

실시간 기체 전자 회절을 사용한 정사면체 대칭 분자의 평형구조 결정

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Direct Evaluation of Equilibrium Structure for Tetrahedrally Symmetric Molecule Using Real-Time Gas Electron Diffraction

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요 약. 누적분석(CA)법과 실시간 기체 전자 회절(GED/RT)을 함께 사용하여 온도 범위 298-673 K에서 정사면체 대칭 분자의 구조 파라미터를 구하고 이를 단순 누적분석(SCA)법과 전통적인 방법으로 얻은 파라미터와 비교하였다. C-F 결합의 평형거리(r_e)를 고분해능 분광법으로 얻은 비조화 힘 장의 정확도를 재는 기준으로 사용하여 다섯 가지 다른 비조화 힘 장의 정확도를 테스트하였다. CA와 SCA로 결정한 CF_4 분자의 C-F 평형 거리는 298 K에서 131.51(4) pm 였다.

주제어: 시간 기체 전자 회절, 누적분석, 평형구조(CF_4)

ABSTRACT. The cumulant analysis (CA) method was expanded to tetrahedrally symmetric molecules. In conjunction with real time gas electron diffraction (GED/RT), the method was applied to study the molecular structural parameters of CF_4 over the temperature range from 298 to 673K. The molecular parameters of CF_4 by the cumulant analysis method were compared with those from the simplified cumulant analysis (SCA) and traditional method. The value of the equilibrium distance (r_e) for bonded distance C-F was used as a criterion for the accuracy of anharmonic force fields obtained from high resolution spectroscopy. The accuracies of five different anharmonic forces fields have been tested by using CA. The equilibrium structural parameters of CF_4 were obtained by CA and SCA. The equilibrium distances (r_e) were 131.51(4) pm by SCA for C-F of CF_4 at 298K.

Keywords: Real Time Gas Electron Diffraction, Cumulant Analysis, Equilibrium Structure (CF_4)

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 1979¹. GED/RT²⁻³ 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,^{4,6} 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 perturbation⁷ or variational⁸ approaches. The method applies to both equilibrium and non-equilibrium molecular ensembles. A simplified-cumulant analysis procedure⁹ 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 (T_d) 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 traditional method. The parameters of CF_4 from CA are compared with those from SCA method and tradition method. The equilibrium distances (r_e) 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 straight forward manner such as mean internuclear distances r_a , and vibrational amplitudes l_a as well as cumulant coefficients γ_n . The temperature dependent vibrational amplitudes l_a of C-F and F...F were obtained with five different force fields.

THEORETICAL PROCEDURES

There exist alternative methods for calculating $I_{m,j}(s)$ by making the vibrational and rotational averages, $\langle \exp[i s(r_i - r_j)] \rangle$.¹⁰ 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 follows¹¹⁻¹⁴:

$$sM(s) = \sum \sum_{i,j=1,N} g_{ij}(s) \exp [Q_{ij}(s)] / r_{e,ij} \{ A_{ij}(s) \sin [s(r_{e,ij} + P_{ij}(s))] + B_{ij}(s) \cos [s(r_{e,ij} + P_{ij}(s))] \} \quad (1)$$

where (omitting the subscripts ij for simplicity)

$$\begin{aligned} Q(s) &= -s^2 \langle \Delta r^2 \rangle_e / 2 + s^4 \langle \Delta r^4 \rangle_e / 24 \\ P(s) &= \langle \Delta r \rangle_e - s^2 \langle \Delta r^3 \rangle_e / 6 \\ A(s) &= 1 - [\langle \Delta r \rangle_e - s^2 \langle \Delta r^3 \rangle_e / 2] / r_e + \dots \\ B(s) &= [-s \langle \Delta r \rangle_e + s^3 \langle \Delta r^3 \rangle_e / 6] / r_e + \dots \end{aligned}$$

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

It is useful to consider the dimensionless cumulant coefficients, γ_n , which are defined (15) by

$$\gamma_n = \langle \Delta r^n \rangle_e / \langle \Delta r^2 \rangle_e^{n/2} \quad n=1, 3, 4, \dots \quad (2)$$

The γ_n values are sensitive functions of the molecular force field and vibrational distribution. By inserting equation 2 into equation 1, one obtains

$$sM(s) = \sum \sum_{i,j=1,N} g_{ij}(s) \exp [Q_{ij}(s)] / r_{e,ij} \{ A_{ij}(s) \sin [s(r_{e,ij} + P_{ij}(s))] + B_{ij}(s) \cos [s(r_{e,ij} + P_{ij}(s))] \} \quad (3)$$

where,

$$\begin{aligned} Q_{ij}(s) &= -s^2 \langle \Delta r^2 \rangle_e / 2 + s^4 \gamma_4 \langle \Delta r^2 \rangle_e^2 / 24 \\ P_{ij}(s) &= \gamma_1 \langle \Delta r^2 \rangle_e^{1/2} - s^2 \gamma_3 \langle \Delta r^2 \rangle_e^{3/2} / 6 \\ A_{ij}(s) &= 1 - [\gamma_1 \langle \Delta r^2 \rangle_e^{1/2} - s^2 \gamma_3 \langle \Delta r^2 \rangle_e^{3/2} / 2] / r_e + \dots \\ B_{ij}(s) &= [-s \langle \Delta r \rangle_e + s^3 \gamma_4 \langle \Delta r^2 \rangle_e^2 / 6] / r_e + \dots \end{aligned}$$

To summarize, the cumulant method establishes a general relationship between diffraction intensity and cumulant averages defined with regard to the $P_{ij}(r)$ or $P_{ij}(r)/r$ functions. This relationship is accurate to any desired degree of approximation. The CA equation is based on geometrically consistent r_e 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_e 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 τ_c and g_m from GED data, extensive parameter correlations were found.¹⁰ 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.¹⁶

Instrumentation and Data Reduction Procedures for GED/RT

The GED/RT system has been described elsewhere.¹⁷⁻¹⁹ 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 molecu-

lar 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 ($50\text{--}280\text{ nm}^{-1}$) 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_2 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.²⁰⁻²² Halofluorocarbons and chlorofluorocarbons can both produce CF_3 radicals. Also fluorocarbons, CFCs, and halofluorocarbons may play a role in green house warming²³⁻²⁴ due to the fact that C-F bonds absorb in the IR frequency range $1000\text{--}1360\text{ cm}^{-1}$. The effec-

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 CF_4 and C_2F_6 have been detected. CF_4 is used in industry for etching, aerodynamic studies, and in chemical lasers. The CF_4 samples were obtained from Alfa (99.7%) and Aldrich (99.9%) and their purity checked by GC/MS.

CF_4 was 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 yielded a smooth intensity profile which was used to correct for slit unevenness, for nonuniformity of response of individual diode channels, and for other constant instrumental imperfections. N_2 gas was used for calibration of the electron diffraction instrument.

For an ideal GED apparatus, the total experimental scattered intensity of a molecule $\bar{I}_{\text{tot}}^{\text{E}}(s)$ is represented as the sum of an atomic background, $\bar{I}_{\text{at}}^{\text{E}}(s)$ and a contribution $\bar{I}_{\text{mol}}^{\text{E}}(s)$ from its internuclear distances. $\bar{J}_{\text{at}}^{\text{E}}(s)$, 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)

$$R_{\text{IJ}}^{\text{E}} = (\bar{I}_{\text{tot}}^{\text{E}} - D) / (\bar{J}_{\text{at}}^{\text{E}} - D) \quad (4)$$

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 $R_{\text{IJ}}^{\text{T}} = \bar{I}_{\text{tot}}^{\text{T}} / \bar{J}_{\text{at}}^{\text{T}}$ where $\bar{I}_{\text{tot}}^{\text{T}} = \bar{I}_{\text{at}}^{\text{T}} + \bar{I}_{\text{mol}}^{\text{T}} - \bar{I}_{\text{int}}^{\text{T}}$, and the symbols have their usual meanings. $\bar{I}_{\text{at}}^{\text{T}}$ is the atomic scattering, $\bar{I}_{\text{mol}}^{\text{T}}$ is the molecular interference, and $\bar{I}_{\text{int}}^{\text{T}}$ is the triatomic contribution. One method of extracting the experimental molecular information is to apply the inverse atomic background ratio, $B_{\text{IJ}}^{\text{T}} = \bar{J}_{\text{at}}^{\text{T}} / \bar{I}_{\text{at}}^{\text{T}}$ to the experimental data. In case the theoretical function J is monatomic, one obtains $B_{\text{IJ}}^{\text{T}} R_{\text{IJ}}^{\text{T}} = 1 - M_{\text{I}}^{\text{T}}(s) - T_{\text{I}}^{\text{T}}(s)$ where $M_{\text{I}}^{\text{T}}(s)$ is the leveled molecular intensity.

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

$$B_{\text{IJ}}^{\text{T}} R_{\text{IJ}}^{\text{E}} = K(s) + R [\bar{M}_{\text{I}}^{\text{E}}(s)] \quad (5)$$

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 resolution. The $K(s)$ and R values are determined that best fit the reduced experimental data to the current theoretical model. Equation 5 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_e , l_j) for the traditional method and the molecular parameters (r_e , l_j , γ_1 , γ_2 and γ_3) 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 reproducibility factor R_r 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.

RESULTS AND DISCUSSIONS

The perturbation theory and variational approaches 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 anharmonic interactions are considerable and the number of vibrational states and Fermi resonances is very large. Thus many factors tend to work against conventional 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 (CFF) 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_4 since there can be only five independent internal-coordinate forces as shown in Table 1.²⁵ The wave numbers of the fundamentals are determined by program NCA^{26a} with the set of constants presented in Table 1. Also the wave numbers from spectroscopic measurements are presented in Table 1.²⁷ 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.^{26b}

Table 1. Harmonic force field parameters of CF_4

| | Force constants ^a | Program NCA ^b | Spectroscopic data ^c |
|------------------|------------------------------|--------------------------|---------------------------------|
| f _{ir} | 7.020 | 913.00 | 908.2 |
| f _{aa} | 1.782 | 432.55 | 434.5 |
| f _{ir'} | 0.770 | 1288.82 | 1282.0 |
| f _{aa'} | 0.281 | 632.80 | 638.0 |
| f _{ra} | 0.777 | | |

^aValues in a/Å from reference [28]. ^bvalues in cm^{-1} from reference [29a]. ^cvalues in cm^{-1} from reference [30]

The scattered electron intensities were recorded in the range $s=70-250\text{ nm}^{-1}$. The complete set of experimental intensity curves of CF_4 was 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_4 molecule has tetrahedral (T_d) symmetry. The equilibrium internuclear distance r_e (C-F) was refined at the first stage of the data analysis, with the non-bonded distance r_e (F...F) dependent on the T_d framework. The experimental intensity curves and RD curves for CF_4 at 298 K and 673 K with force field of Suzuki and Overend (S/O)²⁸ are presented in Figs. 1-4.

Anharmonicity strongly affects molecular spectroscopy including vibrational overtones and combination states. Recently, the anharmonicity for CF_4 has been researched by many groups.^{25,29,30} Five different anharmonic force fields determined from high-resolution spectra were tested using electron diffraction. The results are presented in Figs. 5, 6

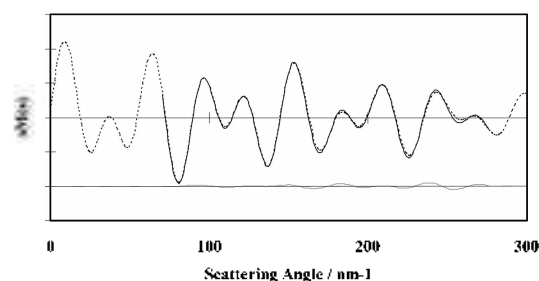


Fig. 1. The Theoretical (dot line) and Experimental (solid line) Intensity for CF_4 at 298 K with Force Field of S/O.

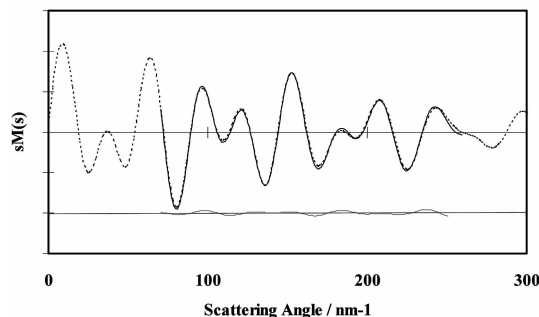


Fig. 2. The Theoretical (dot line) and Experimental (solid line) Intensity for CF_4 at 673 K with Force Field of S/O.

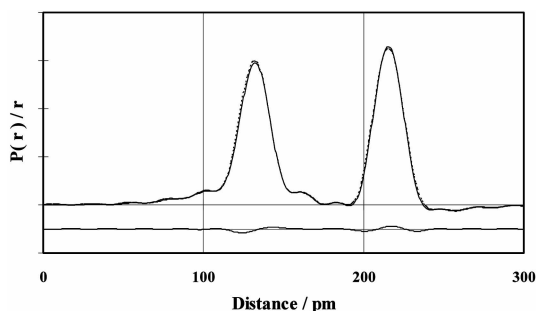


Fig. 3. The Theoretical (dot line) and Experimental (solid line) RD Curves of CF_1 at 298 K with Force Field of S/O.

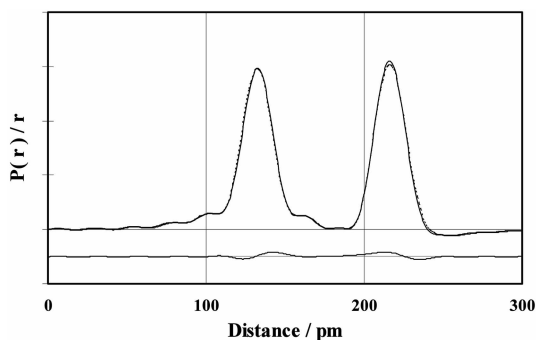


Fig. 4. The Theoretical (dot line) and Experimental (solid line) RD Curves of CF_1 at 673 K with Force Field of S/O.

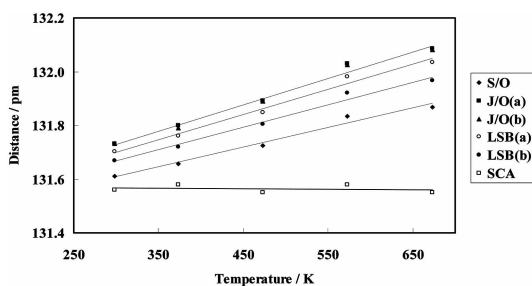


Fig. 5. Equilibrium C-F Distance (r_c) versus Temperature for Five Forces Fields of CF_1 and Simplified-CA.

and in Tables 2. In the force field of reference S/O,²⁸ 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 {J/O(a) and J/O(b)}²⁵ were calculated with very a simple model. They took a quadratic force field in instantaneous

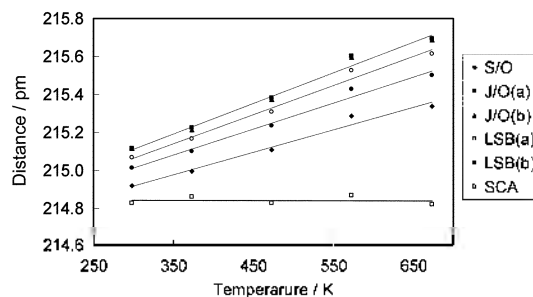


Fig. 6. Equilibrium F...F Distance (r_c) versus Temperature for Five Forces Fields of CF_1 and Simplified-CA.

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)},²⁹ the values of the cubic constants were obtained with the aid of the Kuchitsu-Bartell force field (KBFF).

Among different anharmonic force fields of CF_1 , that of S/O yielded equilibrium distances r_c (C-F) of CF_1 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_c distances but which increase with temperature. The temperature dependent behaviors of the r_c equilibrium distances have a similar positive slope as shown in Fig. 5. In contrast, the equilibrium distances of CF_1 by simplified cumulant analysis are relatively constant.

The equilibrium distances (r_c) are S/O (131.61 pm), J/O(a) (131.73 pm) and J/O(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_1 at 298 K as shown Table 2. From a high resolution diode laser spectrum³⁰ of

Table 2. Experimental equilibrium C-F Distance (r_c)^a of CF₄ with five force fields and SCA

| T/K | S/O | J/O(a) | J/O(b) | LSB(a) | LSB(b) | SCA | R | R _r |
|-----|--------|--------|--------|--------|--------|-----------|------|----------------|
| 298 | 131.61 | 131.73 | 131.73 | 131.70 | 131.67 | 131.56(4) | 0.99 | 6.4 |
| 373 | 131.66 | 131.80 | 131.79 | 131.76 | 131.72 | 131.58(7) | 0.99 | 9.4 |
| 473 | 131.73 | 131.89 | 131.89 | 131.85 | 131.80 | 131.55(7) | 0.96 | 8.2 |
| 573 | 131.84 | 132.03 | 132.03 | 131.98 | 131.92 | 131.58(6) | 0.98 | 9.6 |
| 673 | 131.87 | 132.08 | 132.08 | 132.04 | 131.97 | 131.57(5) | 1.01 | 6.5 |

^aThe values of the r_c (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 (S/O), 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 σ). The values of the index of resolution (R) and the reproducibility factor (R_r in percent) are presented for the S/O force field.

CF₄, the ground state rotational constant is B_v = 0.191688±0.000020 cm⁻¹. The C-F bond length in the ground vibrational state is thus r_0 = 131.752±0.007 pm. In the series of articles, Bartell *et al.*³¹ calculated r_0 = 1.317 Å and a Morse parameter a = 2.02 Å⁻¹ with a modified Urey-Bradley force field.

In CA, various temperature dependent parameters may be calculated in a straight forward manner, e.g., mean internuclear distances r_n , and vibrational amplitudes l_n as well as cumulant coefficients γ_n . 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_n of C-F and F...F with five different force fields and the SCA method all increased. The relative increases of l_n for F...F are much larger than for C-F, in agreement with Bartell's results.^{32,33}

The increases of γ_3 and the decreases of γ_4 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_2) of C-F distance of CF₄ by cumulant analysis^a and SCA

| T/K | S/O | J/O(a) | J/O(b) | LSB(a) | LSB(b) | SCA |
|-----|------|--------|--------|--------|--------|----------|
| 298 | 4.29 | 4.30 | 4.30 | 4.29 | 4.29 | 4.27(6) |
| 373 | 4.31 | 4.32 | 4.33 | 4.32 | 4.32 | 4.32(10) |
| 473 | 4.38 | 4.39 | 4.39 | 4.39 | 4.39 | 4.35(9) |
| 573 | 4.47 | 4.49 | 4.49 | 4.49 | 4.48 | 4.40(8) |
| 673 | 4.59 | 4.61 | 4.61 | 4.61 | 4.60 | 4.47(7) |

The values of the l_2 (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). ^aCalculated values with five different force fields. Column SCA represents the simplified cumulant analysis scheme and numbers in parentheses refer to deviations (1 σ).

Table 4. Experimental vibrational amplitudes (l_2) of F...F distance of CF₄ by cumulant analysis^a and SCA

| T/K | S/O | J/O(a) | J/O(b) | LSB(a) | LSB(b) | SCA |
|-----|------|--------|--------|--------|--------|---------|
| 298 | 5.32 | 5.34 | 5.34 | 5.33 | 5.33 | 5.69(5) |
| 373 | 5.53 | 5.56 | 5.56 | 5.55 | 5.54 | 5.89(8) |
| 473 | 5.86 | 5.89 | 5.89 | 5.88 | 5.87 | 6.25(8) |
| 573 | 6.19 | 6.23 | 6.23 | 6.22 | 6.21 | 6.55(7) |
| 673 | 6.54 | 6.58 | 6.58 | 6.57 | 6.56 | 6.69(6) |

The values of the l_2 (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). ^aCalculated values with five different force fields. SCA represents the simplified cumulant analysis scheme and numbers in parentheses refer to deviations (1 σ).

Table 5. Temperature dependence of the cumulant coefficient γ_3 for C-F with Five Force Fields of CF₄ and SCA.

| T/K | S/O | J/O(a,b) | LSB(a) | LSB(b) | SCA |
|-----|--------|----------|--------|--------|--------|
| 298 | 0.0504 | 0.0004 | 0.0313 | 0.0271 | 0.0861 |
| 373 | 0.0536 | 0.0010 | 0.0339 | 0.0293 | 0.0942 |
| 473 | 0.0608 | 0.0032 | 0.0393 | 0.0341 | 0.1011 |
| 573 | 0.0707 | 0.0056 | 0.0465 | 0.0403 | 0.1166 |
| 673 | 0.0822 | 0.0078 | 0.0545 | 0.0472 | 0.1272 |

The values of γ_3 are given as obtained from analyses of averaged data sets at various temperatures (T/K).

Table 6. Temperature Dependence of the Cumulant Coefficient γ_4 for C-F with Five Force Fields of CF₄ and SCA.

| T/K | S/O | J/O(a, b) | LSB(a) | LSB(b) | SCA |
|-----|---------|-----------|----------|----------|---------|
| 298 | -0.1046 | -0.04930 | -0.07339 | -0.07934 | -0.0421 |
| 373 | -0.1197 | -0.05416 | -0.08179 | -0.08973 | -0.0689 |
| 473 | -0.1457 | -0.06197 | -0.09627 | -0.10745 | -0.1139 |
| 573 | -0.1771 | -0.07086 | -0.11363 | -0.12842 | -0.1638 |
| 673 | -0.2119 | -0.08020 | -0.13267 | -0.15131 | -0.2477 |

The values of γ_4 are given as obtained from analyses of averaged data sets at various temperatures (T/K).

cient 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 γ_3 and the decreases of γ_4 for C-F by SCA are much larger than those by cumulant analysis with five anharmonic force fields.

For comparison of our results (r_s) with five differ-

ent force fields, least-squares refinements were performed with tetrahedral symmetry. These results are presented in Tables 7 and 8. Traditional GED investigations of CF₄ were reported about 1950³⁴ at room temperature. The thermal expansions and anharmonic shrinkage effects in CF₄ were described by Bartell^{32,33} in 1982 but no structural parameters were reported. The C-F distance was reported as 1.317 Å by gas electron diffraction.³⁴ The values of r_s 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 ~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_s) of CF₄ by cumulant analysis with five anharmonic force fields*

| T/K | S/O | J/O(a) | J/O(b) | LSB(a) | LSB(b) |
|-----|--------|--------|--------|--------|--------|
| 298 | 132.17 | 132.14 | 132.14 | 132.16 | 132.16 |
| 373 | 132.27 | 132.23 | 132.23 | 132.25 | 132.25 |
| 473 | 132.41 | 132.36 | 132.36 | 132.38 | 132.39 |
| 573 | 132.60 | 132.54 | 132.54 | 132.57 | 132.57 |
| 673 | 132.72 | 132.65 | 132.64 | 132.68 | 132.69 |

The values of r_s (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.

Table 8. The Comparison of Experimental Thermal Average F...F Distance (r_e) of CF_4 by Cumulant analysis^a with five anharmonic force fields

| T/K | S/O | J/O(a) | J/O(b) | LSB(a) | LSB(b) |
|-----|--------|--------|--------|--------|--------|
| 298 | 215.69 | 215.64 | 215.64 | 215.66 | 215.67 |
| 373 | 215.82 | 215.76 | 215.75 | 215.78 | 215.79 |
| 473 | 216.02 | 215.94 | 215.93 | 215.96 | 215.99 |
| 573 | 216.29 | 216.20 | 216.19 | 216.24 | 216.24 |
| 673 | 216.45 | 216.33 | 216.32 | 216.38 | 216.40 |

The values of r_e (in pm) are given as obtained from analyses of averaged data sets at various temperatures (T/K). ^aAverage uncertainties (standard deviation determined by the results obtained from individual data sets) for experimental distances are 0.08 pm.

experimental 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_6 . In this paper, the CA was expanded to evaluate directly equilibrium molecular structure of tetrahedrally symmetric molecules such as CF_4 and check the anharmonic force fields of CF_4 . In addition, the equilibrium molecular geometry for CF_4 was determined directly from the GED/RT data by SCA without extraneous information from spectroscopy.

The equilibrium mean distance r_e was calculated by the CA with extraneous information from spectroscopy and SCA without extraneous information from spectroscopy. The temperature dependent mean distance r_e 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.

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