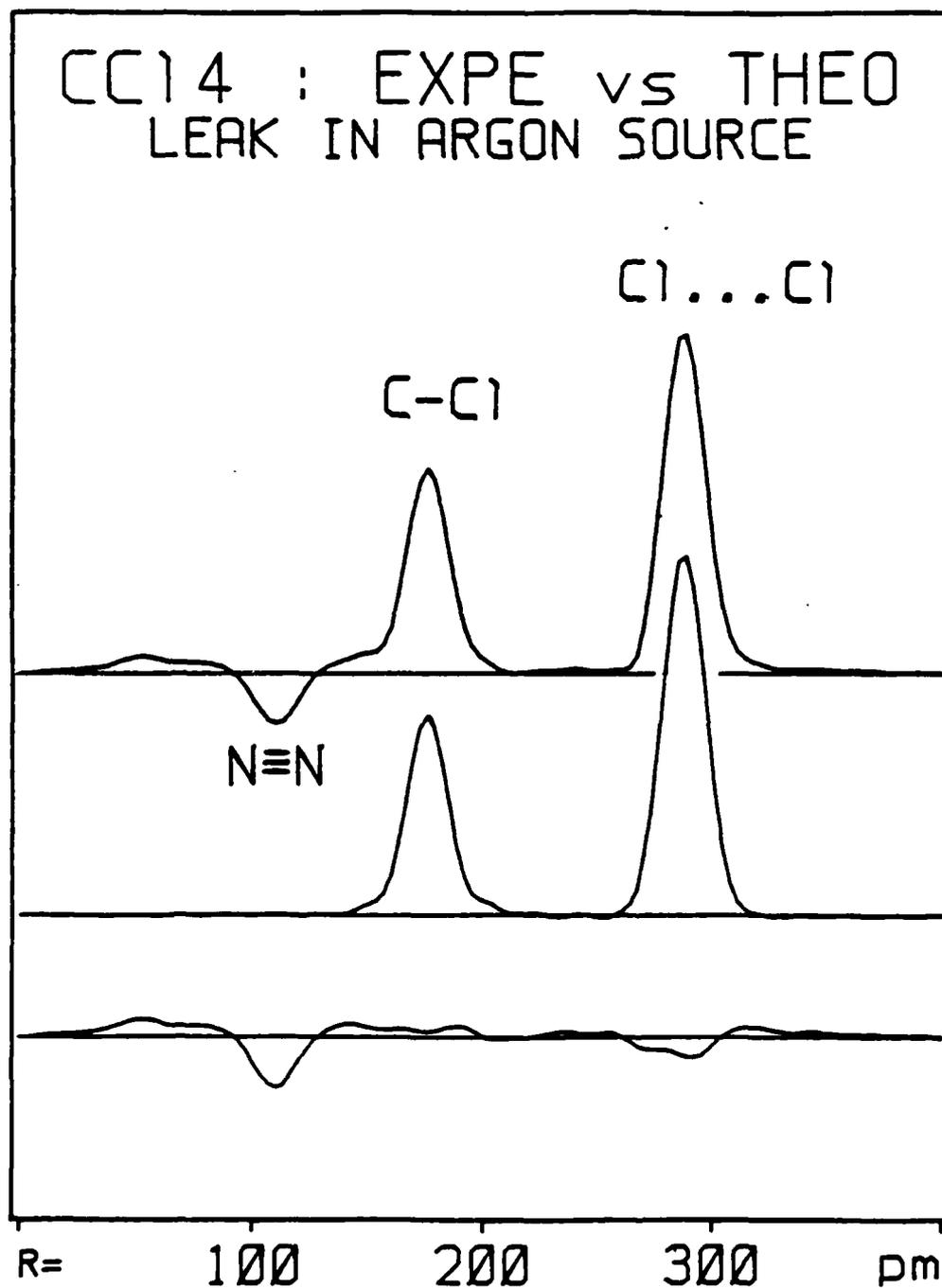


Figure 2.1:3. Experimental (top) and theoretical (bottom) Fourier transformed data for a 15% CO₂/85% N₂ mixture, referenced to 100% N₂. The negative peak at about 110 pm results from the relative overabundance of N₂ in the pure source gas.

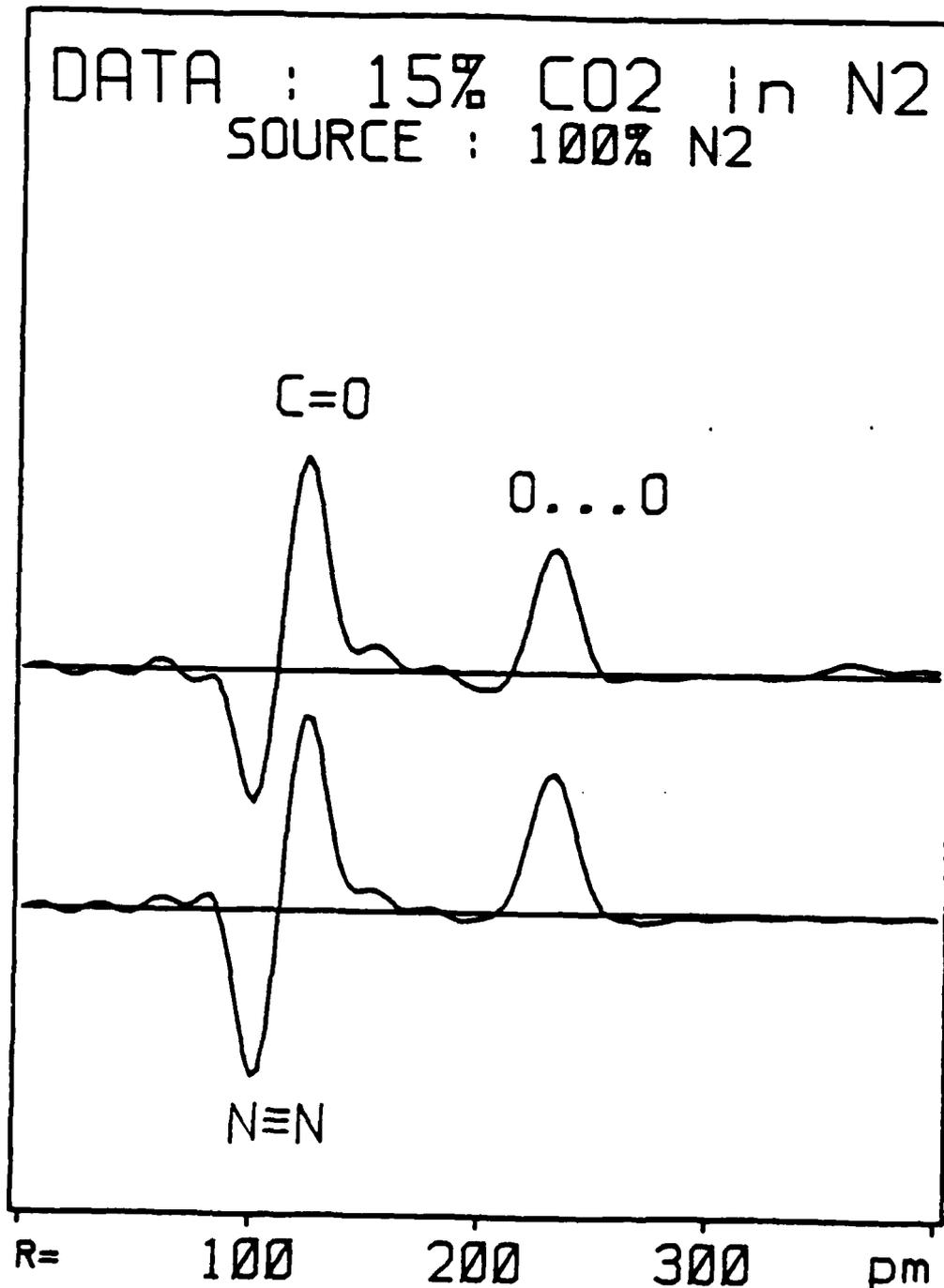
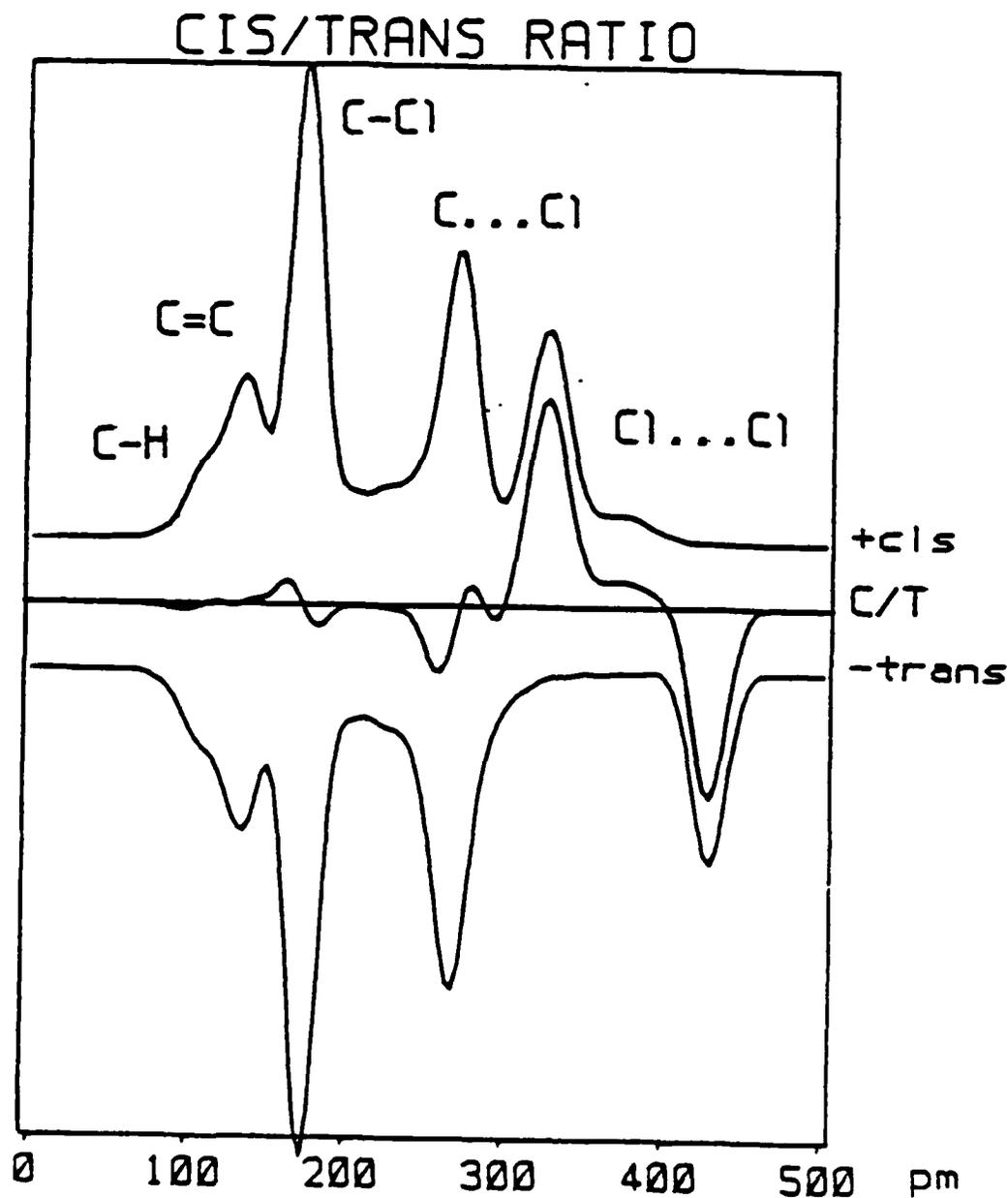


Figure 2.2:4. Experimental Fourier transformed data for cis-1,2-dichloroethene (top); for trans-1,2-dichloroethene (bottom, negative); and the transformed raw data ratio (middle) of the cis isomer divided by the trans isomer. The dramatic isomeric shift of the Cl...Cl intramolecular distance is accompanied by smaller changes in C-Cl and C...Cl internal distances of only a few picometers.



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