Equilibrium Structure for CClF$_3$ Using Real-Time and Time-Resolved Gas Electron Diffraction

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ABSTRACT. The simplified cumulant method was applied to diffraction data of CClF$_3$ to study the equilibrium molecular parameters over a range of temperatures. The molecular parameters of CClF$_3$ by the simplified cumulant method were compared with those from the traditional method. Also the instrumentation of picosecond time resolved electron diffraction (TRED) and the experimental details are described. The total experimental temporal resolution was discussed in terms of the electron pulse width. The TRED system was applied to study the molecular structures for CClF$_3$ at room temperature. The molecular structural parameters CClF$_3$, from TRED are compared with those from GED/RT. The molecular parameters (r$_e$) of bonded C-F and C-Cl for CClF$_3$, by simplified CA are 132.00(2) pm and 175.20(3) pm, respectively, by using GED/RT. From the results of TRED experiments r$_e$ for bonded C-F and C-Cl are 132.23(13) pm and 177.23(19) pm.

Keywords: Molecular Structure, Time-Resolved Electron Diffraction, Gas Electron Diffraction

INTRODUCTION

A real time gas electron diffraction (GED/RT)$^{1,2}$ instrument was constructed with a multichannel photodiode array (PDA) detector, and is thus an online technique. GED/RT has been applied to discriminate among various molecular force fields as derived from high-resolution spectroscopy. In conjunction with cumulant analysis,$^1$ the method determines not only the vibrational average structures, but also the equilibrium molecular geometries. The method applies to both equilibrium and non-equilibrium molecular ensembles. A simplified CA (cumulant analysis) procedure$^3$ was developed recently to allow for data refinements without the need for extraneous information from spectroscopy.
To capture the dynamics of structures in transition states, ultrafast time resolution must be introduced to the diffraction. Previously, it was possible to probe such changes with femtosecond and picosecond spectroscopy to reveal the elementary nuclear motion. The use of an ultrafast laser beam at the scattering center of GED/RT in order to photoexcite the molecules, and at the photocathode to make ultrashort electron pulses, provides a similar pump-and-probe process.

The first time resolved electron diffraction (TRED) system was used to study the structure of radical products formed in the IR multiphoton dissociation of CPF in the microsecond time domain. The temporal resolution was further improved to nanoseconds (ns) by combining a laser initiated electron source with a linear diode array detector to study the 193 nm photodissociation of CS₂ in the time interval from 20-120 ns after excitation. Recently, a TRED system has been reported to observe the UV-dissociation of CF₃I with picosecond (ps) time resolution. Also, the photodissociations of Fe (CO)₅ and CF₃I were studied with picosecond time resolution, but a clear result has not yet been attained. In recent years a number of other dynamic methods such as Time of Flight (TOF) mass spectrometry and Femtosecond Transition-state Spectroscopy (FTS), have probed chemical reactivity in attempts to ascertain critical reactive intermediates and kinetic pathways.

On the theoretical side, time-dependent equations for diffraction intensities have been derived for non equilibrium vibrational distributions for the case of photodissociated CS₂, and for the photoinduced coherent intramolecular dynamics of dissociative and predissociative transient states of ICN, IBr and NaI. Also a new approach was developed to measure directly the quantum state of a molecular ensemble. Only very recently TRED has become available as a new and complementary source of "structural kinetic" information for excited state species. In addition, the simplified-CA method was applied to the diffraction data of CClF₃. The TRED system was used to determine molecular structures for CClF₃. The molecular structural parameters CClF₃ from TRED are compared with those from GED/RT.

**Theoretical Procedures**

There exist alternative methods for calculating Iₚ(s) by making the vibrational and rotational averages, \(<\exp\{i s(r - r_f)\} >\). Displacements of the nuclear positions with respect to their equilibrium positions are expanded in terms of the normal coordinates and vibrational averages taken; then, the average over random orientations of the molecule is obtained. One can get reduced molecular intensities with cumulant average and the vibrational probability density function as follows:

\[ sM(s) = \sum_{ij=1}^{N} g_6(s) \exp \{ Q_i(s) \} \sum_{ij} A_{ij}(s) \sin [s(r_{ei} + P_{ij}(s))] + B_{ij}(s) \cos [s(r_{ei} + P_{ij}(s))] \]  \( (1) \)

where (omitting the subscripts \( i, j \) for simplicity)

\[ Q_i(s) = -s^2 < \Delta r_i^2 > / 2 + s^4 < \Delta r_i^4 > / 24 \]

\[ P_i(s) = < \Delta r_i > - < \Delta r_i^3 > / 6 \]

\[ A_i(s) = 1 - < \Delta r_i > - s^2 < \Delta r_i^2 > / 2 / r_i + ... \]

\[ B_i(s) = -s < \Delta r_i^2 > + s^2 < \Delta r_i^4 > / 6 / r_i + ... \]

Equation (1) provides a basis for least-squares model refinement from GED data. One can adjust the equilibrium internuclear distances \( r_i \) and cumulants \( < \Delta r_i^2 > \) with \( n = 1-4 \). The latter can be assigned a clear meaning in terms of properties determining the vibrational probability density function: \(< r > = r_i + < \Delta r >\) is the mean position, \(< \Delta r_i^2 > = I_{ij}^2\) is the dispersion, \(< \Delta r_i^4 >\) is the skew, and \(< \Delta r_i^4 >\) is the excess, respectively, of the probability density.

It is useful to consider the dimensionless cumulant coefficients, \( g_n \), which are defined by:

\[ \gamma_n = < \Delta r_i^n > / < \Delta r_i^2 > r_i^n \]  \( u = 1, 3, 4, ... \)  \( (2) \)

The \( g_n \) values are sensitive functions of the molecular force field and vibrational distribution. By inserting Eq. (2) into Eq. (1) one obtains

\[ sM(s) = \sum_{ij=1}^{N} g_6(s) \exp \{ Q_i(s) \} \sum_{ij} A_{ij}(s) \sin [s(r_{ei} + P_{ij}(s))] + B_{ij}(s) \cos [s(r_{ei} + P_{ij}(s))] \]  \( (3) \)

where,

\[ Q_i(s) = -s^2 < \Delta r_i^2 > / 2 + s^4 g_6(s) < \Delta r_i^4 > / 24 \]
\[ P_1(s) = g_r \Delta \Lambda^2 >, \quad 1 - s^2 g_r \Delta \Lambda^2 >, \quad 2 / 6 \]
\[ A_2(s) = 1 - s g_r \Delta \Lambda^2 >, \quad 2 s^2 g_r \Delta \Lambda^2 >, \quad 2 / 2 \] / \[ r + \ldots \]
\[ B_2(s) = -s >, \quad s^2 g_r \Delta \Lambda^2 >, \quad 2 / 2 \] / \[ r + \ldots \]

To summarize, the cumulant method establishes a general relationship between diffraction intensity and cumulant averages. This relationship is accurate to any desired degree of approximation. The CA equation is based on geometrically consistent \( r \) parameters and is valid for non-equilibrium systems without extraneous information on harmonic and anharmonic potential constants. The traditional intensity equation is based on \( r \) geometries which are geometrically inconsistent. The molecular parameters obtained by cumulant analysis are more precise than those obtained by the traditional method. Further, the method may be applied to check the validity of anharmonic force fields derived from various spectroscopic investigations.

The simplified version of the CA of GED intensities was developed some time ago. In actual refinements of \( r \) and \( \gamma \) from GED data, extensive parameter correlations were found. Therefore, some approximate constraints between the cumulant coefficients are needed to apply Eq. (3) to GED data analyses without auxiliary spectroscopic calculations.

The least square refinements of molecular intensities can be performed on the basis of Eq. (3) with the approximate constraints. This is the scheme known as simplified CA. This simplified CA retains the conceptual consistency of full CA but allows for GED data refinements without the need for extraneous information or additional computational analysis. The simplified CA procedure can be applied to molecular ensembles at high temperatures and to excited systems. However, the omission of information on vibrational populations and potential constants in the simplified CA procedure is expected somewhat to diminish the accuracy in comparison to the full formalism.

In order to derive theoretical intensity expressions for non-equilibrium systems, one may use the theory afforded by cumulant expansions of the diffraction intensities. This level can be applied in studies of intramolecular vibrational redistribution processes at low levels of vibrational excitation, when the normal mode description of the molecular vibrations is still adequate. The processes of relating the harmonic and anharmonic force constants to electron diffraction intensities and spectroscopic constants are quite involved. First of all, the renormalized frequencies are calculated at the appropriate temperatures. Then, curvilinear internal coordinates are transformed to normal coordinates by a nonlinear transformation. Next the moments are calculated in terms of the potential function in normal coordinate space. Then the cumulants are calculated in internal coordinates and the molecular intensity function is obtained. The refinements are carried out with a Hooke and Jeeves computer algorithm.

**Instrumentation and Experimental Procedures of GED/RT and TRED**

A) Instrumentation and Procedures for GED/RT

The GED/RT system has been described elsewhere. There are three chambers (diffraction, electron and detector) with molecular inlet system and temperature controller. The diffraction and electron chambers are separated from each other and pumped independently. The electron chamber provides a stable high vacuum region for the collimation and positioning of the electron beam. The collimated electron beam interacts with the molecular beam in the diffusion chamber. A PDA is used for on line detection of the diffraction pattern on a fluorescent screen in the detector chamber.

The electron beam with well-defined wavelength is produced in an electron gun with a hot cathode filament of tungsten. The electrons are emitted thermally and are drawn and accelerated by the potential of the anode. The accelerated electrons leave the electron gun through a central hole in the anode. The electron beam is focused onto the registration plane by a magnetic lens.

Most groups still use densitometers which are single channel measuring devices to analyze the electron diffraction data. The method has proven to be successful but the stepping procedure is some-
what time consuming and, like all mechanical processes, it involves inevitable positioning uncertainties. Therefore, a position sensitive multichannel analyzer (PDA) is applied for analyses of the full diffraction pattern in one measurement. The PDA provides precise spatial resolution and offers high sensitivity and a large dynamic range. In the Ge:D/RT instrument, a focused electron beam is crossed by a molecular jet, and the diffraction pattern is displayed on a fluorescent screen. The screen is optically coupled to a photodiode array which records the intensity distribution on-line, in a multichannel mode, and without the intervention of the rotating mechanical sector needed in photographic Ge:D. The diffracted electrons are transformed into photons by the aluminized P20-type phosphor. The PDA is aligned on the opening of the butterfly slit. The PDA consists of a set of 1024 independent silicon photodiodes of pixel size 25 μm by 2.5 mm. The intensity distribution of the diffraction pattern with s range (50–280 nm⁻¹) is obtained and stored in digital form for immediate analysis. The real-time procedure allows for direct comparison of the scattered electron distributions from different substances.

Exposure time is usually 6 seconds at a PDA temperature of −30°C. Raw data output can be viewed immediately on an oscilloscope, or more highly processed data can be displayed on the computer system monitor. Instrumental variables such as the conditions of electron beam and scan state are maintained as constant as possible, and only the sample gas under study is changed. Gold thin film is used for alignment and focusing of the Ge:D/RT system and N₂ is used for calibration purposes. For these studies a sample of CCl₂F₂ (99.0%) was obtained from Aldrich and the purity checked with FT-IR.

CF₃Cl were studied under consistent experimental conditions at various temperatures. Instrumental variables such as electron accelerating voltage, scattering distance, sample temperature, detector temperature, and scan state were maintained as nearly constant as possible, and only the sample under study was changed. Argon gas yields a smooth intensity profile which is used to correct for slit unevenness, for nonuniformity of response of individual diode channels, and for other constant instrumental imperfections. N₂ gas is used for calibration of the electron diffraction instrument.

For an ideal Ge:D apparatus, the total experimental scattered intensity of a molecule Iₓₑ(s) is represented as the sum of an atomic background, Iₓ(s) and a contribution Iₓₑmol(s) from its intramolecular distances. Jₓₑ(s), the experimental intensity of argon, consists only of the featureless background type scattering. For two substances I and J, one defines the experimental ratio of their scattered intensities to be¹⁹

$$R_{E}^{J} = \left( \frac{I_{E}^{J} - D}{J_{E}^{J} - D} \right)\frac{J_{E}^{J}}{I_{E}^{J}}$$  \hspace{1cm} (1)

where D is the detector dark current or PDA signal when no sample gas is entering the diffraction chamber, but the main electron beam is present. The theoretical ratio is Rₓₑ = Iₓₑ / Iₓₑmol where Iₓₑ = Iₓ + Iₓₑmol + Iₓₑscr, and the symbols have their usual meanings. Iₓ is the atomic scattering, Iₓₑmol is the molecular interference, and Iₓₑscr is the tritatomic contribution. One method of extracting the experimental molecular information is to apply the inverse atomic background ratio, Bₓₑ = Iₓₑ / Iₓₑmol to the experimental data. In case the theoretical function J is monatomic, one obtains Bₓₑ = Rₓₑ - 1 + Mₓₑ(s) + Tₓₑ(s) where Mₓₑ(s) is the leveled molecular intensity. Similarly, when the theoretical inverse background ratio is applied to the experimental data, then

$$B_{E}^{J} = K(s) + R [M_{E}^{J}(s)]$$  \hspace{1cm} (2)

where K(s) is a smooth function of the scattering variable s and R is an amplitude scaling constant which may be identified with the index of resolution. The K(s) and R values are determined that best fit the reduced experimental data to the current theoretical model. Eq. (2) is equivalent with the conventional M(s) curve of GED suited for structural analysis. Least-squares analyses are performed on the sM(s) functions of both the traditional and CA
methods until a self-consistent view of the experimental intensities and their theoretical counterparts are obtained. The molecular parameters \((r_n, \lambda_s)\) for the traditional method and the molecular parameters \((r_n, \lambda_s, \gamma_n, \gamma, \text{ and } \gamma_s)\) for CA are obtained over the temperature range from 298K to 673K. As a parameter of accuracy of theoretical fit to the experimental GED data one uses a reduced reproducibility factor \(R_s\), defined as an integral standard deviation over the whole \(s\)-range between experimental and theoretical \(sM(s)\). The radial distribution (RD) curve shows maxima of radial probability which correspond to the internuclear distances.

B) Experimental Apparatus for TRED

The TRED apparatus is shown schematically in Fig. 1 for picosecond TRED. In Fig. 1 the optical pump laser pulses are directed to the diffraction chamber to excite the molecular sample. The probe laser pulses enter the electron chamber to generate picosecond electron pulses. The time delay between the pump and the electron pulses is controlled by a translation stage. The diffraction patterns are recorded with the electronic detection system. The following sections describe the individual components of picosecond TRED.

B. 1) Femtosecond Laser System

The laser system is divided into excimer pump laser, femtosecond laser\(^{25}\), and excimer amplifier. The excimer pump laser (LEXTRA 100, Lambda Physik) is filled with premix XeCl \((80mJ, 15ns\) pulses at 308 nm). The pump energy is distributed among the various dye cells of the femtosecond laser by quartz plates. The energy of the femtosecond system (Lambda Physik, FAMP/LEXtra) including amplified spontaneous emission (ASE) after the second amplifier was 250 \(\mu\)J at 496 nm with 500fs pulse duration. The second harmonic generation in a BBO crystal provided the energy of 10-12 \(\mu\)J at 248 nm, as measured by a Molelectron J4 joulemeter. Also, the wavelength was measured with an Acton Research Corporation, SpectroPro-300I spectrometer.

The amplification of femtosecond pulses was accomplished by a slightly modified excimer laser (Questek). This laser was originally an oscillator with a 20 ns pulse of 100 mJ at 248 nm. The oscillator was converted to an amplifier by replacing the rear resonator mirror with a window. The amplifier

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Fig. 1. The Schematic Diagram of the Picosecond TRED.
was filled with a mixture of 150 mbar F₂, 150 mbar Kr and remainder He to give a total pressure of 2700 mbar. After the first pass, the beam was filtered by a pinhole as shown in Fig. 2, and then sent through the amplifier a second time. By this double-pass amplification scheme, the pulse energy at 248 nm, 500 fs was boosted to 3.5 mJ with no more than 7% amplified spontaneous emission (ASE).

**B. 2) Electron Beam**

The electron gun consists of two electrodes, a magnetic lens and diaphragms as shown in Fig. 3. The cathode is a circular tantalum (1a) disk within a pierce-type electron gun.⁰¹ The emitted electrons are accelerated through a potential of 40 keV. The picosecond electron pulses are reduced to a width of less than 2 mm at the intersection with the molecular beam. The ultrafast electron pulses travel to the diffraction center over a distance of about 50 cm.

The total temporal resolution (tₜᵣₑ) of an ultrafast electron pulse depends on the duration of the initial energy spread of the photoelectrons (Δtₑᵣ), the coulombic dispersion of the electron pulse (Δtₑₑ) due to local space charge (LSC) during its time of flight, the duration of the laser pulse (Δtₕₑ), and a geometry factor (Δtₑᵥ), as shown in Fig. 3. Therefore

\[
(Δtₜᵣₑ)² = (Δtₑᵣ)² + (Δtₑₑ)² + (Δtₑᵥ)² \cdot (Δtₕₑ)²
\]

The geometric effect (Δₜₑᵥ) on the duration of the picosecond electron pulse is calculated by \( (w/c)\tan(αₚ) \), where \( w = 2 \text{ mm} \) is the diameter of the laser beam at the photocathode, \( αₚ = 40° \) is the illumination angle for the laser beam, and \( c \) is the speed of light. The broadening of the pulse due to the initial energy spread is \( -0.5 \text{ ps} \). When electrons are ejected, the electron pulses traveled to the detector with collimation and focusing. After the moment of generation, electron-electron coulombic repulsion causes additional temporal broadening (Δₜₑᵥ). We estimate this space-charge temporal broadening is \( ~4-15 \text{ ps} \). The last term (Δtₑᵥ) corresponds to the temporal duration of the laser pulse which creates the photoelectrons. As mentioned earlier, Δtₑᵥ=0.5 ps. Thus the overall electron pulse duration is in the range Δtₑᵣₑ = 8-19 ps.

**B. 3) Pulsed Inlet System**

TRED consists of two vacuum chambers. The electron chamber is maintained at a vacuum of 10⁻⁶ torr and the diffraction chamber at 10⁻⁴-10⁻⁵ torr. The vacuum is maintained by two diffusion pumps (Edwards Models 160 and 63 Diffistaks) backed by two mechanical pumps (Edwards Model E2M40 and Varian SD 300, respectively).

We have used a modified commercial (Jordan)
supersonic molecular beam pulsed valve (PV) inlet to maximize the scattering intensities for picosecond TRED. The PV consists of a hairpin loop of highly conductive metal and is clamped on both ends with a hole in the bottom plate. A Viton O-ring is placed at the inside of the hole, and sealed by the upper plate. The magnetic repulsion generated by the opposing currents pushes the flexible upper plate away from the O-ring seal and allows gas to flow through the O-ring. The general pulse duration determined by the mechanical response of the upper plate is 30 to 100 ms depending on the pressure and drive current. The maximum repetition rate is 12 Hz. The PV can operate at a maximum 10 atm pressure and about 100°C. The output orifice (d = 0.5 mm) of the jet is extended with a cylindrical channel formed by a stainless hypodermic needle of length 25 mm and inside diameter 0.5 mm to achieve higher molecular densities in the scattering region.

B. 4) Data Acquisition System

The schematic diagram of the data acquisition system is shown in Fig. 4. The diffraction patterns are recorded through an aluminized P-20 phosphor screen coated onto the surface of a vacuum tight fiberoptics faceplate. The phosphor screen is mounted on a standard 10-inch stainless steel flange that provides enough room to place a trap for the main electron beam. The butterfly is used to avoid the over saturation of the signal at small scattering angles and to compensate for signal fall off at larger angles. Furthermore, a linear neutral density filter was designed on the opposite end of the fiber optic coupler. The intensity angular range was nearly equalized with the EF but the signals were still weak for the picosecond experiment. Two fiber optic couplers (Schott) were used for the data acquisition system. The fiber optic couplers consist of a core glass (n = 1.6) and an outside tube of cladding glass which has a lower index of refraction (n = 1.4). Integration over a longer exposure time was previously used to compensate for weak signals but the dark noise became unacceptably large. The use of a microchannel plate (MCP) intensifier (ITL Ltd, MCP-140) has provided good results with shorter exposure times. A microchannel plate (MCP) is an array of $10^4$-105 miniature electron multipliers oriented parallel to one another; typical channel diameters are in the range 10-100 μm. Channel multipliers typically operate at gains of $10^5$-106. The photodiode array (PDA) (RY-2048 diode array, Princeton Instruments) detector consists of 2048 side-by-side elements having pixel dimensions of 25 μm x 2.5 mm. All the diodes in the array are read out after a single integration period and the spectral data stored in the computer memory for display. The CSMA (Princeton Instruments) is a complete control and data collection system. The cooling of the system is essential to reduce the dark current of the PDA. After the system is turned on, it usually takes about two hours for the thermoelectrically

![Fig. 4. Schematic Diagram of the Detector System for TRED.](image-url)
cooled detector to reach its preset temperature of -37°C.

The electron beam is first visualized on the phosphor screen for alignment and focusing, and then placed inside the trap. After the initial alignment, the detector system is butted up against the phosphor screen, and then fine-tuned for the maximum diffraction signals. To align the PV, first the needle is placed on the center of the electron beam, then moved up. The laser pulses are first placed on the PV needle then moved slightly below to complete the intersection of electron pulses, molecular pulses and laser pulses.

RESULTS AND DISCUSSIONS

A) Investigation of Chlorotrifluoromethane (CCIF₃) by GED/RT

A method for direct evaluation of equilibrium molecular geometries from GED/RT intensities was reported previously. Based on a cumulant expansion for the molecular diffraction intensities, the method was applied to determine the equilibrium structures of sulfur hexafluoride SF₆ and selenium hexafluoride. However, information on harmonic and anharmonic potential constants is required for the full cumulant analysis. The simplified CA as reported for SF₆ allows for data refinements without the need for such extraneous information. The molecular parameters [rₑ, λₑ, and γₑ] were refined over a wide temperature range. The application of the new intensity expression to CCIF₃ is important because it avoids the geometrically inconsistent rₑ scheme of the traditional method commonly used in GED investigations. The simplified CA can be applied to equilibrium ensembles at elevated temperatures due to thermal heating or optical pumping, where the traditional method is inoperable.

The results of GED/RT investigations for CCIF₃ comparing the simplified CA and traditional methods are presented. Nₑ (99.998 %) was used as an internal standard for calibration of the GED/RT instrument. The mean equilibrium Nₑ=N distance as determined from the calibration intensity data by excess CA is rₑ=109.74(1) pm. The calculated temperature-dependent distances rₑ, and rₑ, mean amplitudes λₑ and λₑ, and phase shift parameter k agree well with the result of previous work.

The molecule CCIF₃ displays a well resolved distribution of internuclear distances. This molecule has been the subject of three prior photographic electron diffraction studies. The simplified CA analysis was applied to GED intensities of CCIF₃ without spectroscopic information over the temperature range from 298K to 673K. The experimental and theoretical intensity curves for CCIF₃ are compared in Fig. 5. The radial distribution curves are shown in Fig. 6. The molecular parameters at various temperatures of CCIF₃ by simplified CA are presented in Tables 1–3.

The positions, rₑ, of the maximum of the radial distribution peaks (rₑ) = 1.328 ± 0.002Å for C-F, 1.751±0.004 Å for C-Cl, and / FCF = 108.6 ± 0.4°) were reported by Bartell in 1955. The thermal average distances rₑ=1.3257(14) Å for C-F, 1.7489 (39) Å for C-Cl, and / / FCF = 108.6 ± 0.2° were

![Fig. 5. Theoretical and Experimental Intensity Curves of CCIF3 at 298K.](image)

![Fig. 6. Theoretical and Experimental RD Curves of CCIF3 at 298K.](image)
Table 1. The Equilibrium Molecular Parameters for C-F of CCIF₃ by Simplified CA

<table>
<thead>
<tr>
<th>T/K</th>
<th>r₁ (pm)</th>
<th>λ₁ (pm)</th>
<th>γ₁ (%)</th>
<th>γ₂ (%)</th>
<th>R (%)</th>
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The values of the parameters are given from analysis of averaged data sets at each temperature.

Uncertainties in parentheses for r₁ (pm) and λ₁ (pm) are 1σ. The reproducibilities (R) are presented in percent.

Table 2. The Equilibrium Molecular Parameters of C-Cl for CCIF₃ by Simplified CA

<table>
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<tr>
<th>T/K</th>
<th>r₁ (pm)</th>
<th>λ₁ (pm)</th>
<th>γ₁ (%)</th>
<th>γ₂ (%)</th>
<th>R (%)</th>
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The values of the parameters are given from analysis of averaged data sets at each temperature.

Uncertainties in parentheses for r₁ (pm) and λ₁ (pm) are 1σ.

Table 3. The Equilibrium Molecular Parameters for F...F and F...Cl of CCIF₃ by Simplified CA

<table>
<thead>
<tr>
<th>T/K</th>
<th>r₁ (pm)</th>
<th>λ₁ (pm)</th>
<th>r₂ (pm)</th>
<th>λ₂ (pm)</th>
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<td>8.2(3)</td>
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</table>

The values of the parameters are given from analysis of averaged data sets at each temperature.

Uncertainties in parentheses for r₁ (pm) and r₂ (pm) are 1σ.

presented by Oberhammer in 1978. The microwave study of CCIF₃ was reported in 1952 ²⁸ where the values of d₁ = 1.328 ± 0.005Å and d₂ = 1.740 ± 0.0018Å were presented. The stretching and bending anharmonicity of CCIF₃ was studied by Bartell ²⁸, but only the thermal average distances (r₁) at room temperature and bond asymmetry parameters were reported.

The molecular parameters of bonded C-F and C-Cl for CCIF₃ by simplified CA are shown in Tables 1-5; the mean equilibrium distances are r₁ = 132.00 (2) pm and 175.20(3) pm, respectively. As expected, r₁ is essentially independent of temperature as shown in Figures 7-8. As shown in Table 4 the temperature dependent mean distance is r₁ = 132.64 (2) pm for C-F and r₁ = 176.08(6) pm for C-Cl obtained at the room temperature by the traditional method. Also the temperature dependent vibrational amplitudes from the simplified CA are compared with those from the traditional method. The temperature dependent vibrational amplitudes λ₁ of C-F, C-Cl, F...Cl, and F...F also increased and increases of the F...Cl amplitudes much larger than the others. The angles of Cl-C-F are 110.3 ± 0° and 110.0 ± 0.1° by the simplified CA and the traditional methods, respectively. Also, the increases of g₁ and the decreases of g₂ for both nonbonded F...F and Cl-C-Cl are much larger than for bonded C-F.

The data analyses of this study offer the opportunity to directly compare the results obtained by the traditional method and simplified CA. In the traditional method, k asymmetry values are often assumed to be zero which leads to systematic shifts of the r₁ distances. In view of this consideration and the results of this thesis, we expect that simplified
CA provides a more adequate account of the GED/RT experiments. When the simplified CA is applied directly to the GED/RT data, then the equilibrium molecular geometries are refined without information from spectroscopy. The simplified CA scheme may be applied to molecular ensembles at high temperatures and to IR-laser excited systems. Thus, we see its greatest value as establishing the much needed basis for structural kinetic studies of laser excited species by TRED. It will be interesting in the future to compare the results reported in this thesis for CClF, with those obtained from a full cumulant (excess) analysis including spectroscopic information on the molecular force field.

B) TRED Molecular Parameters of CClF,

CCIF, were studied under similar TRED experimental conditions at room temperature. Each frame of data (about 500 channels) contained the complete intensity pattern and required about 20 seconds integration time, and typically 20 to 50 frames were averaged to yield the data sets used for further processing. In a typical experiment, the data set of the molecule to be studied is recorded together with dark current (no gas present), and argon gas (atomic reference), as in GED/RT experiments.

The energy of the 500 fs laser pulses was amplified about 300 times with our modified amplifier. 10% of the amplifier output was directed to the electron chamber to make picosecond amplifier output pulses. After focusing onto the photocathode, the spot diameter is about 2 mm. The other 90% provided the excitation source of molecular samples for the pump-probe experiment. The total temporal broadening (Δt,ms) of the electron pulses was estimated to be ~20 ps.

Measurements of the temporal behavior of the molecular beam were conducted in two different configurations of the pulsed inlet. In the case of "free jet," the molecular pulse length was about 80 μs with argon or SF6 gases. The measured pulse length is very close to the 110 μs pulse predicted by theoretical calculations.

The amplified femtosecond laser pulses yielded stronger diffraction signals than previous experiments for picosecond TRED. The use of the LF allows an increase in quality of diffraction intensities. The diffraction pattern from ~20 ps electron pulses was recorded by the PDA detector during exposure times of ~20 seconds. The total data acquisition time was about 7 minutes.

A lecture bottle of CClF (Aldrich, 99%) was connected directly to the sample inlet of the pulsed valve of TRED to get the molecular structural parameters at room temperature. The ground state picosecond TRED patterns were recorded with 4000 electron pulses. The experimental ratio curve without any smoothing is presented in Fig. 9. The molecular intensity sM(s) and radial distribution curves are shown in Figs. 10 and 11, respectively. The structural parameters for CClF, with GED/RT and TRED are compared in Tables 6 and 7.

From our GED/RT, r, for bonded C-F, C-Cl are 132.64(2) pm and 176.08(6) pm, r, for nonbonded F...F, F...Cl are 215.89(4) pm and 254.20(4) pm,

### Table 4. The Thermal Averaged Molecular Parameters for C-F and C-Cl of CClF, by Traditional Method

<table>
<thead>
<tr>
<th>T/K</th>
<th>r_1 (pm)</th>
<th>λ_1</th>
<th>r_2 (pm)</th>
<th>λ_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>132.64(2)</td>
<td>4.3(1)</td>
<td>176.08(6)</td>
<td>4.8(1)</td>
</tr>
<tr>
<td>373</td>
<td>132.70(3)</td>
<td>4.4(1)</td>
<td>176.15(7)</td>
<td>4.7(1)</td>
</tr>
<tr>
<td>473</td>
<td>132.75(5)</td>
<td>4.5(1)</td>
<td>176.28(5)</td>
<td>5.0(2)</td>
</tr>
<tr>
<td>573</td>
<td>132.79(5)</td>
<td>4.7(1)</td>
<td>176.34(7)</td>
<td>5.1(2)</td>
</tr>
<tr>
<td>673</td>
<td>132.83(4)</td>
<td>4.8(1)</td>
<td>176.43(7)</td>
<td>5.4(3)</td>
</tr>
</tbody>
</table>

The values of the parameters are given from analysis of averaged data sets at each temperature. Uncertainties in parentheses for r (pm) and λ (pm) are 1σ.

### Table 5. The Thermal Averaged Molecular Parameters of F...F and F...Cl for CClF, by Traditional Method

<table>
<thead>
<tr>
<th>T/K</th>
<th>r_1 (pm)</th>
<th>λ_1</th>
<th>r_2 (pm)</th>
<th>λ_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>215.89(4)</td>
<td>5.4(1)</td>
<td>254.20(4)</td>
<td>6.6(1)</td>
</tr>
<tr>
<td>373</td>
<td>215.96(3)</td>
<td>5.6(1)</td>
<td>254.32(3)</td>
<td>6.9(1)</td>
</tr>
<tr>
<td>473</td>
<td>215.94(4)</td>
<td>5.8(1)</td>
<td>254.46(4)</td>
<td>7.4(1)</td>
</tr>
<tr>
<td>573</td>
<td>216.08(6)</td>
<td>6.1(1)</td>
<td>254.68(5)</td>
<td>7.9(1)</td>
</tr>
<tr>
<td>673</td>
<td>216.17(6)</td>
<td>6.5(1)</td>
<td>254.72(5)</td>
<td>8.4(1)</td>
</tr>
</tbody>
</table>

The values of the parameters are given from analysis of averaged data sets at each temperature. Uncertainties in parentheses for r (pm) and λ (pm) are 1σ.
Fig. 9. TRED Experimental Ratio Curves of CCIF3 from 4,000 Electron pulses.

Fig. 10. Theoretical (dot) and Experimental (solid) Intensity Curves of CCIF3 with TRED.

Fig. 11. Theoretical (dot) and Experimental (solid) RD Curves of CCIF3 with TRED.

and the angle of \( \angle \text{ClCF} \) is 110.0 ± 0.1° by the traditional method. From the results of TRED experiments, \( r_i \) for bonded C-F and C-Cl are 132.23(13) pm and 177.23(19) pm; \( r_i \) for nonbonded F...F and F...Cl are 215.90(12) pm and 254.05(14) pm, and the angle \( \angle \text{ClCF} \) is 109.5 ± 0.2°. The vibrational amplitudes \( l_i \) of C-F and F...F are summarized in Tables 6 and 7. When we compare the picosecond TRED results with those of GED/RT, the results of TRED are very close to those of GED/RT. In the future the TRED system can be used for studying transition states and photodissociation processes with picosecond time resolution.

**CONCLUSIONS**

The data analysis of CCIF3 has compared the results obtained by the traditional method and by simplified CA. The equilibrium molecular geometry for CCIF3 was determined directly from the GED/RT data without extraneous information from spectroscopy. When the simplified CA is applied directly to the GED/RT data, then the equilibrium molecular geometries are refined without information from spectroscopy. The simplified CA scheme can be applied to molecular ensembles at high temperatures and to IR-laser excited systems. Thus, we see its greatest value as establishing the much needed basis for structural kinetic studies of laser excited species by TRED. It will be interesting in the future to compare the results reported in this paper with those obtained from a full cumulant (excess) analysis including spectroscopic information on the molecular force field.

In this study, the TRED apparatus was tested and improved. The 500fs laser pulses are amplified, the total temporal broadening of the electron pulses is

### Table 6. The Comparison of Molecular Parameters of C - F and C - Cl for CCIF3, with GED/RT and TRED by Traditional Method at 298K

<table>
<thead>
<tr>
<th></th>
<th>C - F</th>
<th>C - Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_i )</td>
<td>132.64(6)</td>
<td>176.34(2)</td>
</tr>
<tr>
<td>( \lambda_i )</td>
<td>4.3(3)</td>
<td>5.6(3)</td>
</tr>
</tbody>
</table>

### Table 7. The Comparison of Molecular Parameters of F...F and F...Cl for CCIF3, with GED/RT and TRED by Traditional Method at 298K

<table>
<thead>
<tr>
<th></th>
<th>F...F</th>
<th>F...Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_i )</td>
<td>215.89(4)</td>
<td>254.20(4)</td>
</tr>
<tr>
<td>( \lambda_i )</td>
<td>5.4(1)</td>
<td>6.6(1)</td>
</tr>
</tbody>
</table>

The values of the parameters (in pm) are given as obtained from analyses of averaged data. Uncertainties in parentheses for \( r_i \) and \( \lambda_i \) are ±σ.
estimated to be ~20 ps. Current data collection has become routine in picosecond time resolution, collection times have decreased, and the TRID system is applied to study the molecular structures of ground state CCIF, system in picosecond time domain.

REFERENCES