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INTRODUCTION

The photographic measurements have insurmountable problem of inaccuracy because of irregularities of photographic emulsion and chemical processes of development. The technique of direct electron counting with a photomultiplier system was reported in 1979. GED/RT(R) 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 anharmonic part of the potential function contributes significantly to the apparent molecular geometry, and thus can not simply be
ignored in a precise treatment of equilibrium structures. The effects of anharmonicity on the molecular scattering and probability density function have been considered previously by using perturbation or variational approaches. The method applies to both equilibrium and non-equilibrium molecular ensembles. A simplified-cumulant analysis procedure was developed recently to allow for data refinements without the need for extraneous information from spectroscopy.

In this paper, the cumulant analysis method has been expanded to include the direct evaluation of equilibrium geometries of tetrahedrally symmetric \( \left( T_4 \right) \) molecules such as \( CF_4 \). The CA method was applied to analyze the GED-RT data of \( CF_4 \) using five different anharmonic force fields as well as SCA method and tradition method. The parameters of \( CF_4 \) from CA are compared with those from SCA method and tradition method. The equilibrium distances \( \langle r \rangle \) for C-F are presented by using various force fields. By using CA method, various temperature dependent parameters of \( CF_4 \) were calculated in a straightforward manner such as mean internuclear distances \( r_{ij} \) and vibrational amplitudes \( \delta r_{ij} \) as well as cumulant coefficients \( \gamma_n \). The temperature dependent vibrational amplitudes \( \delta r_{ij} \) of C-F and F...F were obtained with five different force fields.

THEORETICAL PROCEDURES

There exist alternative methods for calculating \( \Delta_{\alpha}(s) \) by making the vibrational and rotational averages. \( < \exp[i s (r - r_0)] >_{r} \). 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:\( ^{10,14} \):

\[
Q(s) = \sum_{\alpha = 1}^{N} \exp \left[ Q(s) \right] \langle r_{ij} \rangle \left\{ A(s) \sin [s(r_{ij} + P(s))] + B(s) \cos [s(r_{ij} + P(s))] \right\}
\]

where (omitting the subscripts \( ij \) for simplicity)

\[
Q(s) = -s^{2} \langle \Delta r^{2} \rangle - s^{4} \langle \Delta r^{4} \rangle \quad / 24
\]

\[
P(s) = -s^{2} \langle \Delta r^{2} \rangle \quad / 6
\]

\[
A(s) = -\sum_{\alpha = 1}^{N} \gamma_{n} \langle \Delta r^{2n} \rangle \quad / 6
\]

\[
B(s) = -\sum_{\alpha = 1}^{N} \gamma_{n} \langle \Delta r^{2n} \rangle \quad / 6
\]

Equation 1 provides a basis for least-squares model refinement from GED data. One can adjust the equilibrium internuclear distances \( \varepsilon_{i} \) and cumulants \( \langle \Delta r^{2} \rangle \) with \( n = 1 \sim 4 \). The latter can be assigned a clear meaning in terms of properties determining the vibrational probability density function: \( \langle \Delta r \rangle = \frac{\langle r \rangle + \langle \Delta r \rangle}{2} \) is the mean position, \( \langle \Delta r^{2} \rangle = \frac{\langle r \rangle^{2}}{2} + \langle \Delta r \rangle^{2} \) is the dispersion, \( \langle \Delta r^{4} \rangle = \frac{\langle r \rangle^{4}}{4} + 3 \langle \Delta r \rangle^{2} \langle \Delta r^{2} \rangle \) is the skew, and \( \langle \Delta r^{6} \rangle = \frac{\langle r \rangle^{6}}{6} + 5 \langle \Delta r \rangle^{2} \langle \Delta r^{4} \rangle + 3 \langle \Delta r^{2} \rangle^{3} \) is the excess, respectively, of the probability density.

It is useful to consider the dimensionless cumulant coefficients, \( \gamma_{n} \) which are defined (15) by

\[
\gamma_{n} = \langle \Delta r^{2n} \rangle \quad / \langle \Delta r^{2} \rangle \quad \quad n = 1, 3, 4, \ldots \quad (2)
\]

The \( \gamma_{n} \) values are sensitive functions of the molecular force field and vibrational distribution. By inserting equation 2 into equation 1, one obtains

\[
\sum_{\alpha = 1}^{N} \exp \left[ Q(s) \right] \langle r_{ij} \rangle \left\{ A(s) \sin [s(r_{ij} + P(s))] + B(s) \cos [s(r_{ij} + P(s))] \right\}
\]

where,

\[
Q(s) = -s^{2} \langle \Delta r^{2} \rangle - s^{4} \langle \Delta r^{4} \rangle \quad / 24
\]

\[
P(s) = -s^{2} \langle \Delta r^{2} \rangle \quad / 6
\]

\[
A(s) = -\sum_{\alpha = 1}^{N} \gamma_{n} \langle \Delta r^{2n} \rangle \quad / 6
\]

\[
B(s) = -\sum_{\alpha = 1}^{N} \gamma_{n} \langle \Delta r^{2n} \rangle \quad / 6
\]

To summarize, the cumulant method establishes a general relationship between diffraction intensity and cumulant averages defined with regard to the \( P_{\alpha}(r) \) or \( P_{\beta}(r) \) functions. This relationship is accurate to any desired degree of approximation. The CA equation is based on geometrically consistent \( \varepsilon \) parameters and is valid for non-equilibrium systems without extraneous information on harmonic and anharmonic potential constants. The traditional intensity equation is based on \( \varepsilon \) geometries which are geometrically inconsistent. The molecular parameters obtained by cumulant analysis are more pre-
cise 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 \( g \), from GED data, extensive parameter correlations were found. Therefore, some approximate constraints between the cumulant coefficients are needed to apply equation 3 to GED data analyses without auxiliary spectroscopic calculations.

The least square refinements of molecular intensities can be performed on the basis of equation 3 with the approximate constraints. 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.

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. 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 Data Reduction Procedures for GED/RT

The GED/RT system has been described elsewhere.\(^{15,16}\) 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 diffraction chamber. A position sensitive multichannel analyzer (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. The PDA provides precise spatial resolution and offers high sensitivity and a large dynamic range. In the GED/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 GED. 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 intensity distribution of the diffraction pattern with \( s \) range (50–280 nm\(^{-1}\)) is obtained and stored in digital form for immediate analysis. The molecular inlets have been prepared for high-temperature experiments and the GED experimental temperature is conveniently identified with the temperature of the nozzle at the time of the exposure. Experimental 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 GED/RT system and \( N_{i} \) is used for calibration purposes.

Halofluorocarbons are generally perceived as environmental alternatives to chlorofluorocarbons (CFCs) which have been implicated in the anthropogenic depletion of stratospheric ozone.\(^{25,26}\) Halofluorocarbons and chlorofluorocarbons can both produce CF\(_{3}\) radicals. Also fluorocarbons, CFCs, and halofluorocarbons may play a role in green house warming\(^{19,24}\) due to the fact that C-F bonds absorb in the IR frequency range 1000–1366 cm\(^{-1}\). The effec-

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tiveness of a green house gas depends both on the magnitude of its infrared absorption and on its
atmospheric concentration. Atmospheric concentrations of fully fluorinated compounds are rather low
at present, and in fact only CF₆ and CF₃ have been
detected. CF₆ is used in industry for etching, aero-
dynamic studies, and in chemical lasers. The CF₆
samples were obtained from Aldrich (99.9%) and
and their purity checked by GC/MS.

CF₆ was studied under consistent experimental
conditions at various temperatures. Instrumental
variables such as electron accelerating voltage,
scattering distance, sample temperature, detector
temperature, and scan rate were maintained as nearly
constant as possible, and only the sample under
study was changed. Argon gas yielded a smooth
intensity profile which was used to correct for slit
unevenness, for uniformity of response of indi-
vidual diode channels, and for other constant instru-
mental imperfections. N₂ gas was used for calibration
of the electron diffraction instrument.

For an ideal GED apparatus, the total experimen-
tal scattered intensity of a molecule \( I_{\text{ex}}(s) \) is represen-
ted as the sum of an atomic background, \( I_{\text{a}}(s) \) and a contribu-
tion \( I_{\text{m}}(s) \) from its internuclear dis-
tances. \( I_{\text{a}}(s) \), 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 be (14)

\[
R_{\text{ex}} = \frac{I_{\text{ex}}}{I_{\text{ex}} - D} \cdot \frac{I_{\text{ex}} - D}{I_{\text{m}}(s)} \tag{4}
\]

where \( D \) is the detector dark current or PDA signal
when no sample gas is entering the diffractometer,
but the main electron beam is present. The theo-
retical ratio is \( R_{\text{ex}} = \frac{I_1}{I_2} \), where \( I_{\text{a}} = \frac{I_1}{I_2} \)
and the symbols have their usual meanings. \( I_{\text{a}} \) is the atomic scattering, \( I_{\text{m}} \) is the
molecular interference, and \( I_{\text{m}} \) is the triatomic con-
tribution. One method of extracting the experimen-
tal molecular information is to apply the inverse
atomic background ratio, \( R_{\text{ex}} = \frac{I_1}{I_2} \), to the experimen-
tal data. In case the theoretical function J is
monotonic, one obtains \( B_{\text{ex}} = \frac{I_1}{I_2} - M_{\text{ex}}(s) \),
where \( M_{\text{ex}}(s) \) is the leveled molecular intensity.

Similarly, when the theoretical inverse background
ratio is applied to the experimental data, then

\[
B_{\text{ex}} = K(s) + R \left[ M_{\text{ex}}(s) \right] \tag{5}
\]

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 resolu-
tion. The \( K(s) \) and \( R \) values are determined that best
fit the reduced experimental data to the current theo-
retical model. Equation 5 is equivalent with the
conventional \( M(s) \) curve of GED suited for struc-
tural 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 coun-
terparts are obtained. The molecular parameters \( \varepsilon, \lambda \),
theoretical method and the molecular parameters \( \varepsilon, \lambda, \gamma, \gamma, \gamma, \) and \( \gamma \) for CA are obtained
over the temperature range from 298 K to 673 K.
As a parameter of accuracy of theoretical fit to the
experimental GED data one uses a reduced repro-
ducibility factor \( R \), defined as an integral standard
deviation over the whole \( s \)-range between experi-
mental and theoretical \( sM(s) \). The radial distri-
bution (RD) curve shows maxima of radial proba-
bility which correspond to the internuclear dis-
tances.

**RESULTS AND DISCUSSIONS**

The perturbation theory and variational ap-
proaches have been used for the effect of
anharmonicity on the molecular scattering and probability density function. Using the perturbation
theory, a thermally averaged probability density function is formulated and applied to analyze the
diffraction intensities. The scheme is accurate for molecules with small
anharmonicities, except for cases at high vibrational temperature and / or low vibrational frequency.
The variational method may not be used for vibrationally excited polyatomic systems since anhar-
monic interactions are considerable and the number
of vibrational states and Fermi resonances is very
large. Thus many factors tend to work against con-
tentional solutions of the variational problem at
high temperatures.
There are many approaches to get the molecular parameters by using various force fields. The first type of models is that the internal coordinates do not interact with one another. The only force constants taken into account are those corresponding to stretching, bending, and torsion of chemical bonds, i.e., the so-called valence force field (VFF). The simplified general valence force field (SGVFF) includes the interaction between two valence coordinates if they lie close together. Only next neighboring coordinates can interact and include in the force field. A third model, the central force field (CF) is used only with stretching types of coordinates. The idea of using nonbonding atom interactions has been reconsidered by Urey and Bradley (UBFF) who proposed a new type of force field that can be considered as the sum of the simple VFF and CFF. In the UBFF the diagonal force constants are the usual VFF force constants, whereas the interaction force constants are expressed in terms of nonbonding atom interactions.

It is convenient to express the molecular potential function in terms of internal coordinates. The vibrational problem is solved by using the vibrational Hamiltonian of the molecule. Five nonzero symmetry quadratic force constants are used for CF, since there can be only five independent internal-coordinate forces as shown in Table 1. The wave numbers of the fundamentals are determined by program NCA with the set of constants presented in Table 1. Also the wave numbers from spectroscopic measurements are presented in Table 1. The Cartesian components of the displacements of the nuclei from their equilibrium positions are calculated based on a paper presented by H. A. Jahn in 1938. The scattered electron intensities were recorded in the range $s=70-250$ nm$^{-1}$. The complete set of experimental intensity curves of CF were analyzed in the temperature range from 298 K to 673 K. The temperatures were controlled within $\pm 0.1^\circ$C during the experiments. The ground electronic state of the CF molecule has tetrahedral ($T_4$) symmetry. The equilibrium internuclear distance $r_0 (C-F)$ was refined at the first stage of the data analysis, with the nonbonded distance $r_0 (F-F)$ dependent on the $T_4$ framework. The experimental intensity curves and RD curves for CF at 298 K and 673 K with force field of Suzuki and Overend (S/O) are presented in Figs. 1–4.

Anharmonicity strongly affects molecular spectroscopy including vibrational overtones and combination states. Recently, the anharmonicity for CF has been researched by many groups. Five different anharmonic force fields determined from high-resolution spectra were tested using electron diffraction. The results are presented in Figs. 5, 6.

![Fig. 1. The Theoretical (dot line) and Experimental (solid line) Intensity for CF at 298 K with Force Field of S/O.](image1)

![Fig. 2. The Theoretical (dot line) and Experimental (solid line) Intensity for CF at 673 K with Force Field of S/O.](image2)

<table>
<thead>
<tr>
<th>Table 1. Harmonic force field parameters of CF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force constants</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>$\nu_3$</td>
</tr>
<tr>
<td>$\nu_1$</td>
</tr>
<tr>
<td>$\nu_2$</td>
</tr>
<tr>
<td>$\nu_4$</td>
</tr>
<tr>
<td>$\nu_5$</td>
</tr>
</tbody>
</table>

*Values in cm$^{-1}$ from reference [28], $\nu_3$ values in cm$^{-1}$ from reference [29]. $\nu_3$ values in cm$^{-1}$ from reference [30].
Fig. 3. The Theoretical (dot line) and Experimental (solid line) RD Curves of CF$_4$ at 298 K with Force Field of S/O.

Fig. 4. The Theoretical (dot line) and Experimental (solid line) RD Curves of CF$_4$ at 673 K with Force Field of S/O.

Fig. 5. Equilibrium C-F Distance ($r_e$) versus Temperature for Five Forces Fields of CF$_4$ and Simplified-CA.

Fig. 6. Equilibrium F...F Distance ($r_{ee}$) versus Temperature for Five Forces Fields of CF$_4$ and Simplified-CA.

and in Tables 2. In the force field of reference S/O, the cubic constants were calculated with a Morse potential in each stretching C-F bond, and a Lennard-Jones potential for the interaction energy of the nonbonded F...F atom pair. The anharmonic force fields of Jeannotte and Overend (JO(a) and JO(b)), were calculated with very a simple model. They took a quadratic force field in instantaneous curvilinear coordinates and added cubic and quartic principal bond stretching force field constants modeled on an assumed Morse function. The cubic and the quartic stretching force constants were calculated from the quadratic force constants. Electron diffraction studies of hot molecules have revealed unexpectedly large asymmetries for nonbonded distances, the source of which is not easily characterized by spectroscopy. In the force fields of Bartell (LSB(a) and LSB(b)), the values of the cubic constants were obtained with the aid of the Kuchitsu-Bartell force field (KBF).

Among different anharmonic force fields of CF$_4$, that of S/O yielded equilibrium distances $r_e$ (C-F) of CF$_4$ that increased least over the entire temperature range of the experiments as shown in Figs. 5, 6 and Table 2. The basic model of S/O, taken for the anharmonic part of the intramolecular potential energy function, was the Urey-Bradley potential which included principal interactions between nonbonded atoms in addition to the usual stretching and bending force constants. Force fields LSB(a) and LSB(b) give nearly identical $r_e$ distances but which increase with temperature. The temperature dependent behaviors of the $r_e$ equilibrium distances have a similar positive slope as shown in Fig. 5. In contrast, the equilibrium distances of CF$_4$ by simplified cumulant analysis are relatively constant.

The equilibrium distances ($r_e$) are S/O (131.61 pm), JO(a) (131.73 pm) and JO(b) (131.73 pm), LSB(a) (131.70 pm) and LSB(b) (131.67 pm), and 131.51(4) pm by SCA for C-F of CF$_4$ at 298 K as shown Table 2. From a high resolution diode laser spectrum of
Table 2. Experimental equilibrium C-F distance \( r^e \) of CF\(_4\), with five force fields and SCA

<table>
<thead>
<tr>
<th>T/K</th>
<th>S/O</th>
<th>J/O(a)</th>
<th>J/O(b)</th>
<th>LSB(a)</th>
<th>LSB(b)</th>
<th>SCA</th>
<th>R</th>
<th>R_e</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>131.61</td>
<td>131.73</td>
<td>131.73</td>
<td>131.70</td>
<td>131.67</td>
<td>131.58(4)</td>
<td>0.99</td>
<td>6.4</td>
</tr>
<tr>
<td>373</td>
<td>131.66</td>
<td>131.80</td>
<td>131.79</td>
<td>131.76</td>
<td>131.72</td>
<td>131.58(7)</td>
<td>0.99</td>
<td>5.4</td>
</tr>
<tr>
<td>473</td>
<td>131.73</td>
<td>131.89</td>
<td>131.89</td>
<td>131.85</td>
<td>131.80</td>
<td>131.58(7)</td>
<td>0.96</td>
<td>8.2</td>
</tr>
<tr>
<td>573</td>
<td>131.84</td>
<td>132.03</td>
<td>132.03</td>
<td>131.98</td>
<td>131.92</td>
<td>131.58(6)</td>
<td>0.98</td>
<td>9.6</td>
</tr>
<tr>
<td>673</td>
<td>131.87</td>
<td>132.08</td>
<td>132.03</td>
<td>132.04</td>
<td>131.97</td>
<td>131.57(5)</td>
<td>1.01</td>
<td>6.5</td>
</tr>
</tbody>
</table>

*The values of the \( r_e \) (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). Average uncertainties (standard deviation determined by the results obtained from individual data sets) for experimental distances are 0.05 pm. The anharmonic force fields were taken from Suzuki and Overend (SO), Jeannotte and Overend [J/O(a), J/O(b)] from force field set a and b, and Bartell [LSB(a), LSB(b)] from force field set I and set II. The values of SCA (simplified-CA) are obtained from the simplified-CA method, numbers in parentheses refer to deviations (1\( \sigma \)). The values of the index of resolution (R) and the reproducibility factor (R_e) in percent are presented for the S/O force field.

\( \text{CF}_4 \), the ground state rotational constant is \( B = 0.191688 \pm 0.000020 \text{ cm}^{-1} \). The C-F bond length in the ground vibrational state is thus \( r_e = 131.7524 \pm 0.0007 \text{ pm} \). In the series of articles, Bartell et al.,\(^{21}\) calculated \( r_e = 131.7 \text{ A} \) and a Morse parameter \( a = 2.02 \text{ A}^{-1} \) with a modified Urey-Bradley force field.

In CA, various temperature dependent parameters may be calculated in a straightforward manner, e.g., mean internuclear distances \( r_e \) and vibrational amplitudes \( l_i \), as well as cumulant coefficients \( \gamma_i \). The cumulant coefficients are very sensitive to the force fields, but the vibrational amplitudes are relatively insensitive as seen in Tables 3–6 since they are based on the harmonic part of the potential. The temperature dependent vibrational amplitudes \( l_i \) of C-F and F...F with five different force fields and the SCA method all increased. The relative increases of \( l_i \) for F...F are much larger than for C-F, in agreement with Bartell’s results.\(^{22,33}\)

The increases of \( \gamma_i \) and the decreases of \( \gamma_i \) of bonded C-F for all five force fields and SCA are shown in Tables 5 and 6. The third cumulant coeffi-

Table 3. Experimental vibrational amplitudes \( l_i \) of C-F distance of CF\(_4\), by cumulant analysis\(^*\) and SCA

<table>
<thead>
<tr>
<th>T/K</th>
<th>S/O</th>
<th>J/O(a)</th>
<th>J/O(b)</th>
<th>LSB(a)</th>
<th>LSB(b)</th>
<th>SCA</th>
</tr>
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<tbody>
<tr>
<td>298</td>
<td>3.29</td>
<td>3.20</td>
<td>4.30</td>
<td>4.29</td>
<td>4.29</td>
<td>4.30</td>
</tr>
<tr>
<td>373</td>
<td>3.31</td>
<td>3.32</td>
<td>4.35</td>
<td>4.32</td>
<td>4.32</td>
<td>4.32</td>
</tr>
<tr>
<td>573</td>
<td>3.47</td>
<td>4.49</td>
<td>4.49</td>
<td>4.48</td>
<td>4.48</td>
<td>4.48</td>
</tr>
<tr>
<td>673</td>
<td>3.59</td>
<td>4.61</td>
<td>4.61</td>
<td>4.60</td>
<td>4.60</td>
<td>4.60</td>
</tr>
</tbody>
</table>

The values of the \( l_i \) (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). Calculated values with five different force fields. Column SCA represents the simplified cumulant analysis scheme and numbers in parentheses refer to deviations (1\( \sigma \)).

Table 4. Experimental vibrational amplitudes \( l_i \) of F...F distance of CF\(_4\), by cumulant analysis\(^*\) and SCA

<table>
<thead>
<tr>
<th>T/K</th>
<th>S/O</th>
<th>J/O(a)</th>
<th>J/O(b)</th>
<th>LSB(a)</th>
<th>LSB(b)</th>
<th>SCA</th>
</tr>
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<tbody>
<tr>
<td>298</td>
<td>3.22</td>
<td>3.24</td>
<td>5.34</td>
<td>5.33</td>
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<td>3.53</td>
<td>3.56</td>
<td>5.56</td>
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<tr>
<td>573</td>
<td>6.19</td>
<td>6.23</td>
<td>6.23</td>
<td>6.22</td>
<td>6.21</td>
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<td>6.54</td>
<td>6.58</td>
<td>6.58</td>
<td>6.57</td>
<td>6.56</td>
<td>6.56</td>
</tr>
</tbody>
</table>

The values of the \( l_i \) (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). Calculated values with five different force fields. SCA represents the simplified cumulant analysis scheme and numbers in parentheses refer to deviations (1\( \sigma \)).
The values of \( \gamma_i \) are given as obtained from analyses of averaged data sets at various temperatures (T/K).

### Table 6: Temperature Dependence of the Cumulant Coefficient \( \gamma_i \) for C-F with Five Force Fields of CF, and SCA.

<table>
<thead>
<tr>
<th>T/K</th>
<th>S/O</th>
<th>J/O(a, b)</th>
<th>LSB(a)</th>
<th>LSB(b)</th>
<th>SCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-0.1046</td>
<td>-0.04930</td>
<td>-0.07339</td>
<td>-0.07934</td>
<td>-0.0421</td>
</tr>
<tr>
<td>373</td>
<td>-0.1197</td>
<td>-0.05116</td>
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<td>-0.10745</td>
<td>-0.1139</td>
</tr>
<tr>
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<td>-0.11353</td>
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<td>-0.1638</td>
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<tr>
<td>673</td>
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<td>-0.08920</td>
<td>-0.13207</td>
<td>-0.15131</td>
<td>-0.2477</td>
</tr>
</tbody>
</table>

The values of \( \gamma_i \) are given as obtained from analyses of averaged data sets at various temperatures (T/K).

The coefficient of the C-F bond distance characterizes the skew due to anharmonicity of vibrations; the fourth coefficient indicates the increasing flatness of the probability density with increasing temperature. The third cumulant coefficient for the C-F bond distance for force fields of S/O and LSB is positive and increases significantly with the temperature; the fourth cumulant coefficient is negative and its absolute value increases with temperature. But the third and fourth coefficient for the force field of J/O show little temperature dependence, indicating that the anharmonic part of the force field is somehow deficient. Also, the increases of \( \gamma_1 \) and the decreases of \( \gamma_2 \) for C-F by SCA are much larger than those by cumulant analysis with five anharmonic force fields.

For comparison of our results (\( r_i \)) with five different force fields, least-squares refinements were performed with tetrahedral symmetry. These results are presented in Tables 7 and 8. Traditional GED investigations of CF, were reported about 1950\(^{14} \) at room temperature. The thermal expansions and anharmonic shrinkage effects in CF, were described by Bartell\(^{22,34} \) in 1982 but no structural parameters were reported. The C-F distance was reported as 1.317 Å by gas electron diffraction.\(^23 \) The values of \( r_i \) with five force fields by CA range from 132.17 pm to 132.14 pm for C-F and from 215.69 pm to 215.64 pm for F...F at room temperature.

Routine photographic techniques for GED data collections allow the molecular parameters with uncertainties of about \( \pm 0.3 \) pm. The development of multichannel detector system can reduce the exper-

### Table 7: The comparison of experimental thermal average C-F Distance \( r_i \) of CF, by cumulant analysis with five anharmonic force fields.

<table>
<thead>
<tr>
<th>T/K</th>
<th>S/O</th>
<th>J/O(a)</th>
<th>J/O(b)</th>
<th>LSB(a)</th>
<th>LSB(b)</th>
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</thead>
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<td>132.65</td>
<td>132.64</td>
<td>132.68</td>
<td>132.69</td>
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</tbody>
</table>

The values of \( r_i \) (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). Average uncertainties (standard deviation determined by the results obtained from individual data sets) for experimental distances are 0.05 pm.
imental uncertainties in evaluation of molecular parameters to ~0.1 pm. Therefore more precise and more general theoretical CA was developed to analyze the diffraction data of GED/RT for SF. In this paper, the CA was expanded to evaluate directly equilibrium molecular structure of tetrahedrally symmetric molecules such as CF₄ and check the anharmonic force fields of CF₄. In addition, the equilibrium molecular geometry for CF₄ was determined directly from the GED/RT data by SCA without extraneous information from spectroscopy.

The equilibrium mean distance rₑ was calculated by the CA with extraneous information from spectroscopy and SCA without extraneous information from spectroscopy. The temperature dependent mean distance rₑ was obtained by cumulant analysis with five anharmonic force fields. The CA data analyses of this study offer the opportunity to directly compare the results obtained by the simplified CA.

REFERENCES