VIBRATIONAL CONTRIBUTIONS TO THE SECOND HYPERPOLARIZABILITY OF CF_4

BY

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ABSTRACT

The frequency dependence of the second hyperpolarizability (γ) of CF_4 has been measured in the visible (488 nm $< \lambda <$ 660 nm) by means of gas-phase electric-field-induced second harmonic generation (ESHG). The results of these experiments are compared with the results of other nonlinear optics experiments which have measured γ by third harmonic generation (THG), ESHG and the dc Kerr effect. In order to obtain information about the vibrational contributions to the second hyperpolarizability from this comparison, expressions for the vibrational contributions to γCF_4 have been derived and numerically evaluated for each of these optical processes. It is concluded that vibrational contributions to γCF_4 are negligible for THG, but significant for both the dc Kerr effect and ESHG.

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CHAPTER 1

INTRODUCTION: HISTORY AND PRESENT INTEREST

The world we are living in is a "nonlinear" colorful world. Studies of nonlinear phenomena have a long history. Even in optics, the Faraday effect was discovered in 1845 and the Kerr effect in 1875. "Nonlinear optics" is usually used to refer to those phenomena involving light waves, which must be described in terms containing other than the first power of the electric and magnetic field strengths. In physics, many important phenomena depend on the electric dipole moments induced in atoms or molecules by externally applied electric fields. On the other hand, many nonlinear optical processes can provide much information related to the polarizability and hyperpolarizability. However, since nonlinear optical phenomena are really observable only if the electric field is large enough for the nonlinearity of the polarization to appear, nonlinear optics became a subject of great common interest only after the laser was invented.[1] The remarkable first observation of a nonlinear optical effect was made by Franken, Hill, Peters and Weinreich in 1961 when they observed optical second-harmonic

generation (SHG) using a ruby laser. Since then many important nonlinear optical processes including third-harmonic generation (THG), the dc Kerr effect and four-wave mixing (FWM) have been widely observed in solids, liquids and gases.[1,2] At the same time a number of semi-classical theoretical treatments of high order polarizabilities including those by Bloembergen et al. in 1962 and Ward in 1965 appeared.[1,3,4]

Here, what we are concerned about is the vibrational contribution to the second hyperpolarizability of a certain molecule. The third-order nonlinear susceptibility $\chi^{(3)}$, which mediates a wide range of nonlinear-optical processes, is the macroscopic expression of the microscopic second hyperpolarizability tensor γ.[1-4] Perturbation theory gives a single expression for γ, and the hyperpolarizabilities corresponding to each of the various nonlinear optical processes are just special cases of this general expression.[5-7] The underlying unity of the fundamental theoretical description is obscured in practice because γ for each nonlinear optical process has a characteristically different balance of contributions from the electronic, vibrational and rotational degrees of freedom of each molecule.[8-10] Recently there has been much theoretical interest and

activity directed towards gaining an understanding of the various contributions to γ for various small molecules by means of ab initio calculations.[11-15] On the other hand, since the particular γ tensors mediating the various processes are merely instances of a general γ tensor differing only in their frequency arguments, it should be possible to disentangle the contributions of the various molecular mechanisms by experimentally studying the frequency dependence of γ. In this thesis we will present experimental measurements of the frequency dependence of γ for CF_4 made by means of electric-field-induced second harmonic generation (ESHG) and a comparison of these results with the results of previous measurements from several other nonlinear-optics experiments on the same molecule. In order to get information about the vibrational contributions to the second hyperpolarizability from this comparison, we have also derived and numerically evaluated the expressions of vibrational contributions to γ_{CF_4} for the nonlinear-optical processes of THG, ESHG and the dc Kerr effect.

CHAPTER 2

VIBRATIONAL CONTRIBUTION TO THE SECOND HYPERPOLARIZABILITY

The theory applied in this work includes two parts: one is the theory of hyperpolarizability in which we are interested, and the other is the theory by which the molecular hyperpolarizability is extracted from our experimental observations of dc electric-field-induced second-harmonic generation (ESHG). Details of the latter can be found in Refs.(16-20). In this chapter we will derive the expressions for vibrational contributions to the second hyperpolarizability for different nonlinear optical process.

2.1 ... Quantum Mechanical Expression For The Second Hyperpolarizability

Hyperpolarizability has been well studied using quantum mechanical theory during the 1970's. Equivalent expressions for the hyperpolarizability have been derived using perturbation theory with the help of the method of

averages, the density matrix or Feynman diagrams.[1,5] The expression of γ used as a starting point here is from perturbation theory and the average method due to Orr and Ward in 1971.[5] This expression is applicable when damping may be ignored and is suitable for use even in the static limit:

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3} \sum_P \times \Big\{ \sum_m{}' \sum_n{}' \sum_p{}' \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1-\omega_2)(\Omega_{pg}-\omega_1)} - \sum_m{}' \sum_n{}' \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1)(\Omega_{ng}+\omega_2)} \Big\} \qquad (2.1.1)$$

where

$$\omega_\sigma = \omega_1 + \omega_2 + \omega_3 \quad , \qquad (2.1.2)$$

and Σ_p denotes the sum over terms obtained by permuting the frequencies $-\omega_\sigma$, ω_1, ω_2 and ω_3, together with their associated spatial subscripts α, β, γ and δ. The primed sums over intermediate states exclude the ground state $|g\rangle$. This expression is valid for nondipolar molecules such as CF_4. For arbitrary ω_1, ω_2 and ω_3, Eq.(2.1.1) gives 48 permuted terms as follows:

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1-\omega_2)(\Omega_{pg}-\omega_1)} - \sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1-\omega_3)(\Omega_{pg}-\omega_1)}$$

$$- \sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_2-\omega_1)(\Omega_{pg}-\omega_2)} - \sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_2-\omega_3)(\Omega_{pg}-\omega_2)}$$

$$- \sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_3-\omega_2)(\Omega_{pg}-\omega_3)} - \sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_3-\omega_1)(\Omega_{pg}-\omega_3)}$$

$$\sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1)(\Omega_{ng}+\omega_2)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_1)(\Omega_{ng}+\omega_3)}$$

$$- \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_2)(\Omega_{ng}+\omega_1)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_2)(\Omega_{ng}+\omega_3)}$$

$$- \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_3)(\Omega_{ng}+\omega_2)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg}-\omega_\sigma)(\Omega_{ng}-\omega_3)(\Omega_{ng}+\omega_1)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}+\omega_1+\omega_3)(\Omega_{pg}+\omega_\sigma)} - \sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}+\omega_1+\omega_2)(\Omega_{pg}+\omega_\sigma)}$$

$$- \sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}+\omega_1+\omega_3)(\Omega_{pg}-\omega_2)} - \sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}+\omega_1+\omega_2)(\Omega_{pg}+\omega_\sigma)}$$

$$- \sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}-\omega_2-\omega_3)(\Omega_{pg}-\omega_2)} - \sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}-\omega_3-\omega_2)(\Omega_{pg}-\omega_3)}$$

$$\sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}+\omega_\sigma)(\Omega_{ng}+\omega_2)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}+\omega_\sigma)(\Omega_{ng}+\omega_3)}$$

$$- \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}-\omega_2)(\Omega_{ng}-\omega_\sigma)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}-\omega_3)(\Omega_{ng}+\omega_2)}$$

$$- \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg}+\omega_1)(\Omega_{ng}-\omega_3)(\Omega_{ng}-\omega_\sigma)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}+\omega_2+\omega_3)(\Omega_{pg}-\omega_1)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}-\omega_1)(\Omega_{ng}-\omega_\sigma)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}-\omega_1-\omega_3)(\Omega_{pg}-\omega_1)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}-\omega_1)(\Omega_{ng}+\omega_3)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}+\omega_2+\omega_3)(\Omega_{pg}+\omega_\sigma)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}+\omega_\sigma)(\Omega_{ng}+\omega_1)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}+\omega_2+\omega_1)(\Omega_{pg}+\omega_\sigma)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}+\omega_\sigma)(\Omega_{ng}+\omega_3)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}+\omega_2+\omega_1)(\Omega_{pg}-\omega_3)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}-\omega_3)(\Omega_{ng}-\omega_\sigma)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}-\omega_1-\omega_3)(\Omega_{pg}-\omega_3)} - \sum_{m,n} \frac{\langle g|\mu|m\rangle\langle m|\mu|g\rangle\langle g|\mu|n\rangle\langle n|\mu|g\rangle}{(\Omega_{mg}+\omega_2)(\Omega_{ng}-\omega_3)(\Omega_{ng}+\omega_1)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}-\omega_1-\omega_2)(\Omega_{pg}-\omega_1)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}-\omega_1)(\Omega_{ng}+\omega_2)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}+\omega_2+\omega_3)(\Omega_{pg}-\omega_1)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}-\omega_1)(\Omega_{ng}-\omega_\sigma)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}-\omega_2-\omega_1)(\Omega_{pg}-\omega_2)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}-\omega_2)(\Omega_{ng}+\omega_1)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}+\omega_1+\omega_3)(\Omega_{pg}-\omega_2)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}-\omega_2)(\Omega_{ng}-\omega_\sigma)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}+\omega_1+\omega_3)(\Omega_{pg}+\omega_\sigma)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}+\omega_\sigma)(\Omega_{ng}+\omega_2)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}+\omega_2+\omega_3)(\Omega_{pg}+\omega_\sigma)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg}+\omega_3)(\Omega_{ng}+\omega_\sigma)(\Omega_{ng}+\omega_1)}$$

The vibrational contribution to the total γ is the sum of all those terms for which at least one of the intermediate states is a vibrationally excited state in the ground electronic manifold of states.[9,21]

2.2 ... Expression For γ^{V}_{THG} For CF_4

In the case of third-harmonic generation (THG) the vibrational hyperpolarizability γ^{V} is obtained by substituting

$$(-\omega_\sigma;\ \omega_1,\ \omega_2,\ \omega_3) = (-3\omega;\ \omega,\ \omega,\ \omega) \qquad (2.2.1)$$

to get the 48 permuted terms:

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - 2\omega)(\Omega pg - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - \omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - 2\omega)(\Omega pg - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - \omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - 2\omega)(\Omega pg - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - \omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - 2\omega)(\Omega pg - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - \omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - 2\omega)(\Omega pg - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - \omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - 2\omega)(\Omega pg - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg - 3\omega)(\Omega ng - \omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg + \omega)(\Omega ng + 2\omega)(\Omega pg + 3\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg + \omega)(\Omega ng + 3\omega)(\Omega ng + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg+3\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+3\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng-3\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng-3\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng-3\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+3\omega)(\Omega pg+3\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+3\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg+3\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+3\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng-3\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng-3\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg+3\omega)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng+3\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg+3\omega)} - \sum_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+3\omega)(\Omega ng+\omega)}$$

Each of these terms may be classified according to whether one, two or three of the intermediate states m, n, p are vibrationally excited states of the ground electronic manifold. Thus, seven distinct groups of terms arise from each of the permuted terms of Eq.(2.1.1) involving the triple sum over states, while only three groups of terms arise from each of the permuted terms of Eq.(2.1.1) involving the double sum over states. The THG signal measured in the laboratory is related to the XXXX component of the isotropically averaged molecular hyperpolarizability tensor. If the dominant contributions to the hyperpolarizabilities are from transitions whose frequencies are remote from all relevant field and polarization frequencies, then Kleinman symmetry applies and the hyperpolarizabilities are approximately invariant to interchange of polarization and field coordinate subscripts.[4] In the special case of third- harmonic generation, it may be noted that Kleinman symmetry holds exactly due to the intrinsic permutation symmetry ($\omega_1 = \omega_2 = \omega_3 = \omega$)[18]. Furthermore, since the x, y, z directions are equivalent for a T_d symmetry group molecule such as CF_4, one may write

$$\gamma_{THG} = \langle\gamma\rangle_{XXXX} = \gamma_{xxxx} - 2/5\ \Delta\gamma \quad , \qquad (2.2.3)$$

where $\langle\ \rangle$ denotes the isotropic average,

$$\Delta\gamma = (\gamma_{xxxx} - 3\gamma_{xxyy}) \quad , \qquad (2.2.4)$$

and the upper case (lower case) spatial indices refer to the laboratory (molecular) frame. For an atom $\Delta\gamma = 0$. At the present level of approximation it should be adequate to assume $\Delta\gamma = 0$ for CF_4 as well, from which it follows that $\gamma^{v}_{THG} = \gamma^{v}_{XXXX}$. By considering only the tensor component γ_{xxxx}, the number of distinct terms is reduced from 240 to just 40.

In order to proceed further in evaluating γ^{v}_{THG}, one notes that the following approximate relations hold for the transition frequencies and dipole matrix elements of the principal electronic and vibrational transitions for CF_4:

$$\Omega_e \sim 10\,\omega \sim 100\,\Omega_v \qquad (2.2.5a)$$

$$|\mu_e| \approx 10\,|\mu_v| \qquad (2.2.5b)$$

$$|\mu_e|^2/\,\Omega_e \approx |\mu_v|^2/\,\Omega_v \qquad (2.2.5c)$$

where Ω_e, ω, Ω_v, are electronic, optical and vibrational transition frequencies and μ_e and μ_v are typical electronic and vibrational transition matrix elements. Eq.(2.2.5c) follows from Eq.(2.2.5a) and (2.2.5b) and it essentially states that the electronic and vibrational contributions to the static polarizability are about equal. Characterizing all the electronic and vibrational transitions by μ_e, Ω_e and μ_v, Ω_v is a crude approximation, but it allows one to easily

obtain a simple result for γ^{V}_{THG}. From Eq.(2.2.5a), the denominators of the terms in the expression for γ^{V}_{THG} may be written so as to involve only Ω_V:

$$\Omega_v - 3\omega \approx -3\Omega_v \times 10 \quad ,$$

$$\Omega_e - 3\omega \approx \Omega_v \times 100 \quad , \text{ etc.} \qquad (2.2.6)$$

Similarily, employing Eq.(2.2.3) allows one to write all the numerators so that they involve only μ_v (ie. $\langle g|\mu|m\rangle \simeq 10\mu_v$ if gm is an electronic transition). Then every term of γ^{V}_{THG} is simply proportional to μ_v^4/Ω_v^3. The terms arising from the triple sum over states in Eq.(2.1.1) all sum to zero, while the term inside the double sum in Eq.(2.1.1) gives just $(-64/1000)\,\mu_v^4/\,\Omega_v^3$. Thus, one obtains the following expression for γ^{V}_{THG}:

$$\gamma^{V}_{THG} = (64/1000)\,(\Sigma'_m\,|\mu^x_{mg}|^2)^2/\,(\hbar\,\Omega_v)^3. \qquad (2.2.7)$$

As mentioned before this derivation uses some relatively crude approximations, but it is still significant because at least it allows one to estimate the order of magnitude of γ^{V}_{THG}.

2.3 ... Expression For γ^{V}_{ESHG} For CF_4

In the case of ESHG, the situation is rather different from that of THG. Substituting

$$(\omega_\sigma ; \omega_1 , \omega_2 , \omega_3) = (-2\omega ; \omega , \omega , 0) , \qquad (2.3.1)$$

one may again write out the 48 permuted terms and one finds that more than half of the terms have the factors $(\Omega_v - \omega')$ in the denominator with $\omega' = 0$ (indicated by * on the top left of the terms):

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - 2\omega)(\Omega_{pg} - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{ng} + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{pg} - \omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{ng})}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - 2\omega)(\Omega_{pg} - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg} - 2\omega)\Omega_{ng} - \omega)\Omega_{ng} + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{pg} - \omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{ng})}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{pg})} - \sum_{m,n}^{*} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng})(\Omega_{ng} + \omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)(\Omega_{pg})} - \sum_{m,n}^{*} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng})(\Omega_{ng} + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} + \omega)(\Omega_{pg} + 2\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} + 2\omega)(\Omega_{ng} + \omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} + 2\omega)(\Omega_{pg} + 2\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} + 2\omega)(\Omega_{ng})}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} + \omega)(\Omega_{pg} - \omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} - \omega)(\Omega_{ng} - 2\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} - \omega)(\Omega_{pg} - \omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} - \omega)(\Omega_{ng})}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} - \omega)(\Omega_{pg})} - \sum_{m,n}^{*} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng})(\Omega_{ng} + \omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega ng-2\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega pg-\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)\Omega ng-\omega)(\Omega ng-2\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega pg-\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega ng)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega pg+2\omega)} - \sum_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg+2\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega ng)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-2\omega)(\Omega ng)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng-\omega)(\Omega pg)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega ng+\omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega pg-\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng-2\omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng-2\omega)(\Omega pg-\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega pg-\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng-2\omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega pg+2\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+2\omega)(\Omega ng+\omega)}$$

$$\sum_{m,n,p}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega pg+2\omega)} - \sum_{m,n}^{*} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+2\omega)(\Omega ng+\omega)}$$

Since for typical vibrational and optical frequencies, $\Omega_v << \omega$, terms with a factor of the form $(\Omega_v - 0)$ in the denominator will be strongly enhanced over all the other terms. Retaining only enhanced terms one obtains the following expressions for the relevant tensor components of γ^v_{ESHG}:

$$\gamma^v_{\alpha\beta\beta\alpha}(-2\omega;\omega,\omega,0)$$

$$= \hbar^{-1} \sum_m{}' \frac{2\mu^\alpha_{gm}(\beta_{\alpha\beta\beta})_{mg}}{\Omega_{mg}}$$

$$+ \hbar^{-3} \sum_m{}' \sum_n{}' \left\{ \frac{\mu^\alpha_{gm}\mu^\alpha_{mg}\ \mu^\beta_{gn}\ \mu^\beta_{ng} + 2\mu^\alpha_{gm}\ \mu^\beta_{mg}\ \mu^\beta_{gn}\ \mu^\alpha_{ng}}{\omega^3} \right.$$

$$\left. + \frac{2\mu^\alpha_{gm}\ \mu^\alpha_{mg}\ \mu^\beta_{gn}\ \mu^\beta_{ng} - 2\mu^\alpha_{gm}\ \mu^\beta_{mg}\ \mu^\beta_{gn}\ \mu^\alpha_{ng}}{\Omega_{mg}\ \omega^2} \right\}$$

(2.3.3)

and

$$\gamma^v_{\alpha\beta\alpha\beta}(-2\omega;\omega,\omega,0) = \gamma^v_{\alpha\alpha\beta\beta}(-2\omega;\omega,\omega,0)$$

$$= \hbar^{-1} \sum_m{}' \frac{\mu^\beta_{gm}(\beta_{\alpha\alpha\beta})_{mg} + \mu^\beta_{gm}\ (\beta_{\beta\alpha\alpha})_{mg}}{\Omega_{mg}}$$

$$+ \hbar^{-3} \sum_m{}' \sum_n{}' \left\{ \frac{2\mu^\beta_{gm}\mu^\alpha_{mg}\ \mu^\alpha_{gn}\ \mu^\beta_{ng} + \mu^\beta_{gm}\ \mu^\beta_{mg}\ \mu^\alpha_{gn}\ \mu^\alpha_{ng}}{\omega^3} \right.$$

$$\left. + \frac{\mu^\beta_{gm}\ \mu^\alpha_{mg}\ \mu^\alpha_{gn}\ \mu^\beta_{ng} - \mu^\beta_{gm}\ \mu^\beta_{mg}\ \mu^\alpha_{gn}\ \mu^\alpha_{ng}}{\Omega_{mg}\ \omega^2} \right\}$$

(2.3.4)

where $|m\rangle$, $|n\rangle$ are vibrational excited states of the ground

electronic manifold, and $(\beta_{\alpha\beta\beta})_{gp}$ are components of the hyper-Raman transition hyperpolarizability tensor defined by[22]

$$(\beta_{\alpha\beta\gamma})_{gp} = 2\hbar^{-2} \sum_m{}' \sum_n{}' \left\{ \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} - \omega)} + \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle}{(\Omega_{mg} + \omega)(\Omega_{ng} + 2\omega)} + \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle}{(\Omega_{mg} - 2\omega)(\Omega_{ng} - \omega)} \right\} . \qquad (2.3.5)$$

The experimentally measured quantity in our ESHG experiment is $\langle\gamma\rangle_{XXXX}$. The isotropically averaged γ tensors for ESHG and the dc Kerr effect have only two independent components: $\langle\gamma\rangle_{XXXX}$ and $\langle\gamma\rangle_{XYYX}$. For both ESHG and the dc Kerr effect the relation

$$\langle\gamma\rangle_{XXYY} = \langle\gamma\rangle_{XYXY} \qquad (2.3.6a)$$

holds, as well as the more general relation

$$\langle\gamma\rangle_{XXXX} = \langle\gamma\rangle_{XXYY} + \langle\gamma\rangle_{XYYX} + \langle\gamma\rangle_{XYXY} . \qquad (2.3.6b)$$

Making use of the equivalence of the x, y, z directions for a tetrahedral molecule, one may write the two independent components of $\langle\gamma\rangle$ in terms of the three independent components of γ as follows:

$$\langle\gamma\rangle_{XXXX} = 1/5 \left(3\gamma_{xxxx} + 4\gamma_{xxyy} + 2\gamma_{xyyx} \right) \qquad (2.3.6c)$$

$$\langle\gamma\rangle_{XYYX} = 1/5 \left(\gamma_{xxxx} - 2\gamma_{xxyy} + 4\gamma_{xyyx} \right) \qquad (2.3.6d)$$

where the lower case indices denote components in the molecule fixed frame. Substituting Eqs.(2.3.3, 2.3.4) into Eqs.(2.3.6c, d), and considering that for the spherical top molecule CF_4 the following relations are satisfied:[23, 25]

$$\beta_{xxx} = \beta_{yyy} = \beta_{zzz} \qquad (2.3.7a)$$

$$\beta_{xyy} + \beta_{zzx} = \beta_{yzz} + \beta_{xxy} = \beta_{zxx} + \beta_{yyz} \qquad (2.3.7b)$$

$$\beta_{xyy} = \beta_{yyx},\ \beta_{xzz} = \beta_{zzx},\ \beta_{yzz} = \beta_{zzy} \quad , \qquad (2.3.7c)$$

one obtains the following expression of γ^{v}_{ESHG} for CF_4:

$$\gamma^{v}_{ESHG} = \frac{12}{5}\,\hbar^{-1} \sum_{m}{}' \frac{\mu^{x}_{gm}\,(\,\beta_{xxx} + \beta_{xyy} + \beta_{zzx}\,)_{mg}}{\Omega_{mg}} + \frac{27}{5}\,\hbar^{-3} \sum_{m}{}' \sum_{n}{}' \frac{\left|\mu^{x}_{gm}\right|^2 \left|\mu^{x}_{gn}\right|^2}{\omega^3} \quad . \qquad (2.3.8)$$

At optical frequencies, the second term of Eq.(2.3.8) should be very small and the first term is expected to be dominant.

2.4 ... Expression For γ^{v}_{Kerr} For CF_4

The second hyperpolarizability related to the dc Kerr effect is defined by

$$\gamma_{Kerr} = (-\omega;\ 0,\ 0,\ \omega) \quad . \qquad (2.4.1)$$

Substituting

$$(-\omega_\sigma;\ \omega_1,\ \omega_2,\ \omega_3) = (-\omega;\ 0,\ 0,\ \omega)$$

in Eq.(2.1.1), one can also write out the 48 frequency permuted terms for γ^{V}_{Kerr}. One finds that in this case there appear terms with two of the factors $(\Omega_V-\omega')$ in the denominator having $\omega'=0$ (indicated by ** on the top left of the terms):

$$\overset{**}{\sum_{m,n,p}} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng)(\ pg)} - \overset{**}{\sum_{m,n}} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{\Omega mg\ -\omega)(\Omega ng)(\Omega ng)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)\Omega pg)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng)(\Omega ng\ +\omega)}$$

$$\overset{**}{\sum_{m,n,p}} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg\ -\omega)(\Omega ng)\Omega pg)} - \overset{**}{\sum_{m,n}} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg\ -\omega)\Omega ng)(\Omega ng)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)\Omega pg)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)(\Omega ng\ +\omega)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)(\Omega pg\ -\omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)(\Omega ng)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)\Omega pg\ -\omega)} - \sum_{m,n} \frac{\langle g|\mu_\alpha|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg\ -\omega)(\Omega ng\ -\omega)(\Omega ng)}$$

$$\sum_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng\ +\omega)(\Omega pg\ +\omega)} - \overset{**}{\sum_{m,n}} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng\ +\omega)(\Omega ng)}$$

$$\overset{**}{\sum_{m,n,p}} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng)(\Omega pg\ +\omega)} - \sum_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng\ +\omega)(\Omega ng\ +\omega)}$$

$$\overset{**}{\sum_{m,n,p}} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng\ -\omega)(\Omega pg)} - \overset{**}{\sum_{m,n}} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng)(\Omega ng\ -\omega)}$$

$$\overset{**}{\sum_{m,n,p}} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg)\Omega ng\ -\omega)(\Omega pg)} - \overset{**}{\sum_{m,n}} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg)(\Omega ng)(\Omega ng\ +\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega pg-\omega)} - \sum^{**}_{m,n,p} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng)(\Omega pg-\omega)}$$

$$\sum^{**}_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\beta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng-\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega pg)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng)(\Omega ng-\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega pg)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg)(\Omega ng)(\Omega ng+\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega pg+\omega)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\delta|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega ng)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\delta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng)(\Omega pg+\omega)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\delta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg)(\Omega ng+\omega)(\Omega ng+\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng)(\Omega pg-\omega)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng-\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega pg-\omega)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\gamma|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\delta|g\rangle}{(\Omega mg)(\Omega ng-\omega)(\Omega ng)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega pg)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega ng)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng+2\omega)(\Omega pg)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\beta|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega ng-3\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega pg)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\alpha|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega ng)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\alpha|p\rangle\langle p|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega pg)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\alpha|n\rangle\langle n|\mu_\gamma|g\rangle}{(\Omega mg+\omega)(\Omega ng)(\Omega ng-\omega)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|n\rangle\langle n|\mu_\gamma|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega pg+\omega)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\beta|g\rangle\langle g|\mu_\gamma|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega ng)}$$

$$\sum^{**}_{m,n,p} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|n\rangle\langle n|\mu_\beta|p\rangle\langle p|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega pg+\omega)} - \sum^{**}_{m,n} \frac{\langle g|\mu_\delta|m\rangle\langle m|\mu_\gamma|g\rangle\langle g|\mu_\beta|n\rangle\langle n|\mu_\alpha|g\rangle}{(\Omega mg+\omega)(\Omega ng+\omega)(\Omega ng)}$$

These terms are expected to be greatly enhanced over all other terms and therefore dominate the expression for γ^{V}_{Kerr}. Retaining only the doubly enhanced terms results in the following expressions for the relevant tensor components of γ^{V}_{Kerr}:

$$\gamma^{V,\alpha}_{\alpha\beta\beta\alpha}(-\omega;0,0,\omega) = 2\hbar^{-2}\left\{ \sum_m{}' \sum_n{}' \frac{2\alpha^{\alpha\alpha}_{gm}\,\mu^{\beta}_{mn}\,\mu^{\beta}_{ng} + \mu^{\beta}_{gm}\,\alpha^{\alpha\alpha}_{mn}\,\mu^{\beta}_{ng}}{\Omega_{mg}\,\Omega_{ng}} - \sum_m{}' \frac{\alpha^{\alpha\alpha}_{gg}\,\mu^{\beta}_{gm}\,\mu^{\beta}_{mg}}{\Omega_{mg}\,\Omega_{mg}} \right\} \tag{2.4.3a}$$

and $$\gamma^{V,\alpha}_{\alpha\beta\alpha\beta}(-\omega;0,0,\omega) = \gamma^{V,\alpha}_{\alpha\alpha\beta\beta}(-\omega;0,0,\omega)$$

$$= \hbar^{-2}\left\{ \sum_m{}' \sum_n{}' \frac{2\,\alpha^{\alpha\beta}_{gm}\,\mu^{\beta}_{mn}\,\mu^{\alpha}_{ng} + 2\,\alpha^{\beta\alpha}_{gm}\,\mu^{\alpha}_{mn}\,\mu^{\beta}_{ng}}{\Omega_{mg}\,\Omega_{ng}} + \sum_m{}' \sum_n{}' \frac{\mu^{\alpha}_{gm}\,\alpha^{\beta\alpha}_{mn}\,\mu^{\beta}_{ng} + \mu^{\beta}_{gm}\,\alpha^{\alpha\beta}_{mn}\,\mu^{\alpha}_{ng}}{\Omega_{mg}\,\Omega_{ng}} - \sum_m{}' \frac{2\,\alpha^{\alpha\beta}_{gg}\,\mu^{\alpha}_{gm}\,\mu^{\beta}_{mg}}{\Omega_{mg}\,\Omega_{mg}} \right\} \tag{2.4.3b}$$

where $$\alpha^{\alpha\beta}_{mn} = \hbar^{-1} \sum_p{}' \langle m|\mu_\alpha|p\rangle\langle p|\mu_\beta|n\rangle \frac{2\Omega_{pg}}{\Omega^2_{pg} - \omega^2} \tag{2.4.4}$$

is the Raman transition polarizability.

The dc Kerr effect birefringence measured in the laboratory is related to the isotropically averaged molecular hyperpolarizability tensor through the definition

$$\gamma_{Kerr} = 3/2 \; [\; \langle\gamma\rangle_{XXXX} - \langle\gamma\rangle_{XYYX} \;] \quad , \qquad (2.4.5)$$

where the notation is the same as in the calculations for γ^{v}_{THG} and γ^{v}_{ESHG}. Substituting Eqs.(2.4.3a, b) into Eqs.(2.3.6a, b) and Eq.(2.4.5), and recalling that

$$\mu^{x}_{gm} = \mu^{y}_{gm} \; , \; \alpha^{xy}_{gg} = 0$$

and

$$\alpha^{xy}_{gm} = \alpha^{yx}_{gm} \; ,$$

one obtains the following expression for γ^{v}_{Kerr} of CF_4:

$$\gamma^{v,\alpha}_{Kerr} = \frac{18}{5} \hbar^{-2} \sum_{m}{}' \sum_{n}{}' \frac{2 \, \alpha^{xy}_{gm} \, \mu^{y}_{mn} \, \mu^{x}_{ng} + \mu^{x}_{gm} \, \alpha^{xy}_{mn} \, \mu^{y}_{ng}}{\Omega_{mg} \; \Omega_{ng}} \; .$$

(2.4.6)

If one carefully retains the terms with only one of the factors $(\Omega_{v}-\omega')$ in the denominator having $\omega'=0$, as well as the doubly enhanced terms which gave rise to Eq.(2.4.6), one obtains the following additional contribution to γ^{v}_{Kerr} which involves the hyper-Raman β:

$$\gamma^{\nu,\beta}_{Kerr} = \frac{4}{15}\hbar^{-1}\sum_{m}{}' \frac{2\,\mu^{x}_{gm}(\beta_{xxx} + \beta_{xyy} + \beta_{zzx})_{mg} + \mu^{z}_{gm}(\beta_{xyy} + \beta_{zzx})_{mg}}{\Omega_{mg}} \quad . \tag{2.4.7}$$

The relations of Eq.(2.4.4) have been employed in obtaining this result.

The expressions given in Eqs.(2.3.8, 2.4.6, 2.4.7) allow one to calculate γ^{ν} for ESHG and the dc Kerr effect.

The nature of the final expressions for γ^{ν} and the manner in which they were derived may be clarified by reference to Fig.(2.1). The terms of Eq.(2.1.1) have been classified in Fig.(2.1) according to possible sequences of the vibrationally or electronically excited intermediate states $|m\rangle$, $|n\rangle$ and $|p\rangle$ in the terms which contribute to γ^{ν}. Making use of Eqs.(2.3.5, 2.4.4) allows sequences of electronic transition dipoles in Fig.(2.1a) to be collapsed into vibrational transition polarizabilities and hyperpolarizabilities as shown in Fig.(2.1b). Eqs.(2.3.8, 2.4.6, 2.4.7) result when the calculation is done with due regard for spatial subscripts in the numerator and frequency arguments in the denominator; account is taken of molecular symmetry, and the microscopic molecular result is isotropically averaged. The numerical evaluation will be

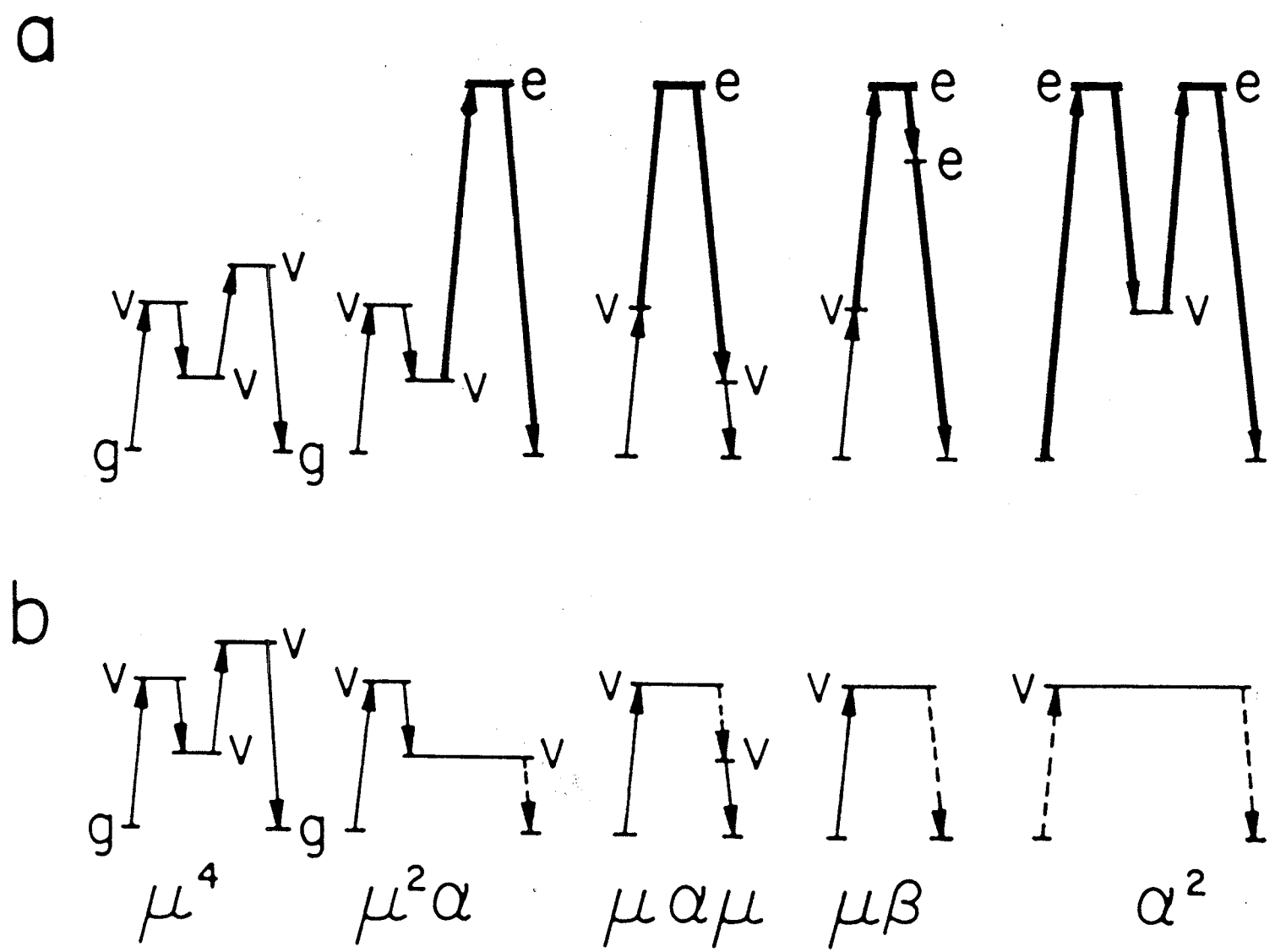
given in chapter 5. It may be noted that the various diagrams in Fig.(2.1) do not contribute equally to γ^{V} , and the allowed terms in the calculation will depend on the particular molecule. For CF_4 all terms are allowed, but the $\mu\mu\alpha$ and $\mu\alpha\mu$ and $\mu\beta$ terms are dominant for the nonlinear optical processes that we have considered.

Figure 2.1

Diagrams for the five essential types of terms which contribute to γ^{v}.

(a). The arrows denote transition dipole matrix elements between states of the molecule. The states are labeled v or e according to whether they are vibrationally or electronically excited. All diagrams start and end at the molecular ground state g. Heavier arrows are drawn for electronic transitions.

(b). Summing over the sequences of electronic transitions in (a) gives diagrams involving transition matrix elements of the Raman or hyper-Raman polarizabilities α or β (dashed arrows). Thus, the diagrams for γ^{v} may be expressed in terms of vibrational transitions only, at the expense of containing matrix elements for all lower order processes.


a
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g
g
μ^4
$\mu^2\alpha$
$\mu\alpha\mu$
$\mu\beta$
α^2

CHAPTER 3

EXPERIMENT

The experimental technique employed in this work is that of dc ESHG. This process was observed in gases, liquids and solids with high-power pulsed lasers during the 1960's and 1970's.[1-4] The technique of periodic phase matching, developed by D.P. Shelton and A.D. Buckingham at the beginning of the 1980's, allowed measurements to be made with a gas sample excited by a low-power laser beam.[16] The theory relating to this dc ESHG experiment has been well described in Refs.(10,16,17).

3.1...Experimental System For dc ESHG

The basic idea in a dc ESHG experiment is to make mesurements of the ratios of hyperpolarizabilities for the sample molecules against the reference molecules. As long as one knows the hyperpolarizability of the reference molecules, one obtains the hyperpolarizability of the sample molecules. In this experiment, the optical-field and static-field polarizations are parallel, so the measurements

are related to the XXXX component of the orientationally averaged tensor $\gamma_{\alpha\beta\delta\gamma}$. The ratio of hyperpolarizabilities for a sample gas B and a reference gas A is obtained from

$$\gamma_B/\gamma_A = (S_B^{(2\omega)}/S_A^{(2\omega)})^{1/2} (\rho_B n'_B / \rho_A n'_A)^{-1} , \qquad (3.1.1)$$

where $S^{(2\omega)}$ is the peak signal of the second harmonic, ρ is the number density and n' is defined by

$$n' = \{ (n_0^2+2)/3 \}\{ (n_\omega^2+2)/3 \}^2\{ (n_{2\omega}^2+2)/3 \} / n_\omega^2 n_{2\omega} . \qquad (3.1.2)$$

A schematic diagram of the optical system and the detection system is shown in Fig.(3.1). The fundamental CW light beam from a Rhodamine-6G or DCM dye laser (COHERENT CR-599 Dye Laser) pumped by an argon-ion laser (COHERENT CR-6 Innova Plasma Tube Ion Laser), or from the argon-ion laser directly, is redirected by plane mirrors. Then a well defined horizontal linear polarization state of the laser beam is selected by a Glan-laser prism polarizer. A filter is used to eliminate the unwanted second-harmonic light generated in the birefringent filter of the dye laser (The wavelength selector of the dye laser is a low-loss crystalline-quartz birefringent filter inserted in the three-mirror cavity.). The power of the laser beam is usually around 0.6-0.8 W at one of seven different wavelengths. The wavelengths of the laser beam from the dye laser are calibrated by Na or Ne atomic emission lines using spectral

lamps and a Jarrell-Ash 1m spectrometer. The laser beam is weakly focused, with a confocal parameter of about 20 cm, at the center of the gas cell to satisfy the requirement that the laser beam pass unobstructed through the long and narrow gap between the electrodes of the sample cell.

The sample gas cell is a cylinder with two optical windows supported on optically flat mounts at normal incidence to the beam. Inside the cell, there is a periodic electrode array in which a frequency-doubled beam is produced by passing a laser beam through the gas sample. The electrode array consists of 150 pairs of steel wires of 1.59 mm diameter and at a 2.69 mm center-to-center spacing. The length of the array is about twice the confocal parameter of the focused laser beam. Details of the construction of the electrode array can be found in Ref.(19). In this experiment the applied field is typically about 1.8 kV/mm. The gas cell is constructed to withstand high pressure. However in these experiments the pressure of the sample gas varies in the range of 2-6 atm. The pressure of gas is measured by a capacitance manometer (MKS Baratron) calibrated by the manufacturers and with a stated accuracy of 0.15%. The temperature is monitored inside the cell by a thermistor in direct contact with the gas, with accuracy

±0.2 K.

After transmission through the sample cell, the laser beam is recollimated and sent through a double prism monochromator which eliminates most of the visible fundamental while passing the ultraviolet second harmonic signal. The Brewster angle dispersing prisms pass light polarized in the horizontal plane with negligible attenuation. A final filter (SCHOTT UG-5 OR CORNING CS7-54) eliminates the residual fundamental. The second-harmonic signal is detected by a photon counter with an uncooled EMI model No.9893QB/350 photomultiplier tube. The background in this experiment is usually about 0.5 cps, while the peak signal of the second-harmonic is around several hundred cps.

3.2 ... Sample Preparation And Effect Of Impurities

In this study, CF_4 is the sample while N_2 is the reference gas. Both gases are taken from Matheson. The purity of the N_2 gas is 99.999% while that of the CF_4 is better than 99.9%. A Ramam spectroscopic assay of the sample gas has been done in this laboratory using the Ar^+

laser (λ=514.5 nm) and a Jarrell-Ash 1m spectrometer. From the standard theory, the concentration of the impurity can be calculated from the following equation:

$$\rho_i/\rho_s = \frac{(I_i/I_s)(d\sigma/d\Omega)_s/(d\sigma/d\Omega)_{Q,N}}{(d\sigma/d\Omega)_i/(d\sigma/d\Omega)_{Q,N}} \qquad (3.2.1)$$

where I is the peak signal in the Raman spectrum measured in the laboratory, and $(d\sigma/d\Omega)$ is differential cross section. The subscripts "i" and "s" used in Eq.(3.2.1) denote "impurity" and "sample" respectively. Here "sample" refers to CF_4. A tabulation of $(d\sigma/d\Omega)i/(d\sigma/d\Omega)_{Q,N_2}$ can be found in Ref.(26). The calculation shows that the impurity of the CF_4 sample gas is less than 0.058%:

CF_3Cl < 0.021%

CHF_3 < 0.005%

N_2 < 0.018%

O_2 < 0.012%

H_2O < 0.0018%

Using the published measurements[27,28] of the refractive index dispersion and the third-order susceptibility, and adding the contributions to the third-order susceptibility due to each of the impurities, one may estimate that the effect of the impurities will be to shift the measured

hyperpolarizability by less than 0.1% compared to that of pure CF_4. This effect is smaller than the accuracy of the ratio determination in this experiment.

3.3 ... Signal Curve and Data Analysis

The second-harmonic signal varies with the coherence length of the gas. The peak signal occurs when the coherence length of the gas matches the fixed spacing of the electrodes. The coherence length is adjusted by varying the gas pressure which is related to the gas density. Typical normalized experimental data of S against P are shown in Fig.(3.2), where S is the normalized strength of second-harmonic signal and P is the normalized pressure of gas. Using least squares fitting of a polynomial

$$S = \Sigma_n A_n P^n$$

to the measurements of S versus P, one finds that the data are very well represented regardless of taking the maximum power of n as N = 2, 3 or 4, provided only data taken symmetrically within about 10% of the peak signal are included. The difference in the peak values obtained with

fitting polynomials with N = 2, 3 or 4 is only 10^{-6} for ΔS_{peak} and 10^{-5} for ΔP_{peak}. Based on this analysis, we simply choose a quadratic to fit the data taken symmetrically within around 10% of the peak. This provides a method to accurately determine the peak signal and the optimum pressure while avoiding fitting errors.

Measurements were made in coupled triplets (ABABA...) in order to cancel drifts. The sample densities were computed from the measured pressures and temperatures by iteratively solving the virial equation of state:

$$\rho_{n+1} = P / RT(1 + B\rho_n + C\rho_n^2) \qquad (3.3.1)$$

where P is the pressure of the gas, T is the temperature, R is the universal gas constant and B and C are the second and third virial coefficients, respectively. Experimental virial coefficients for different real gases at different temperatures can be found in Ref.(29). In this experiment, the temperature is around 293 K, so we take

$$B = -4.46 \text{ cm}^3/\text{mole}, \quad C = 1063 \text{ cm}^6/\text{mole}^2 \qquad (3.3.2)$$

for N_2 gas and

$$B = -88.5 \text{ cm}^3/\text{mole}, \quad C = 6100 \text{ cm}^6/\text{mole}^2 \qquad (3.3.3)$$

for CF_4. The density ρ usually converges with five iterations or less. Details of the computer programs are presented in the Appendix.

The estimated total experimental uncertainty of a hyperpolarizability-ratio measurement is obtained by convolving the statistical uncertainty for an average of usually five triplets of runs with the uncertainty of the density determinations due to the limited accuracy of the pressure gauge. The accuracy of the ratio determined in this experiment is estimated to be about 0.4%.

Figure 3.1

Experimental system

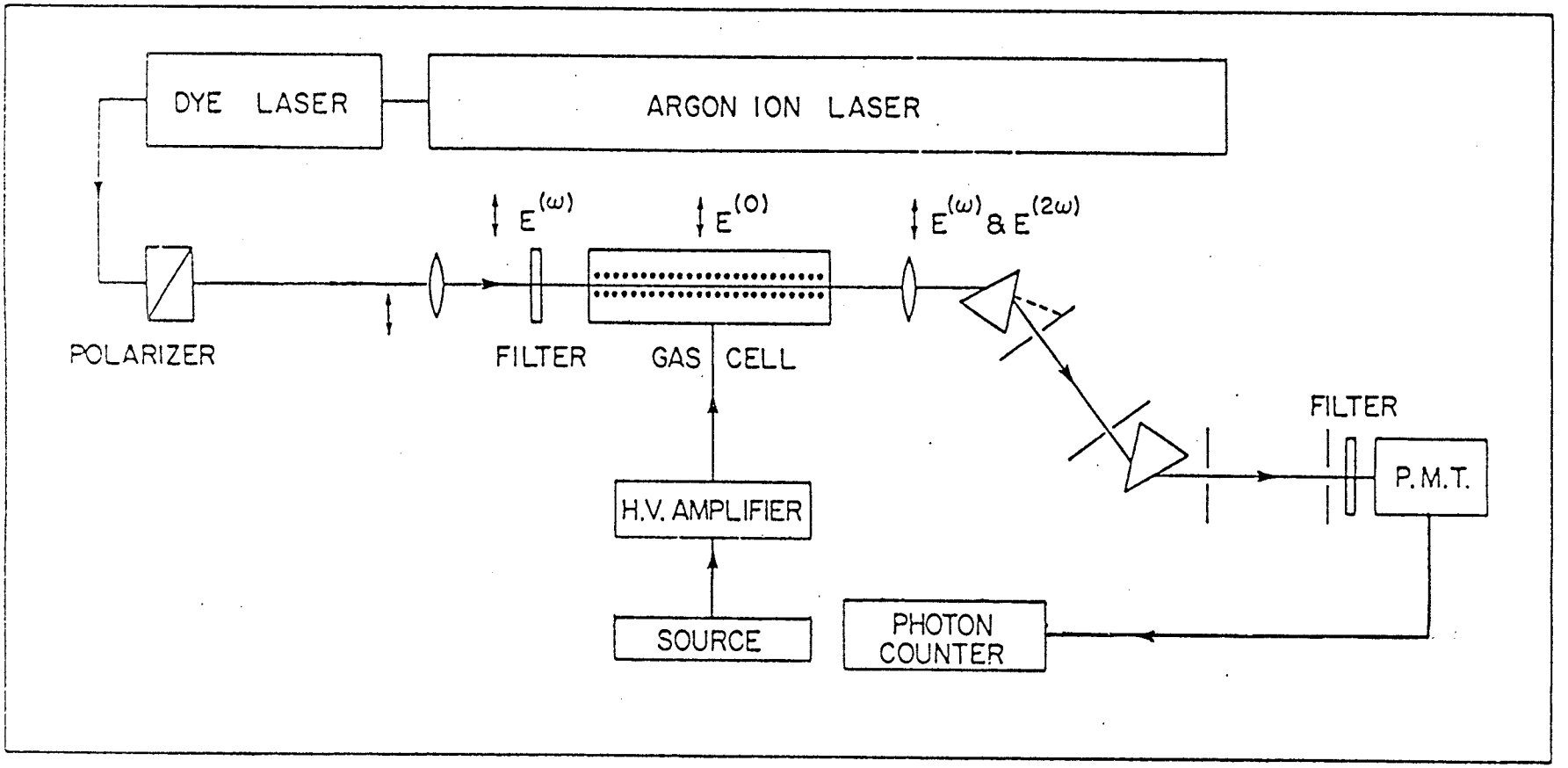
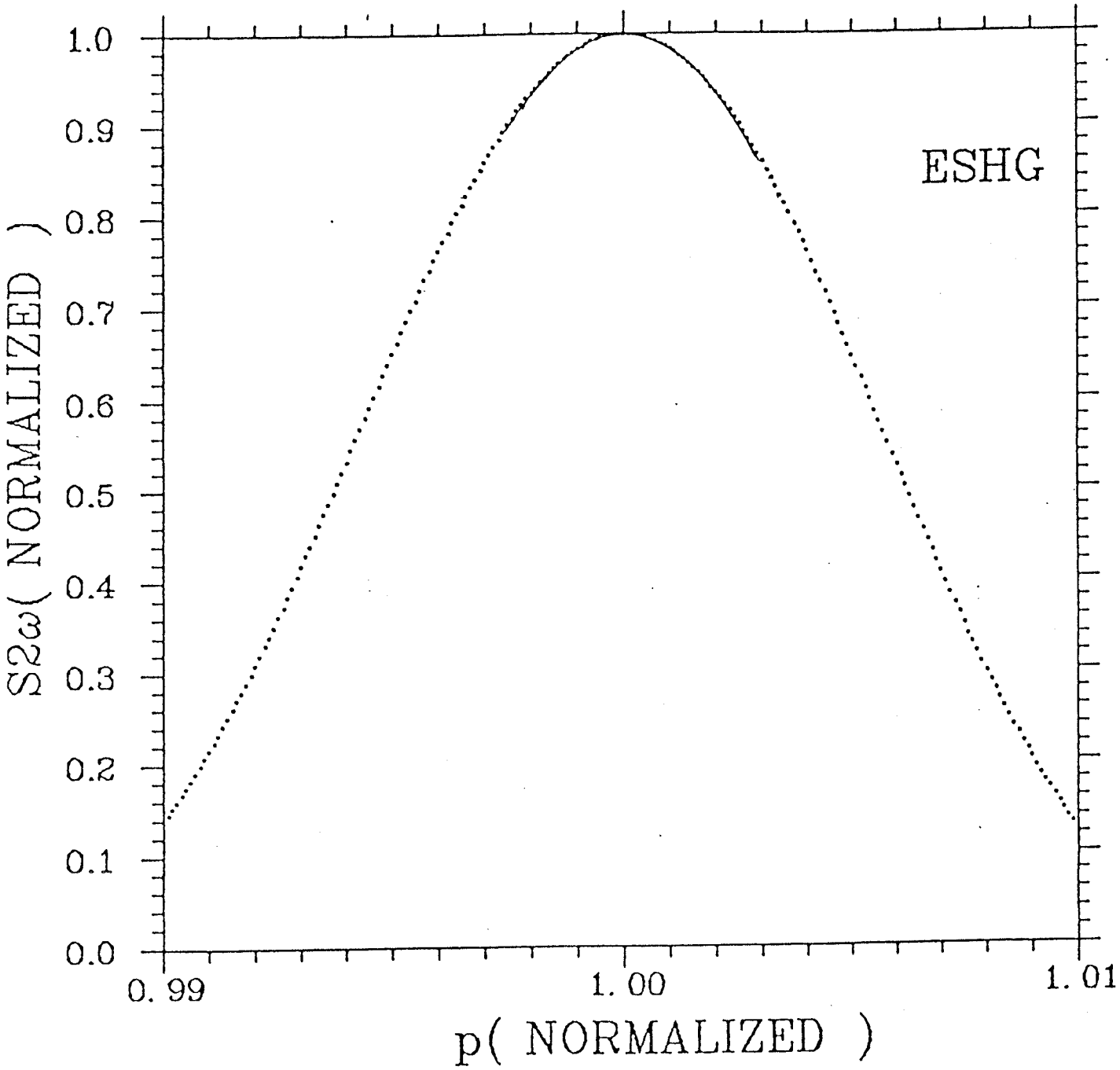

DYE LASER
ARGON ION LASER
$E^{(\omega)}$
$E^{(0)}$
$E^{(\omega)}$ & $E^{(2\omega)}$
POLARIZER
FILTER
GAS CELL
FILTER
P.M.T.
H.V. AMPLIFIER
SOURCE
PHOTON COUNTER

Figure 3.2

Signal Curve And Least Squares Fitting Polynomial

In this figure, points denote experimental data and the solid line denotes the quadratic curve fitted to the data taken symmetrically within about 10% of the peak signal. In this case, $\chi^2 \approx 0.001$.


ESHG
S2ω(NORMALIZED)
p(NORMALIZED)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.99
1.00
1.01

CHAPTER 4

EXPERIMENTAL RESULTS

The experiment gives the ratio of the peak signal for CF_4 and N_2 . To obtain the ratio of the hyperpolarizabilities, one needs to apply a local field correction factor. In this chapter, first we will calculate the local field correction factor and then give the second hyperpolarizability of CF_4 from this experiment.

4.1 ... Local Field Correction Factor

The ratio $\gamma_{CF_4}/\gamma_{N_2}$ can be obtained by using Eq.(3.1.1) and Eq.(3.1.2). Eq.(3.1.2) is

$$n' = [(n_0^2+2)/3][(n_\omega^2+2)/3]^2[(n_{2\omega}^2+2)/3]/n_\omega^2 n_{2\omega}$$

where n_0 is the static refractive index of the gas, n_ω is the refractive index of the gas at frequency ω and $n_{2\omega}$ is that at the doubled frequency, all evaluated at the gas density which gives phase matching. The final factor $n_\omega^2 n_{2\omega}$ is not strictly a local field factor but it appears in the

expression for the ESHG signal. Taking $n = 1+\delta$ ($\delta<<1$) and neglecting the higher orders of δ, which is a good approximation in the experiment, one obtains a compact form for n' :

$$n' = (n_0^4 n_\omega^3 n_{2\omega})^{1/6} . \qquad (4.1.1)$$

It is considered as a local field correction factor in obtaining the ratio $\gamma_{CF_4}/\gamma_{N_2}$. From the relation

$$n_\omega(T,P) - 1 = \alpha(\omega)\rho(T,P)/2\varepsilon_0 \qquad (4.1.2a)$$

one may derive the following equation:

$$[n_\omega(T_2,P_2) - 1] = [n_\omega(T_1,P_1) - 1]\rho(T_2,P_2)/\rho(T_1,P_1) , \qquad (4.1.2b)$$

where T is the temperature of the gas and P the pressure. The mole density $\rho(Ti,Pi)$ corresponds to $n_\omega(Ti,Pi)$. For N_2, n_ω and $n_{2\omega}$ can be found from the tabulated values at standard conditions in Ref.(31) with linear interpolation to the seven frequencies corresponding to the ESHG experiment. For CF_4, n_ω can also be found in the same way, but $n_{2\omega}$ is not available in the table.

To obtain $n_{2\omega}$ for CF_4, one may use Eq.(4.1.2a) together with

$$\alpha(2\omega) = \alpha(\omega) + \Delta\alpha(\omega) \qquad (4.1.3)$$

where

$$\Delta\alpha(\omega) = \alpha(2\omega) - \alpha(\omega) \qquad (4.1.4)$$

is the linear polarizability dispersion. Applying Eq.(4.1.2a) for $n_{2\omega}$, one may write

$$n_{2\omega}(T,P) - 1 = \alpha(2\omega)\,\rho(T,P)/2\varepsilon_0 \,. \qquad (4.1.5)$$

From Eq.(4.1.5) and Eq.(4.1.2a), one gets

$$[n_{2\omega}(T,P) - 1] - [n_{\omega}(T,P) - 1] = \Delta\alpha\,\rho(T,P)/2\varepsilon_0 . \qquad (4.1.6)$$

It can be expressed in an alternative way when using Eq.(4.1.2a):

$$n_{2\omega}(T,P) - n_{\omega}(T,P) = \Delta\alpha\,[n_{\omega}(T,P) - 1]/\alpha(\omega) \,. \qquad (4.1.7)$$

Let $\rho(T_1,P_1)$ denote the mole density measured for n_ω in Ref.(31) and $\rho(T_2,P_2)$ denote the phase-matching density in our ESHG experiment. Substituting Eq.(4.1.2b) in Eq.(4.1.7), one obtains

$$n_{2\omega}(T_2,P_2) = n_{\omega}(T_2,P_2) + \Delta\alpha\{n_{\omega}(T_1,P_1)-1\}\frac{\rho(T_2,P_2)}{\rho(T_1,P_1)\alpha(\omega)} \qquad (4.1.8)$$

It is adequate to simply use the value given in Refs.(8, 31) for $\lambda = 632.8$ nm,

$$\alpha(\omega) = 3.172 \times 10^{-40} C^2 m^2 J^{-1}, \qquad (4.1.9)$$

and

$$n_{\omega}(T_1,P_1) - 1 = 451.242 \times 10^{-6}, \qquad (4.1.10)$$

to calculate $n_{2\omega}$. Finally,

$$n_{2\omega} = n_{\omega} + 1.423 \times 10^{36}\Delta\alpha(\omega)\rho(T_2,P_2)/\rho(T_1,P_1) \,. \qquad (4.1.11)$$

To apply Eq.(4.1.11) to calculate $n_{2\omega}$ for CF_4, one needs

$\Delta\alpha(CF_4)$. However, in the ESHG experiment the wave-vector mismatch ΔK is determined by the difference in the refractive index of the sample between ω and 2ω expressed by

$$\Delta K = 2K_\omega - K_{2\omega} = 4\pi(n_\omega - n_{2\omega})/\lambda_\omega$$

$$= -\frac{2\pi}{\lambda_\omega \varepsilon_0}(\Delta\alpha)\rho(T,P) + o(\rho^2) \quad . \quad (4.1.12)$$

This implies that at the phase-matching case,

$$\text{i.e.} \quad \Delta K = \text{constant} ,$$

one can obtain the linear polarizability dispersion ratio by

$$\Delta\alpha_{CF_4} / \Delta\alpha_{N_2} = \rho_{N_2} / \rho_{CF_4} \qquad (4.1.13)$$

using phase-matching densities measured in the ESHG experiment. Further, employing the measured values of $\Delta\alpha_{N_2}$ in Ref.(30) at the corresponding frequencies one can obtain $\Delta\alpha_{CF_4}$ from Eq.(4.1.13), and then $n_{2\omega}$ can be calculated from Eq.(4.1.11).

For the static refractive index, from Eq.(4.1.2a) one obtains

$$n_0 - 1 = \alpha(0)\rho/2\varepsilon_0 \qquad (4.1.14)$$

Employing the published data in Refs.(32, 33):

$$\alpha_{CF_4}(0) = 4.270 \times 10^{-40} C^2 m^2 J^{-1} \quad (4.1.15)$$

$$\alpha_{N_2}(0) = 1.935 \times 10^{-40} C^2 m^2 J^{-1} \quad (4.1.16)$$

one gets

$$n_0(CF_4) = 1 + (1.452 \times 10^{-5} m^3/\text{mole})\ \rho(T_2,P_2) \quad (4.1.17)$$

and

$$n_0(N_2) = 1 + (6.580 \times 10^{-6}\ m^3/mole)\ \rho(T_2,P_2)\ . \quad (4.1.18)$$

The local field correction parameters have been listed with $\Delta\alpha_{CF_4}$ in Table (4.1). They are seen to result in very small corrections, within the range of 0.05% to 0.17%.

4.2 ... Dispersion of The Second Hyperpolarizability of CF_4 From ESHG Experiment

The results for ratios $\gamma_{CF_4}/\gamma_{N_2}$ measured at seven wavelengths in the experiment are given in Table (4.2). To obtain γ_{CF_4} from the measured ratios, we have employed the previous measurements of γ_{N_2}/γ_{He} in Ref.(18) and the ab initio results for γ_{He} for calibration. The ab initio results for γ_{He} [34] were calculated by Sitz and Yaris in 1968. Over the range of frequencies employed in the present measurements, these results are adequately represented by

$$\gamma_{He} = 42.6\ \text{a.u.}\ [1 + (2.94 \times 10^{-10}\ cm^2)\nu^2]\ . \quad (4.2.1)$$

On the other hand, from the previous work of Ref.(35), the ratios γ_{N_2}/γ_{He} over the same frequency range can be well represented by

$$\gamma_{N_2}/\gamma_{He} = 20.30\ [1 + (6.55 \times 10^{-10}\ cm^2)\nu^2]\ , \quad (4.2.2)$$

where ν is given in cm^{-1} and 1 a.u.= $6.2360 \times 10^{-65} C^4 m^4 J^{-3}$. An uncertainty of ±0.4% due to γ_{N_2}/γ_{He} calibration has been assumed in assigning the error bars for γ_{CF_4}. The ab initio result for γ_{He} are thought to be accurate to 1%.[35] No allowance has been made for the uncertainty of γ_{He} in arriving at the experimental results for γ_{CF_4} given in Table (4.2). The experimental results for γ_{CF_4} are plotted versus ν^2 in Fig.(4.1). They are adequately represented by a straight line. The previous results are also plotted in Fig.(4.1). These results are seen to be in good agreement with the present ESHG measurements for γ_{CF_4}.

Figure 4.1

The values of CF_4 measured in the present ESHG experiments (filled circles) and in previous experiments (open circles) are plotted versus ν^2. The straight line is a fit of the function

$$\gamma = A (1 + B\nu^2)$$

to the data of the present experiments. The coefficients of the fit are

$$A = 60.03 \times 10^{-63} \ C^4 m^4 J^{-3}$$

and

$$B = 7.93 \times 10^{-10} \ cm^2,$$

where ν is given in cm^{-1}.

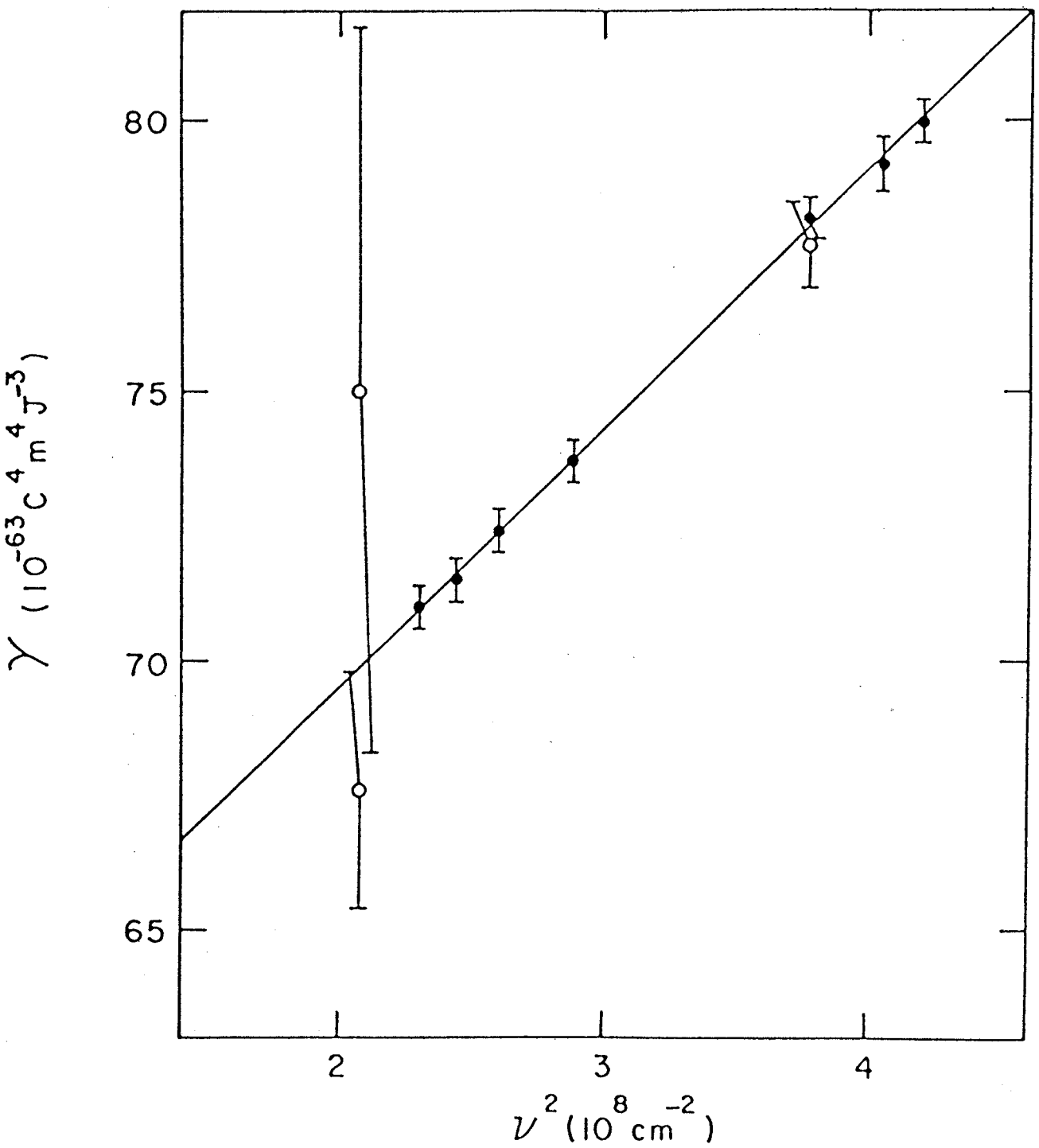

80
75
70
65
2
3
4
γ ($10^{-63} c^4 m^4 J^{-3}$)
ν^2 ($10^8 cm^{-2}$)

Table 4.1

Local field correction factor.

λ (nm)	CF_4 ($10^{-41} C^2 m^2 J^{-1}$)	$n'(CF_4)$	$n'(N_2)$	$n'(CF_4)/n'(N_2)$
488.0	1.498	1.001531	1.000785	1.00075
496.5	1.444	1.001612	1.000829	1.00078
514.5	1.339	1.001799	1.000930	1.00087
589.0	1.019	1.001984	1.001442	1.00054
621.7	0.9193	1.003186	1.001714	1.00147
640.2	0.8701	1.003468	1.001880	1.00158
659.8	0.8234	1.003777	1.002045	1.00173

Table 4.2

Experimental results for γ of CF_4 measured by ESHG over the visible.

λ (nm)	ν (cm^{-1})	$\gamma CF_4/\gamma N_2$	γCF_4 ($10^{-63} C^4 m^4 J^{-3}$)
488.0	20486	1.036 ± 0.003	80.0 ± 0.4
496.5	20135	1.036 ± 0.004	79.2 ± 0.5
514.5	19430	1.046 ± 0.003	78.2 ± 0.4
589.0	16973	1.060 ± 0.002	73.7 ± 0.4
621.7	16080	1.068 ± 0.004	72.4 ± 0.4
640.2	16615	1.067 ± 0.004	71.5 ± 0.4
659.8	15152	1.072 ± 0.004	71.0 ± 0.4

CHAPTER 5

DISCUSSION: γ^{v}_{THG}, γ^{v}_{ESHG} AND γ^{v}_{Kerr} FOR CF_4

Our purpose in this work is to analyze the vibrational contributions to the second hyperpolarizability of CF_4. We have derived the expressions of γ^{v} for CF_4 in different nonlinear processes and obtained the results for γ from an ESHG experiment. Next we will give a numerical estimation and discussion of $\gamma^{v}_{CF_4}$.

5.1 ... γ^{v}_{THG} And γ^{v}_{ESHG} For CF_4

5.1.1 ... Previous Results for γ_{CF_4} in THG, ESHG and the dc Kerr effect

Before proceeding with the numerical evaluation of γ^{v}, it is useful to compare the experimental measurements for several different third-order optical processes, ignoring for the moment the contribution due to γ^{v}. It has been suggested in Refs.(10, 36) that far below resonance the

electronic contributions to γ for the various third-order nonlinear optical processes will obey the relation

$$\gamma^e(\omega_\sigma;\omega_1,\omega_2,\omega_3) = \gamma\ (0;\ 0,\ 0,\ 0) \times (1 + C\omega_L^2) \qquad (5.1.1)$$

where

$$\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2 + \omega_3^2 \qquad (5.1.2)$$

is the effective laser frequency. If it is the case that the electronic contributions to γ_{CF_4} are dominant, the values of γ_{CF_4} experimentally determined by means of different nonlinear optical processes should all fall on the same straight line when plotted versus ν_L^2.

The previously published values of γ_{CF_4} from the dc Kerr effect,[37,38] ESHG[16,39,40] and THG[41] experiments have been collected in Table (5.1) and have been plotted versus ν_L^2 in Fig.(5.1). The straight line drawn there is the least squares fit of Eq.(5.1.1) to the experimental ESHG results of the present work. Two discordant values of γ_{CF_4} from the dc Kerr effect experiments are given in Table (5.1), but only one has been plotted in Fig.(5.1). The earler measurement in Ref.(37) was made on a sample of relatively low purity, only 98%, the chief impurity being air. One may estimate that the effect of 2% air as an impurity will be to increase the apparent value of γ_{CF_4} by 10%. A similar systematic error would arise from as little as 0.1% of typical fluoromethane

Table 5.1

Hyperpolarizability of CF_4 previously measured by several nonlinear optical processes.

Process	λ (nm)	ν_L^2 (10^8 cm^{-2})	γ_{CF_4} ($10^{-63}C^4m^4J^{-3}$)
dc Kerr	632.8	4.99	92.8 ± 5.2 [a]
	632.8	4.99	77.0 ± 6.0 [b]
ESHG	694.3	12.45	75.0 ± 6.7 [c]
	694.3	12.45	67.6 ± 2.2 [d]
	514.5	22.66	77.7 ± 0.8 [e]
THG	694.3	24.89	73.5 ± 3.7 [f]

a. From Ref.(37)

b. From Ref.(38)

c. From Ref.(39)

d. From Ref.(40)

e. Recalculated from the result given in Ref.(16), using the more accurate value of γ_{CH_4} from Ref.(36) for calibration.

f. From Ref.(41)

impurities. The effect of impurities would be revealed by a spurious temperature dependence of the measured γ_{CF_4}, but the measurements of Ref.(37) were made at only a single temperature. The later measurement in Ref.(38), on the other hand, used a sample of much higher purity (99.7%) and demonstrated temperature independence of the measured value of γ_{CF_4} over the temperature range 269-322 K. On the basis of these considerations, we have rejected the result of Ref.(37) in favor of the result of Ref.(38), which alone has been plotted in Fig.(5.1). Comparing the dc Kerr and THG measurements with the straight line fitted to the ESHG measurements, one finds that the dc Kerr measurement falls about 20% above , while the THG measurement result falls about 7% below the straight line. These differences are well outside the error bars of the various measurements, which clearly indicates that there is a different balance of vibrational contributions for different processes.

5.1.2 ... γ^{V}_{THG} And γ^{V}_{ESHG} For CF_4

To evaluate the vibrational contribution to γ_{THG} for

CF_4 using Eq.(2.2.7) derived in chapter 2, we employ the dipole matrix elements given in Table (5.2). These matrix elements for CF_4 are obtained from experimental measurements of infrared absorption and Raman scattering using the standard theory. The sum

$$\Sigma'_m |\mu^x_{mg}| = 1.3 \times 10^{-60} C^2 m^2 \qquad (5.1.3)$$

is dominated (95% contribution) by the ν_3 vibrational fundamental. Using the ν_3 vibrational transition frequency as Ω_v in Eq.(2.2.7), one gets

$$\gamma^v_{THG} \approx 1.1 \times 10^{-63} C^4 m^4 J^{-3} \qquad (5.1.4)$$

This is only about 1% of the total γ. The accuracy of Eq.(5.1.4) may be difficult to assess, but even if it were in error by a factor of three, γ^v_{THG} would still be very small compared to γ^e for CF_4. It indicates that γ^v_{THG} is almost negligible in comparison to the electronic contribution, and suggests that the vibrationally corrected γ_{THG} may be used to calibrate the electronic contributions to the other processes for CF_4. Following this idea and taking γ^v_{ESHG} as the vertical distance between the ESHG line and the vibrationally corrected THG point, the vibrational contribution to γ_{ESHG} is estimated to be $7.1 \times 10^{-63} C^4 m^4 J^{-3}$. It may be seen from Eq.(2.3.8) that there is a term of γ^v_{ESHG} which varies as ω^{-3}. However, evaluating this term using the

matrix elements given in Table (5.2), one finds that it is only $0.14 \times 10^{-63} C^4 m^4 J^{-3}$. This is negligible. Therefore, at optical frequencies the vibrational contribution to γ_{ESHG} is nearly independent of ω. Subtracting the value of γ^v_{ESHG} from the γ_{ESHG} data to obtain γ^e_{ESHG} only causes a parallel translation of the straight line shown in Fig.(5.1). The estimate of γ^e obtained by a parallel translation of the γ_{ESHG} line until it passes through the γ^e_{THG} point is shown as the dashed line in Fig.(5.1). Deviations of the measured values of γ from this dashed line are to be interpreted as vibrational contributions. If this analysis is correct, γ^v calculated from Eq.(2.3.8) for ESHG and Eqs.(2.4.6, 2.4.7) for the dc Kerr effect must agree with the experimental values which are obtained from Fig.(5.1).

Evaluation of γ^v_{ESHG} from Eq.(2.2.14) would be straight forward, except that there have been no measurements of the hyper-Raman β for CF_4 that we need for our analysis. However, there have been measurements of the hyper-Raman spectra of various other CX_4 compounds.[42,44] Therefore, we will use the measurements[43] and calculations[45] which have been made for CH_4 for guidance.

5.1.3 ...Hyper-Raman β

The hyper-Raman spectrum of CH_4 was recorded by Verdieck and Peterson in 1970.[43] The spectrum shows that the intensity of the hyper-Rayleigh line and the ν_3 Stokes hyper-Raman line are of the same order, and that all other transitions are much weaker. What the experiment measured is the XXX component of the isotropically averaged β^2, which may be expressed in terms of the hyperpolarizability components in the molecule fixed frame by the expression:[23]

$$\langle\beta^2\rangle_{XXX} = (1/35)\ \{\ 5\Sigma_\alpha\ \beta^2_{\alpha\alpha\alpha} + 6\Sigma_{\alpha\neq\beta}\ \beta_{\alpha\alpha\alpha}\beta_{\alpha\beta\beta} + 9\Sigma_{\alpha\neq\beta}\ \beta^2_{\alpha\alpha\beta} + 6\Sigma_{\substack{\alpha,\beta,\gamma \\ \text{cyclic}}}\ \beta_{\alpha\alpha\beta}\beta_{\beta\gamma\gamma} + 12\ \beta^2_{\alpha\beta\gamma}\ \} \qquad (5.1.4)$$

Assuming that the hyper-Rayleigh and the Stokes hyper-Raman scattering have equal intensities, and that

$$\beta_{xxx} = \beta_{xyy} = \beta_{zzx} \qquad (5.1.5)$$

is valid for a CX_4 molecule, Eq.(5.1.4) may be applied to obtain the following relation between the magnitude of the hyper-Raman and hyper-Rayleigh hyperpolarizability components:

$$\left|\langle\beta\rangle_{ZZZ}\right|(\nu_3) \approx 1/3\ \left|\langle\beta\rangle_{XYZ}\right|(\text{Rayleigh}). \qquad (5.1.6)$$

Hyper-Rayleigh scattering by a tetrahedral molecule is mediated by the single nonvanishing hyperpolarizability component β_{xyz}, whose magnitude was estimated theoretically by Buckingham and Stephan to be $7.8 \times 10^{-52} C^3 m^3 J^{-2}$ for CH_4. Hyper- Raman scattering is mediated by several components of the transition hyperpolarizability. Eq.(2.3.8) for γ^{v}_{ESHG} involves the following combination of transition hyperpolarizability components:

$$\beta_{eff} = \beta_{zzz} + \beta_{zxx} + \beta_{yyz}, \qquad (5.1.7)$$

which may be evaluated by means of Eq.(5.1.5) to obtain

$$|\beta_{eff}| = |\beta_{xyz}| = 7.8 \times 10^{-52} C^3 m^3 J^{-2} \qquad (5.1.8)$$

for CH_4. With this value of β_{eff}, and using the transition matrix elements given in Ref.(8), one obtains from Eq.(2.3.8) the estimate

$$\gamma^{v}_{ESHG} = 3 \times 10^{-63} C^4 m^4 J^{-3} \qquad (5.1.9)$$

for CH_4. This is only 1% of the total γ_{ESHG} of CH_4. In a similar fashion, using Eq.(2.3.8) and the matrix elements of Table (5.2) and the observed difference

$$\gamma_{ESHG} - \gamma^{e}_{THG} = 7.1 \times 10^{-63} C^4 m^4 J^{-3}, \qquad (5.1.10)$$

one deduces

$$|\beta_{eff}| \approx 1.3 \times 10^{-52} C^3 m^3 J^{-2} \qquad (5.1.11)$$

for the ν_3 mode of CF_4. One may note that this value is 6× smaller than the corresponding value for CH_4.

5.2 ... γ^{v}_{Kerr} for CF_4

5.2.1 ... The Nature of The Vibrations For CF_4

Before attempting to evaluate γ^{v}_{Kerr}, it is useful to consider in more detail the nature of the vibrations for CF_4. As a spherical top molecule, CF_4 has fundmentals ν_1, ν_2, ν_3 and ν_4 with the symmetry assignments a_1, e, f_2 and f_2 in the T_d group respectively. The normal vibrations corresponding to ν_1, ν_2, ν_3 and ν_4 have been shown in Fig.(5.2). All of the four fundamentals are Raman active, while only ν_3 and ν_4 are infrared active. The symmetry of a combination or overtone level is obtained from the direct product of irreducible representations, and will be a sum of a_1, a_2, e, f_1 and f_2 terms. The transitions with nonvanishing dipole matrix elements are just those for which the symmetry species f_2 appear at least once in the direct product of the representations of the initial and final levels of the transition. The three degenerate components of a mode of f_2 symmetry may taken as vibrations in the x,y and z directions, in which case only a single transition dipole matrix element and a single pair of transition polarizability matrix elements are nonvanishing for each vibrational component, as shown in Fig.(5.2). The

vibrational components and the corresponding nonvanishing matrix elements are

$$x: \quad \mu^x, \quad \alpha^{yz} = \alpha^{zy} \qquad (5.2.1a)$$

$$y: \quad \mu^y, \quad \alpha^{zx} = \alpha^{xz} \qquad (5.2.1b)$$

and

$$z: \quad \mu^z, \quad \alpha^{xy} = \alpha^{yx} \qquad (5.2.1c)$$

The nonvanishing matrix elements also satisfy

$$\mu^x = \mu^y = \mu^z \qquad (5.2.2a)$$

and

$$\alpha^{xy} = \alpha^{yz} = \alpha^{zx} \qquad (5.2.2b)$$

Note that only vibrations of f_2 symmetry contribute to the final expressions for γ^v_{ESHG} and γ^v_{Kerr}, Eqs.(2.3.8, 2.4.6, 2.4.7), and that the 3-fold degeneracy of such vibrations has already been accounted for by making use of Eq.(2.3.6) for the isotropic averages. However, when symmetry species f_2 appears n times in the representation of a particular vibrational overtone or combination transition, then one must multiply the matrix element by an extra degeneracy factor n. Furthermore, in the harmonic approximation, the matrix element for the hot band transition v_i, $v_j \rightarrow v_i$, v_j+1 is proportional to (v_j+1). Such a simple result is not obtained for overtone and combination transitions, which are not allowed in the harmonic approximation. So for

simplicity we have assumed that an overtone or combination transition starting from an excited level has the same matrix element as the same transition starting from the ground state.

5.2.2 ... γ^{v}_{Kerr} - Significant But Not Large

The evaluation of γ^{v}_{Kerr} from Eqs.(2.4.6) and (2.4.7) makes use of the matrix elements given in Table (5.2) and the hyper-Raman β deduced when considering γ^{v}_{ESHG}. Evaluation of Eq(2.4.6) is performed by writing out diagrams with three successive transitions $g \rightarrow m \rightarrow n \rightarrow g$, using matrix elements selected from Table (5.2). The number of diagrams used for calculation is about 100 altogether. Taking all the matrix elements to be positive when computing the diagrams, and noting that many of the required matrix elements correspond to hot band transitions, one obtains:

$$\gamma^{v,\alpha}_{Kerr} = 20.2 \times 10^{-63} C^{4} m^{4} J^{-3}. \qquad (5.2.3)$$

When Eq.(2.4.7) is evaluated and added, the final result is:

$$\gamma^{v}_{Kerr} = 23.0 \times 10^{-63} C^{4} m^{4} J^{-3}. \qquad (5.2.4)$$

One sees that Eq.(2.4.7) involving the hyper-Raman β makes

only a small contribution to the total. Subtracting Eq. (5.2.4) from the measured value of γ_{Kerr} one obtains γ^{v}_{Kerr} which has been plotted as the open triangle in Fig.(5.1). The error bar of the plotted point overlaps the dashed line representing γ^{e}, just as required by our analysis.

The calculated value of γ^{v}_{Kerr} finally permits a clear test of our calculations of γ^{v}. We had proceeded by attributing the difference between the γ^{e}_{THG} and γ_{ESHG} measurements to γ^{v}_{ESHG}. However, the theoretical expression for γ^{v}_{ESHG} is proportional to the unknown hyper-Raman β for CF_4, so the calculation for γ^{v}_{ESHG} ends up being used to determine the free parameter β. For γ^{v}_{Kerr}, no further unknown parameters enter the calculation and so one may carry through the comparison of theory and experiment in order to judge the accuracy of the calculation. Thus, the fact that all the vibrationally corrected measurements fall on the same line seems to support the adequacy of our analysis. It should be noted, however, that the calculated γ^{v}_{Kerr} is likely to be an overestimate since all matrix elements were assumed to be positive in the evaluation of the theoretical expressions. One may expect that there will be a cancellation of terms if some matrix elements are negative, which may significantly reduce the calculated

value of γ^{v}_{Kerr}. Nevertheless, the numerical results obtained here are much more reliable than those previously obtained by Elliott and Ward in 1984.[8] Their calculation gave

$$\gamma^{v}_{Kerr} = 3\gamma^{e} ,$$

which is about 10× too large.

Figure 5.1

Experimental values of γ_{CF_4} measured by the dc Kerr effect (triangles), ESHG (circles) and THG (square) are plotted versus ν_L^2 (defined by Eq.(5.1.2)). The filled symbols are the directly measured values of γ, while the open symbols are the corresponding results after subtracting the calculated vibrational contributions to obtain the purely electronic contribution γ^e. Note that the vibrational contribution is very small for THG. In Fig. (5.1), the solid line is the straight line which was fit to the ESHG data , while the dashed line is the corresponding straight line fit to the vibrationally corrected ESHG data points. All the measurements of γ^e (open symbols) fall on the dashed straight line to within the error bars, as predicted by Eq.(5.1.1).

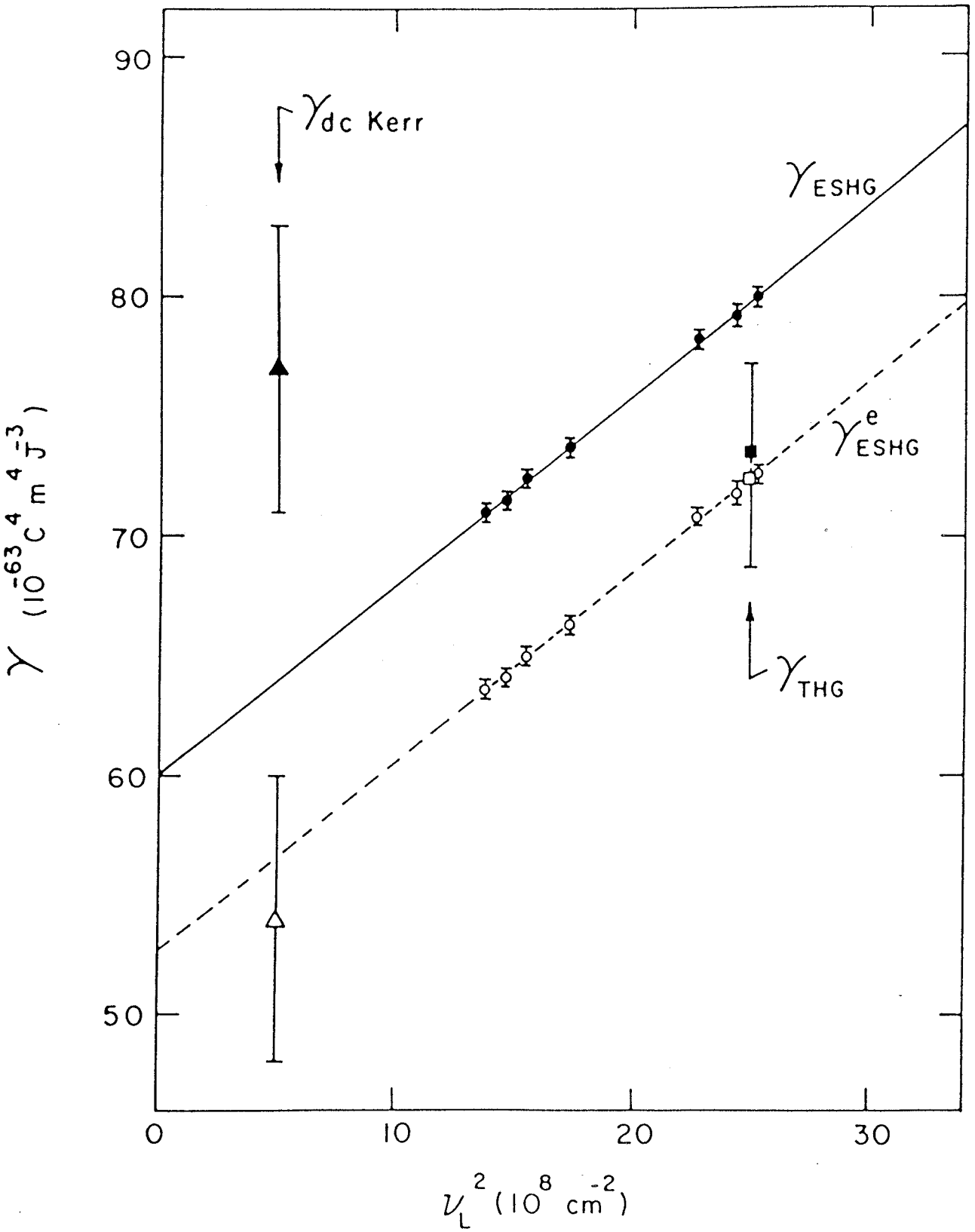
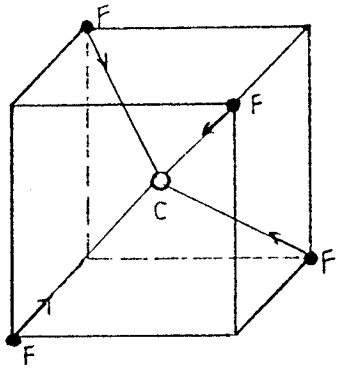
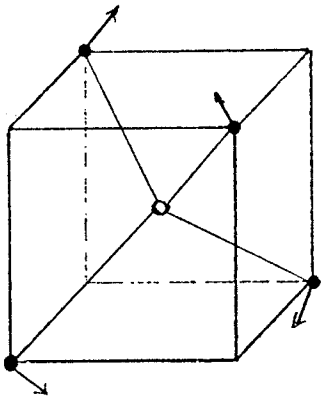

90
80
70
60
50
0
10
20
30
$\gamma_{dc\ Kerr}$
γ_{ESHG}
γ^{e}_{ESHG}
γ_{THG}
γ (10^{-63} C^4 m^4 J^{-3})
ν_L^2 (10^8 cm^{-2})

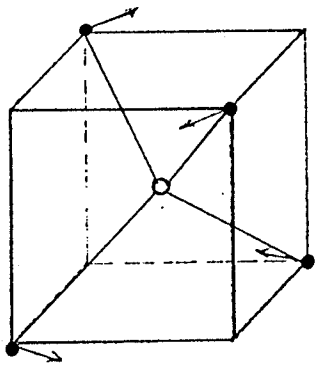
Figure 5.2

The normal vibrations with symmetry a_1, e, f_2, and f_2 of the molecule CF_4.[46]

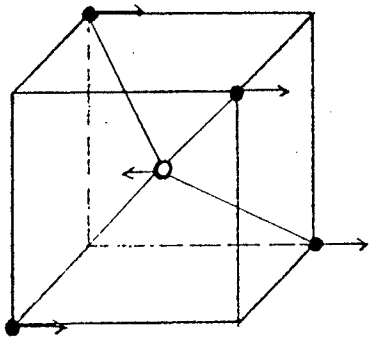


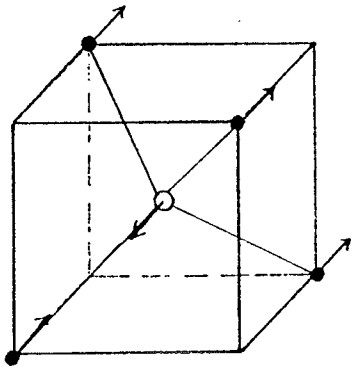
A_1 (ν_1)

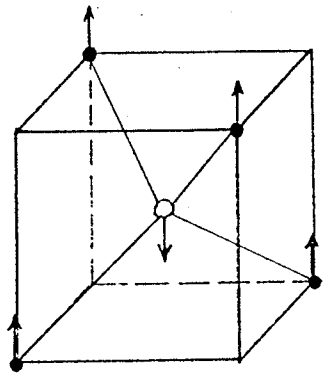




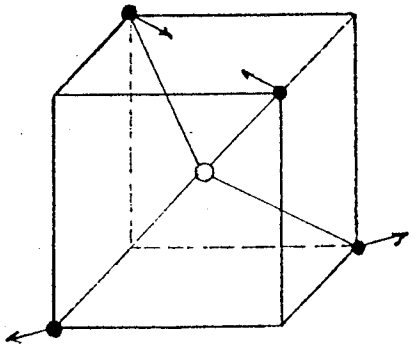
E (ν_2)

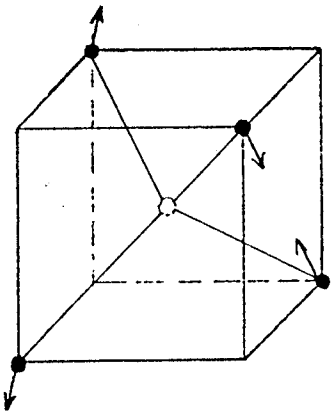


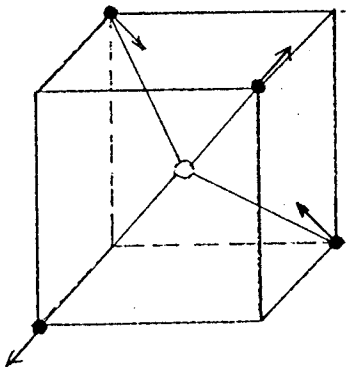




F_2 (ν_3)







F_2 (ν_4)

Table 5.2

Matrix elements for transitions from the ground state for the CF_4 molecule. The symmetry species for the upper level of each transition are given in the column labeled species. The matrix elements have been deduced from infrared absorption and Raman scattering data as outlined in Refs.(8, 26, 46-49). The observables in a Raman scattering experiment are the mean polarizability and the anisotropy, usually denoted by "a" and "γ". Summing over degenerate modes, these may be written as

$$a = 1/3\ (\alpha^{xx}+\alpha^{yy}+\alpha^{zz})$$

and

$$\gamma^2 = (\alpha^{xx}-\alpha^{yy})^2 + 9(\alpha^{xy})^2$$

in terms of the independent components of the transition polarizability tensor for CF_4.

Assign.	species	ν_{gm} (cm^{-1})	$\lvert\mu^{x}_{gm}\rvert^{a}$ (10^{-32} C m)	$\lvert\alpha^{xy}_{gm}\rvert^{b}$ (10^{-42} $C^2m^2J^{-1}$)
ν_1	a_1	908	0.	0.[c]
ν_2	e	435	0.	0.[d]
ν_3	f_2	1283	112.0	2.20
ν_4	f_2	631	16.0	2.43
$2\nu_2$	a_1+e	869	0.	0.[e]
$2\nu_3$	a_1+e+f_2	2566	7.66	0.04[f]
$2\nu_4$	a_1+e+f_2	1264	7.98	0.21[g]
$\nu_1+\nu_3$	f_2	2187	4.43	
$\nu_1+\nu_4$	f_2	1536	8.86	
$\nu_2+\nu_3$	f_1+f_2	1718	3.49	
$\nu_2+\nu_4$	f_1+f_2	1067	3.94	
$\nu_3+\nu_4$	a_1+e+f_1+f_2	1915	3.95	
$\nu_1+\nu_3+\nu_4$	a_1+e f_1+f_2	2819	1.12	

Assign.	species	ν_{gm} (cm^{-1})	$\lvert\mu^{x}_{gm}\rvert^{a}$ (10^{-32} C m)	$\lvert\alpha^{xy}_{gm}\rvert^{b}$ (10^{-42} $C^2m^2J^{-1}$)
$3\nu_4$	$a_1+f_1+2f_2$	1896	0.18	
$3\nu_3$	$a_1+f_1+2f_2$	3850	0.48	
$\nu_1+3\nu_3$	$a_1+f_1+2f_2$	4753	0.19	
$2\nu_3+\nu_4$	$a_1+e+2f_1+3f_2$	3198	0.56	
$\nu_1+2\nu_3+\nu_4$	$a_1+e+2f_1+3f_2$	4102	0.24	
$\nu_3+2\nu_4$	$a_1+e+2f_1+3f_2$	2547	5.10	
$\nu_1+\nu_3+2\nu_4$	$a_1+e+2f_1+3f_2$	3450	0.69	
$2\nu_1+\nu_3$	f_2	3091	0.61	
$2\nu_1+\nu_4$	f_2	2440	1.50	
$\nu_1+2\nu_4$	a_1+e+f_2	2168	1.37	
$2\nu_2+\nu_3$	f_1+2f_2	2153	1.08	
$\nu_3-\nu_1$ [h]	f_2	373	1.32	
$2\nu_3-\nu_2$ [i]	a_1+e+f_2	2131	0.61	
$3\nu_4-\nu_2$ [i]	$a_1+f_1+2f_2$	1459	3.07	

a. The matrix elements for the four fundamental transitions are the values calculated by Elliott and Ward from the infrared absorption data of Refs.(50-53). The remaining matrix elements were obtained from the overtone and combination band intensities read from the spectrum given in Ref.(50) and calibrated against the ν_4 band. The accuracy of the latter values is ±10-20% at best. The transition dipole $|\mu^x_{gm}|$ is nonzero for the f_2 symmetry species only.

b. The polarizability matrix elements for the four fundamentals are essentially the values calculated by Elliott and Ward from the Raman scattering data of Refs.(54-57). The overtone intensities were measured in the course of the Raman spectroscopic assay of our sample. The intensities were calibrated against the intensity of the nearest fundamental of the same symmetry. The transition polarizability α^{xy}_{gm} is nonzero for the f_2 symmetry species only.

c. For this vibration of a_1 symmetry the only nonzero transition polarizability is

$$1/3\ |\alpha^{xx}+\alpha^{yy}+\alpha^{zz}| = 7.1 \times 10^{-42}\ C^2m^2J^{-1}\ .$$

d. For this vibration of e symmetry the only nonzero transition polarizability is

$$|\alpha^{xx}-\alpha^{yy}| = 6.4 \times 10^{-42}\ C^2m^2J^{-1}\ .$$

e. Since the $2\nu_2$ band is strongly polarized and the a_1 symmetry species is in Fermi resonance with ν_1, one may assume that the intensity is dominated by the a_1 species, giving

$$1/3\ |\alpha^{xx}+\alpha^{yy}+\alpha^{zz}| = 1.44 \times 10^{-42}\ C^2m^2J^{-1}\ .$$

f. This is an upper bound arrived at by assuming that the Raman intensity is due to only the f_2 species.

g. Since the $2\nu_4$ band is depolarized and the f_2 species is in Fermi resonance with ν_3, we assumed that the intensity is dominated by the f_2 species.

h. Lower level is $\nu_1 = 1$.

i. Lower level is $\nu_2 = 1$.

CHAPTER 6

CONCLUSION

The experimental measurements of γ made by ESHG and a method for combining these measurements with those from other nonlinear optics experiments have been presented here. All the experimental data are consistent with the decomposition of γ into electronic and vibrational parts, where γ^e is strongly frequency dependent but γ^v is essentially constant for each nonlinear optical process. Combining measurements and theoretical calculations, one finds that for CF_4, γ^v / γ^e = 1%, 10% and 30% corresponding to THG, ESHG and the dc Kerr effect respectively. This fact indicates that vibrational contributions to γ_{CF_4} are negligible for THG, but significant for both the dc Kerr effect and ESHG. Accurate data on the frequency dependence of γ_{THG} and γ_{Kerr} would allow a better test of the calculations and analysis in this thesis.

The estimate of the value of the hyper-Raman β of CF_4 which is obtained as a by-product of this work allows one to predict that the hyper-Raman spectrum of CF_4 will be 40x weaker than that of CH_4. A measurement of the hyper-Raman

spectrum of CF_4 would provide another test of the above analysis. Ultimately, a measurement of γ^{V}_{ESHG} may provide a means for the accurate absolute calibration of the hyper-Raman β.

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APPENDIX

PROGRAMS FOR THE CALCULATIONS

IN THE THESIS

```
0001                PROGRAM DENSITYCF4.FOR
0002
0003      C   This program is used to calculate the density
              of CF4.
0004      C   B and C are the second and third virial
              coefficient, respectively, in cm**3/mole and
0005      C   cm**6/mole**2.
0006      C   The input data are the pressure "P" in torr
0007      C   and temperature "T" in "K".
0008      C   The final output is the density of CF4 in
              mole/m**3.
0009      C   To exit the program type L=6.
0010      C   To use this program for another gas, change
0011      C   the virial coefficients B and C.
0012
0013                B=-88.5
0014                C=6100
0015      1         WRITE (6,2)
0016      2         FORMAT (2X,23HPLEASE PUT IN DATA *P*.)
0017                READ (5,20) P
0018      3         WRITE (6,4)
0019      4         FORMAT (2X,23HPLEASE PUT IN DATA *T*.)
0020                READ (5,30) T
0021      5         WRITE (6,7)
0022      7         FORMAT (2X,40HPLEASE PUT IN THE DATA
                    GROUP NUMBER *L*.)
0023                READ (5,40) L
0024      20        FORMAT (F10.4)
0025      30        FORMAT (F10.4)
0026      40        FORMAT (I1)
0027      50        D=P/(62363.68*T)
0028                DI=D/(1+B*D+C*D*D)
0029                DO 10 I=1,10
0030                DF=D/(1+B*DI+C*DI*DI)
0031                IF(ABS(DF-DI)-1E-8) 100,100,80
0032      80        DI=DF
0033                GOTO 10
0034      10        CONTINUE
0035      100       DF=DF*1E6
0036                WRITE (6,150)L,DF
0037      150       FORMAT (2X,3HCF4,2X,3HNO(,I1,1H),2X,
                    8HDENSITY=,F10.4,2X,8HMOL/M**3)
0038      160       IF(L-5) 1,180,180
0039      180       STOP
0040                END
```

```
0001            PROGRAM  AVD.FOR
0002
0003     C  This program  is  used for fitting the data in an ESHG
           experiment.
0004     C  The  experimental  data  are  contained  in the arrays
           X(J) and Y(J) which are collected in the file
0005     C  FOR003.DAT and read by AVD.FOR.
0006     C  X(J) is  the pressure  (P)  and  Y(J)  is  the  signal
0007     C  count (S2w) at the corresponding pressure.
0008     C  "N"  is the degree of the fitting  polynomial,  chosen
           by the user.  "JI" is the number  of  data used.   "P"
0009     C  is the intial estimate  of  the  peak  pressure.   The
0010     C  values of "N","JI" and "P" are to be entered following
0011     C  a prompt by the program.
0012     C  The  program will give  the coefficients of the normal
           equations, the coefficients  of the fitting polynomial,
0013     C  the   differences  between   the  polynomial  fit  and
0014     C  experimental  data,  X^2 and  the peak values of S2w and
0015     C  P (divided  by 1000).   To  exit  the  program,  enter
0016     C  N=16.
0017
0018            IMPLICIT REAL*8 (A-H,O-Z)
0019            DIMENSION X(15),Y(15),S(30),Q(30),T(20),
                          A(20,20),B(20,20),R(15)
0020            DIMENSION E(15),P(15),D(15),AP(15),AY(15),
                          SGA(15),RD(15),AAY(15),AAP(15),
0021              +       AD(15)
0022
0023     C  READ THE DATA WHICH IS THE ORIGINIAL DATA DIVIDE
           BY 1000.
0024     C  WRITE THE DATA.
0025     C  J IS THE NUMBER OF THE DATA.
0026
0027     1      READ (003,10) (X(J),Y(J),J=1,10)
0028     10     FORMAT (1X,2F7.4)
0029     2      WRITE (6,5) (X(J),Y(J),J=1,10)
0030     5      FORMAT (2X,'P=',F6.4,5X,'S2W=',F7.3)
0031     21     WRITE (6,23)
0032     23     FORMAT (33H**PLEASE CHOOSE POWER NUMBER *N*.)
0033     25     READ (5,35) N
0034            IF (N-15) 26,26,300
0035     26     WRITE (6,27)
0036     27     FORMAT (33H**PLEASE CHOOSE DATA NUMBER *JI*.)
0037            READ (5,36) JI
0038     35     FORMAT (I2)
0039     36     FORMAT (I3)
0040
0041     C  CALCULATE THE COEFFICIENTS OF THE NORMAL EQUATIONS.
0042
0043     37     WRITE (6,38)
0044     38     FORMAT (2X,3HTHE,1X,4HDATA,1X,2HOF,1X,
                       13HM*S*EQUATIONS)
0045     45     NI=2*(N+1)
0046            DO 22 K=2,NI
0047            S(K)=0
0048            DO 11 J=1,JI
0049            S(K)=S(K)+X(J)**(K-2)
0050     11     CONTINUE
0051            Q(K)=S(K)
0052            WRITE (6,30) K,Q(K)
0053     22     CONTINUE
0054     30     FORMAT (10X,2HQ(,I2,2H)=,1X,D25.18)
0055            NN=N+1
0056            M=NN+1
0057            DO 44 K=1,NN
```

```
0058                T(K)=0
0059                DO 33 J=1,JI
0060                T(K)=T(K)+Y(J)*X(J)**(K-1)
0061      33        CONTINUE
0062                A(K,N+2)=T(K)
0063                B(K,N+2)=A(K,N+2)
0064                WRITE (6,40) K,N+2,B(K,N+2)
0065      44        CONTINUE
0066      40        FORMAT (10X,2HA(,I2,I2,2H)=,1X,D25.18)
0067                DO 55 I=1,NN
0068                DO 55 J=1,NN
0069                B(I,J)=S(I+J)
0070                WRITE (6,50) I,J,B(I,J)
0071      55        CONTINUE
0072      50        FORMAT (10X, 2HA(,I2,I2,2H)=,1X,D25.18)
0073
0074      C   A(I,J) IS THE COEFFICIENTS OF NORMAL EQUITIONS.
0075
0076      56        WRITE (6,57)
0077      57        FORMAT (2X,3HTHE,1X,12HCOEFFICIENTS,1X,
                    2HOF,1X,9HEQUATIONS)
0078      60        WRITE (6,70) ((B(I,J),J=1,M),I=1,NN)
0079      70        FORMAT (2X,D24.18,3X,D24.18,3X,D24.18)
0080
0081      C   NOW SOLVE THE NORMAL EQUATIONS.
0082
0083                DO 66 K=1,NN
0084                BMAX=0
0085                DO 77 I=K,NN
0086                IF (BMAX-DABS(B(I,K))) 80,77,77
0087      80        BMAX=DABS(B(I,K))
0088                L=I
0089      77        CONTINUE
0090                EPS=1D-15
0091                IF (BMAX.LT.EPS) STOP4444
0092                IF (L.EQ.K) GOTO 90
0093                DO 88 J=K,M
0094                TT=B(L,J)
0095                B(L,J)=B(K,J)
0096      88        B(K,J)=TT
0097      90        TT=1.0/B(K,K)
0098                K1=K+1
0099                DO 99 J=K1,M
0100                B(K,J)=B(K,J)*TT
0101                DO 99 I=K1,NN
0102      99        B(I,J)=B(I,J)-B(I,K)*B(K,J)
0103      66        CONTINUE
0104                DO 111 IK=2,NN
0105                I=M-IK
0106                I1=I+1
0107                DO 111 J=I1,NN
0108      111       B(I,M)=B(I,M)-B(I,J)*B(J,M)
0109      112       DO 115 K=1,NN
0110                R(K)=B(K,M)
0111                WRITE (6,100) K,R(K)
0112      115       CONTINUE
0113      100       FORMAT (2X,8HSOLUTION,5X,
                    2HS(,I2,2H)=,D24.18)
0114
```

```
0115     C  SOLUTION TO THE LEAST SQUARES PROBLEM HAS
            BEEN OBTAINED.
0116     C  R(K) IS THE COEFFICIENTS OF THE FIT FUNCTION.
0117     C  NOW COMPARE THE SOLUTION WITH THE ORIGINAL DATA.
0118
0119           WRITE (6,105)
0120     105   FORMAT (14X,8H*ERRORS*,23X,5H*SUM*)
0121           DO 222 I=1,JI
0122           XI=X(I)
0123           P(I)=0
0124           DO 333 K=1,NN
0125           QI=R(K)*XI**(K-1)
0126           P(I)=P(I)+QI
0127     333   CONTINUE
0128           AP(I)=DABS(P(I))
0129           AY(I)=DABS(Y(I))
0130           D(I)=DABS(AP(I)-AY(I))
0131           E(I)=D(I)/AP(I)
0132           WRITE (6,125) I,E(I),I,AP(I)
0133     125   FORMAT (10X,2HE(,I3,2H)=,D18.9,7X
               3HAP(,I3,2H)=,D18.9)
0134     222   CONTINUE
0135
0136     C  NOW ESTIMATE THE FIT FUNCTION.
0137     C  AAP(I) IS THE FUNCTION VALUE.
0138     C  AAY(I) IS THE DATA OF S2W.
0139     C  XK IS CIGMA((Y-YI)**2/ABS(YI)).
0140
0141     223   XK=0
0142           DO 331 I=1,JI
0143           AAP(I)=AP(I)*1000
0144           AD(I)=(D(I)*1000)
0145           RD(I)=AD(I)**2
0146           AAY(I)=AY(I)*1000
0147           XK=XK+RD(I)/AAY(I)
0148     331   CONTINUE
0149     133   WRITE (6,134) (RD(I),AAY(I),
               AAP(I),AD(I),I=1,JI)
0150     134   FORMAT (5X,'(Y-YI)**2=',D12.6,2X,
0151          +  'YI=',D12.6,2X,'Y=',D12.6,2X,
               'ABS(Y-YI)='F7.2)
0152     332   ND=JI-N-1
0153           CHI=XK/ND
0154           WRITE (6,335) XK,ND,CHI
0155     335   FORMAT (5X,'*SIGMA*=',D12.6,4X,
               '*ND*=',I3,
0156          +  4X,'*CHISQ*=',F7.3)
0157           WRITE (6,110)
0158           DO 444 I=1,NN
0159           IR=I-1
0160           WRITE (6,120) IR,R(I)
0161     444   CONTINUE
0162     110   FORMAT (2X,36H  THE COEFFICIENTS OF
               FIT*POLYNOMIAL)
0163     120   FORMAT (10X,2HR(,I2,2H)=,2X,D18.9)
0164
0165     C  NOW FIND THE PEAK.
0166     C  XN IS THE INITIAL ESTIMATE.
0167
0168     121   WRITE (6,122)
0169     122   FORMAT (2X,8H**PLEASE,1X,6HCHOOSE,
               1X,4H*P*.)
0170     130   READ (5,140)XN
0171     103   IF (XN.EQ.0.) ASSIGN 300 TO I
```

```
0172                IF (XN.EQ.22222.) ASSIGN 21 TO I
0173                IF (XN.LT.11111.) ASSIGN 145 TO I
0174                GO TO I,(300,21,145)
0175     140        FORMAT (F10.2)
0176     145        L=0
0177                EPX=1D-7
0178     150        L=L+1
0179                IF (L-200) 155,155,210
0180     155        X1=XN
0181                SUM=0
0182                DO 555 I=1,NN
0183                SMR=R(I)*X1**(I-1)
0184                SUM=SUM+SMR
0185     555        CONTINUE
0186     160        DSUM=0
0187                DO 666 J=2,NN
0188                DSMR=(J-1)*R(J)*X1**(J-2)
0189                DSUM=DSUM+DSMR
0190     666        CONTINUE
0191     161        DDSUM=0
0192                DO 667 K=3,NN
0193                DDSMR=(K-1)*(K-2)*R(K)*X1**(K-3)
0194                DDSUM=DDSUM+DDSMR
0195                IF (DDSMR) 667,210,667
0196     667        CONTINUE
0197     165        XN=X1-DSUM/DDSUM
0198     170        WRITE (6,190)
0199                WRITE (6,200) L,SUM,DSUM,XN
0200     175        AXN=DABS(XN)
0201                AX1=DABS(X1)
0202                DX=AXN-AX1
0203                IF (DABS(DX)-EPX) 220,220,150
0204     190        FORMAT (7X,1HL,13X,3HS2W,20X,4HDSUM,
                    20X,1HP)
0205     200        FORMAT (5X,I4,4X,D18.9,4X,D18.9,4X,D18.9)
0206     210        WRITE (6,215)
0207                GOTO 130
0208     215        FORMAT (5X,7H*FAIL*.,4X,8H**PLEASE,1X,
                    6HCHOOSE,1X,
0209               +          7HANOTHER,1X,2HP./5X,10H** 0= STOP/
0210               +       5X,25H**22222= CHOOSE ANOTHER N/
0211               +       5X,15H**<11111= GO ON)
0212     220        GOTO 21
0213     300        STOP
0214                END
```

```
0001                PROGRAM GAMA
0002
0003      C   This program  is  used  to calculate the
0004      C   vibrational hyperpolarizability  for the
0005      C   dc Kerr effect.  In the  program,  A, B,
0006      C   and C are the data  arrays corresponding
0007      C   to αuu, uαu and uuα terms, respectively.
0008      C   The data for a  single term specified by
0009      C   A, B  or  C  consists  of  three  matrix
0010      C   elements,    two    intermediate   state
0011      C   degeneracies     and     two     transition
0012      C   frequencies, in that order.  The program
0013      C   GAMA.FOR reads these data from the files
0014      C   FOR051.DAT, FOR052.DAT  and  FOR053.DAT.
0015      C   The output of the program is  a  list of
0016      C   the    input    data,    the    calculated
0017      C   contribution  to the hyperpolarizability
0018      C   for each term,  and the final result for
0019      C   the vibrational second hyperpolarizability
0020      C   denoted by "GAMA".

0021                DIMENSION A(25,7),B(21,7),C(25,7),AA(25),
0022               +  BB(25),CC(25)
0023
0024                READ (51,10) ((A(I,J),J=1,7),I=1,25)
0025                READ (52,20) ((B(I,J),J=1,7),I=1,21)
0026                READ (53,30) ((C(I,J),J=1,7),I=1,25)
0027      10        FORMAT (7F9.5)
0028      20        FORMAT (7F9.5)
0029      30        FORMAT (7F9.5)
0030                WRITE (6,11)
0031                WRITE (6,12) (I,(A(I,J),J=1,7),I=1,25)
0032      11        FORMAT (2X,'NO.',2X,'ALFA(gn)',5X,'U(np)'
0033               +  ,5X,'U(pg)',3X,'g(n)',2X,'g(p)',3X,
                      'V(gn)',4X,'V(pg)')
0034      12        FORMAT (2X,I2,2X,F9.5,2X,F9.5,2X,F9.5,2X,
0035               +  F3.0,3X,F3.0,4X,F5.0,3X,F5.0)
0036                WRITE (6,22)
0037                WRITE (6,24) (I,(B(I,J),J=1,7),I=1,21)
0038      22        FORMAT (2X,'NO.',4X,'U(gm)',5X,'ALFA(mp)'
0039               +  ,4X,'U(pg)',3X,'g(m)',2X,'g(p)',3x,
                      'V(gm)',4X,'V(pg)')
0040      24        FORMAT (2X,I2,2X,F9.5,2X,F9.5,2X,F9.5,2X,
0041               +  F3.0,3X,F3.0,4X,F5.0,3X,F5.0)
0042                WRITE (6,33)
0043                WRITE (6,36) (I,(C(I,J),J=1,7),I=1,25)
0044      33        FORMAT (2X,'NO.',5X,'U(gm)',5X,'U(mn)',
0045               +  4X,'ALFA(ng)',2X,'g(m)',3X,'g(n)',2X,'
                      V(mg)',3X,'V(ng)')
0046      36        FORMAT (2X,I2,2X,F9.5,2X,F9.5,2X,F9.5,2X,
0047               +  F3.0,3X,F3.0,4X,F5.0,3X,F5.0)
0048
0049      C NOW CALCULATE THE TERMS IN THE BRACKET OF GAMA.
0050
0051                X=9.123*1000
0052
0053      C PART (A).  NO.1 - 25  DIVIDE  BY  3
0054      C BECAUSE OF THE VIBERATIONAL SYMMETRY.
0055
0056                SUMA=0
0057      41        DO 42 I=1,25
```

```
0058                AA(I)=X*A(I,1)*A(I,2)*A(I,3)*A(I,4)
0059              + *A(I,5)/(A(I,6)*A(I,7)*3.0)
0060                SUMA=SUMA+AA(I)
0061          42    CONTINUE
0062
0063          C PART (B). NO.1 - 15 DIVIDE BY 3 AND
                NO. 16 - 21 DIVIDE BY 9 BECAUSE OF
0064          C THE VIBERATIONAL SYMMETRY.
0065
0066          50    SUMB=0
0067                DO 55 I=1,15
0068                BB(I)=X*B(I,1)*B(I,2)*B(I,3)*B(I,4)*
0069              + B(I,5)/(B(I,6)*B(I,7)*3.0)
0070                SUMB=SUMB+2.0*BB(I)
0071          55    CONTINUE
0072          56    DO 57 I=16,21
0073                BB(I)=X*B(I,1)*B(I,2)*B(I,3)*B(I,4)*
0074              + B(I,5)/(B(I,6)*B(I,7)*9.0)
0075                SUMB=SUMB+2.0*BB(I)
0076          57    CONTINUE
0077
0078          C PART (C). SIMILAR TO PART (A).
0079
0080          60    SUMC=0
0081          67    DO 68 I=1,25
0082                CC(I)=X*C(I,1)*C(I,2)*C(I,3)*C(I,4)*
0083              + C(I,5)/(C(I,6)*C(I,7)*3.0)
0084                SUMC=SUMC+CC(I)
0085          68    CONTINUE
0086                WRITE (6,70) (I,AA(I),I,BB(I),I,
                    CC(I),I=1,25)
0087                WRITE (6,75) SUMA,SUMB,SUMC
0088          70    FORMAT(2X,'A(',I2,')=',F9.6,3X,'B('
                    ,I2,')=',
0089              + F9.6,3X,'C(',I2,')=',F9.6)
0090          75    FORMAT (4X,'SUMA='F9.6,1X,'10**(-62)
                    C4M4J-3',
0091              + /4X,'SUMB=',F9.6,1X,'10**(-62)C4M4J-3'
0092              + ,/4X,'SUMC=',F9.6,1X,'10**(-62)C4M4J-3')
0093                SUM=SUMA+SUMB+SUMC
0094                WRITE (6,80) SUM
0095          80    FORMAT (4X,'GAMA=',F9.6,1X,'10**
                    (-62)C4M4J-3')
0096          90    STOP
0097                END
```