Nuclear relaxation contribution to static and dynamic (infinite frequency approximation) nonlinear optical properties by means of electrical property expansions: Application to HF, CH₄, CF₄, and SF₆

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(Received 4 August 1997; accepted 8 December 1997)

Electrical property derivative expressions are presented for the nuclear relaxation contribution to static and dynamic (infinite frequency approximation) nonlinear optical properties. For CF₄ and SF₆, as opposed to HF and CH₄, a term that is quadratic in the vibrational anharmonicity (and not previously evaluated for any molecule) makes an important contribution to the static second vibrational hyperpolarizability of CF₄ and SF₆. A comparison between calculated and experimental values for the difference between the (anisotropic) Kerr effect and electric field induced second-harmonic generation shows that, at the Hartree–Fock level, the nuclear relaxation/infinite frequency approximation gives the correct trend (in the series CH₄, CF₄, SF₆) but is of the order of 50% too small. © 1998 American Institute of Physics. [S0021-9606(98)04310-4]

I. INTRODUCTION

It is now well established¹⁻³ that nuclear motions can make major contributions to polarizabilities and hyperpolarizabilities. In fact, these contributions can exceed the electronic term not only in the static limit⁴ but at optical frequencies⁵ as well.

In recent articles (to which the reader is directed for references) Bishop and Dalskov⁶ and Luis et al.⁷ have provided a survey of the various approaches available for computing the nuclear contribution (apart from rotations, which are usually ignored as they are here). From a theoretical perspective there are two general procedures that are relevant for this paper. One of these might be called time-dependent perturbation theory and the other the method of time-independent property expansions.

The time-dependent perturbation theory approach has been developed by Bishop and Kirtman (BK).⁸⁻⁹ It is the only procedure that is applicable at all optical frequencies. On the other hand, in the static limit one can arrive at the same formulas by expanding the potential energy⁷ and induced dipole moment as a double power series in the normal coordinates and the static electric field(s). This is the time-independent property expansion method. The specific connections between the perturbation and expansion methods have been analyzed for a diatomic molecule by Martí and Bishop.¹⁰

From the viewpoint of the property expansion method it is natural to divide the total static hyperpolarizability arising from nuclear motions into two sets of terms,¹¹ one of which has been referred to as the nuclear relaxation contribution and the other as the "vibrational" or "curvature" contribution. The nuclear relaxation contribution is due to the change in the induced dipole moment caused by the field-induced relaxation of the equilibrium geometry. The curvature contribution is due to the change in zero-point vibrational energy caused directly by the field and indirectly by the geometry relaxation. This contribution is sometimes referred to as "vibrational" but should not be confused with the vibrational hyperpolarizability, which is defined by:

\[ \text{vibrational hyperpolarizability} = \text{ZPVA} \]

where ZPVA is the zero-point vibrational averaging correction to the electronic hyperpolarizability. In this paper we will be dealing almost entirely with the nuclear relaxation component.

It is interesting⁷,¹² that, in the property expansion formulation, the nuclear relaxation contribution to the static (hyper-)polarizability is completely accounted for by considering only those terms in the double expansion of the potential energy \( V \), that involve the derivatives

\[ \phi^{[1...i_n,j_1...j_m]} = \frac{1}{n!m!} \left( \frac{\partial^{n+m} V(Q_1, ..., Q_{3N-6}, F_x, F_y, F_z)}{\partial Q_1 ... \partial Q_{3N-6} \partial F_x \partial F_y \partial F_z} \right)_{Q=0,F=0}, \]

where \( Q \) are the normal coordinates; \( F_x, F_y, F_z \) are the Cartesian components of the electric field; and \( n + m \leq 2 \) for linear polarizability (\( \alpha \)), 3 for first hyperpolarizability (\( \beta \)), and 4 for second hyperpolarizability (\( \gamma \)). We also note that the relaxation contribution contains the leading vibrational (hyper)polarizability perturbation terms of each type as discussed below. From a perturbation theory point of view, the
major terms in the remaining curvature contribution are those due to ZPVA. The latter are of order (0,1), (1,0) and higher, where the first number in parentheses is the order of electrical anharmonicity and the second number is the order of mechanical anharmonicity. In order to estimate the ZPVA correction one needs the fifth derivatives $a_{23}$ for $\beta$ and the sixth derivatives $a_{24}$ for $\gamma$ (in both cases $Q_0 = Q_1$).

From the computational perspective, all of the static hyperpolarizability contributions due to nuclear motion can be evaluated either by using the above derivatives or by applying finite field techniques.$^{11,13–17}$ The finite field procedure has the advantage of computational efficiency, particularly for large molecules. However, it does not permit an analysis of the individual terms that are obtained by examining the derivatives. The derivatives, in turn, may be evaluated either numerically or analytically depending upon the availability of appropriate software.

There is one other circumstance where time-dependent perturbation theory and time-independent property expansions connect, namely at the “infinite (optical) frequency” limit. Bishop, Hasan, and Kirtman (BHK)$^{18}$ have presented a simple finite field procedure which yields, in that limit, the nuclear relaxation contribution to the most common nonlinear optical processes. They presented an analysis in terms of perturbation theory but their method was also related to a double expansion of the static induced linear polarizability and first hyperpolarizability (rather than the dipole moment). One purpose of our paper is to present an explicit derivation in terms of the derivatives [see Eq. (2)] involved in these expansions. A major part of the motivation for doing so is to set the stage for possible extensions of the BHK finite field procedure to include the curvature contribution as well.

The nuclear relaxation/infinite frequency treatment is an important special case because it is expected to give a reasonable approximation for the “exact” optical frequency vibrational hyperpolarizability. Both theoretical and computational arguments have been made to support this view. In the BK perturbation theory treatment the various terms appearing in the expression for the vibrational hyperpolarizability are classified according to type (see later) and the lowest-order terms of each type constitute the nuclear relaxation contribution.$^6$ From the perspective of property expansions we have already noted, in connection with the static limit, that the nuclear relaxation expressions are complete with respect to derivatives of total order $\leq 4$ for $\gamma$. This remains true in the infinite frequency approximation; in fact, in that case only one of the derivatives with $n + m = 4$ appears. Finally, in numerical tests of the nuclear relaxation/infinite frequency approximation on five small molecules Bishop and Dalskov$^5$ found this treatment to be adequate in all instances where the effect of nuclear motions is important.

The second purpose of this paper is to carry out a few applications of the nuclear relaxation formulas obtained by the property expansion method for the two limiting cases (static, infinite frequency) that have been mentioned. In the infinite frequency limit these formulas are identical to those already derived by perturbation theory.$^{8,9,18}$ However, there are no previous $ab$ initio calculations on CF$_4$ or SF$_6$ and to our knowledge these are two of only three polyatomic molecules for which experimental measurements$^{19}$ of the contributions due to nuclear motion are available. In the static limit, perturbation theory expressions have not been given previously for some of the higher-order terms which have, therefore, not been evaluated for any polyatomic molecule. We find that in certain cases one particular higher-order term can be quite important.

II. DERIVATION

We follow a procedure similar to that employed in previous work$^7$ dealing with a static field. In fact, the initial steps are identical: (i) The potential energy, $V$, is expanded about the field-free equilibrium geometry using a double power series through fourth order in the normal coordinates $Q = (Q_1, Q_2, \ldots, Q_{3N-6}(0))$ and the field strength vector $F = (F_x, F_y, F_z)$; and (ii) the normal coordinate displacements due to the field are obtained by iterative solution of the stationary condition for the field-dependent equilibrium geometry.

From the potential energy expansion in step (i) one can derive analogous expansions for the dipolar electrical properties:

$$\mu_a = \left( \frac{\partial V(Q,F)}{\partial F_a} \right)_{Q=0,F=0},$$

$$\alpha_{ab} = \left( \frac{\partial^2 V(Q,F)}{\partial F_a \partial F_b} \right)_{Q=0,F=0},$$

etc.

If one replaces the normal coordinates that appear in these expressions by the field-dependent displacements determined in step (ii) the result is a power series expansion in $F$. After subtraction of the pure electronic terms, i.e., those terms that do not contain nuclear derivatives, the expansion of $\mu$ gives the nuclear relaxation contribution to the static polarizability, $\alpha_{ab}^{nr}(0;0)$, hyperpolarizabilities, $\beta_{abc}^{nr}(0;0,0)$, and $\gamma_{abcd}^{nr}(0;0,0,0)$, according to the Taylor series definition$^{20}$

$$\Delta \mu_a = \sum_{b}^{x,y,z} \alpha_{ab}^{nr}(0;0) F_b + \frac{1}{2} \sum_{b,c}^{x,y,z} \beta_{abc}^{nr}(0;0,0) F_b F_c + \frac{1}{6} \sum_{b,c,d}^{x,y,z} \gamma_{abcd}^{nr}(0;0,0,0) F_b F_c F_d.$$ (4)

Here the prime in $\mu_a$ is used as a reminder that the pure electronic terms have been removed. The numerical values in parentheses indicate the frequencies associated with the particular process in the conventional notation ($-\omega_a; \omega_1, \ldots$) where the frequencies $\omega_1, \ldots$ correspond to the fields $F_b, \ldots$ (in order) and $\omega_a$ corresponds to $F_a$. In terms of the derivatives in Eq. (2),

$$\alpha_{ab}^{nr}(0;0) = \frac{1}{2} \sum_{i=1}^{3N-6} P_{ab} a_i^{a_i} a_i^{b_i},$$ (5)
\[ \beta_{abc}^{(0,0)} = \sum_{i=1}^{3N-6} P_{abc}^{i,ab} q_1^{i,c} - \sum_{ij} P_{abc}^{ij,a} q_1^{i,d} q_1^{j,c} + \sum_{ijk} P_{abcd}^{ijk} q_1^{i,c} q_1^{j,d} q_1^{k,b} q_1^{l,c} \] (6)

and

\[ \gamma_{abcd}^{(0,0)} = \sum_{i} P_{abcd}^{i,ab} \left( \frac{a_{11}}{2a_{20}} q_1^{i,d} + \frac{a_{12}}{2a_{20}} q_2^{i,c} \right) - \sum_{ij} P_{abcd}^{ij,a} \left( \frac{a_{21}}{2a_{20}} q_1^{i,d} + \frac{a_{12}}{2a_{20}} q_2^{i,d} \right) \] (8)

where the notation

\[ q_1^{k,a} = \frac{a_{11}}{2a_{20}}, \quad q_2^{k,ab} = \frac{a_{12}}{2a_{20}} \] (8)

has been introduced and \( P_{ab} \ldots \) indicates a sum over all the perturbations of the indices \( a \) \( b \) \ldots

As BHK\textsuperscript{18} have demonstrated the corresponding expansions for \( \Delta \alpha_{ab}^{(0,0)} \) and \( \Delta \beta_{ab}^{(0,0)} \) yield the nuclear relaxation contributions to several nonlinear optical (NLO) processes in the infinite frequency approximation [see BHK Eqs. (7), (8), (10), and (11)]:

\[ \Delta \alpha_{ab}^{(0,0)} = \sum_{c} \beta_{abc}^{(0,0)} (\omega, \omega, 0) \rightarrow_{\omega \rightarrow \infty} F_c \]
\[ + \frac{1}{2} \sum_{c,d} \gamma_{abcd}^{(0,0)} (\omega, \omega, 0) \rightarrow_{\omega \rightarrow \infty} F_c F_d \] (9)

and

\[ \Delta \beta_{abc}^{(0,0)} = \sum_{d} \gamma_{abcd}^{(0,0)} (\omega, \omega, 0) \rightarrow_{\omega \rightarrow \infty} F_d \] (10)

Following exactly the same procedure that was used for \( \Delta \mu^\prime \) [i.e., steps (i) and (ii) above followed by expansion of \( \alpha \) or \( \beta \)] we find

\[ \beta_{abc}^{(0,0)} (\omega, \omega, 0) = \sum_{i=1}^{3N-6} 2a_{12}^{i,ab} q_1^{i,c} \] (11)

\[ \gamma_{abcd}^{(0,0)} (\omega, \omega, 0) \rightarrow_{\omega \rightarrow \infty} = \sum_{i} P_{abcd}^{i,ab} \left( 6a_{13}^{i,ab} q_1^{i,d} + 2a_{12}^{i,ab} q_2^{i,c} \right) - \sum_{ij} P_{abcd}^{ij,a} \left( 2a_{12}^{ij,a} q_1^{i,d} + 4a_{11}^{ij,a} q_1^{j,d} q_1^{l,b} \right) \]
\[ - \sum_{ijk} P_{abcd}^{ijk} \left( 6a_{30}^{ijk} q_1^{i,j} q_1^{j,k} q_1^{k,b} q_1^{l,c} \right) + \sum_{ijk} P_{abcd}^{ijk} \left( 9a_{30}^{ijk} q_1^{i,j} q_1^{j,k} q_1^{k,b} q_1^{l,c} \right) \] (12)

for the dynamic nuclear relaxation contributions in the infinite frequency approximation. Equations (11), (12), and (13) correspond, respectively, to the Pockels effect, Kerr effect, and electric field induced second-harmonic generation (ESHG). The expressions for these quantities can also be deduced directly from the BK perturbation treatment by taking the \( \omega \rightarrow \infty \) limit of the terms listed in Table I of BHK.\textsuperscript{18}

We note that \( \alpha_{ab}^{(0,0)} (\omega, \omega, \omega) \), \( \beta_{ab}^{(0,0)} (2\omega, \omega, \omega) \), and \( \gamma_{ab}^{(0,0)} (2\omega, \omega, \omega, \omega) \) all vanish in the infinite frequency approximation. The only major nonlinear optical process that remains, therefore, is the intensity-dependent refractive index (IDRI). From the BK perturbation treatment the terms in IDRI that survive in the infinite frequency limit\textsuperscript{1} have the form \( \alpha_{ab}^{(0,0)} \) or, in derivative notation, they contain the products \( \alpha_{12}^{ij,a} q_2^{i,c} \). Extracting these products from the formula for IDRI given in BHK we find

\[ \gamma_{abcd}^{(0,0)} (2\omega, \omega, \omega, \omega) \rightarrow_{\omega \rightarrow \infty} = \sum_{i} \left( 6a_{13}^{i,ab} q_1^{i,d} \right) \] (13)

\[ \gamma_{abcd}^{(0,0)} (2\omega, \omega, \omega, \omega) \rightarrow_{\omega \rightarrow \infty} = 8 \sum_{i} \left( a_{12}^{i,ab} q_2^{i,c} \right) \] (14a)

with an analogous expression for the average value (see later). More generally, for an arbitrary component it can be demonstrated\textsuperscript{31} that

\[ \gamma_{abcd}^{(0,0)} (\omega, \omega, \omega, \omega) = 4 \sum_{i} \left( a_{12}^{i,ab} q_2^{i,c} + a_{12}^{i,ab} q_2^{i,b} \right) \] (14b)

Table I shows compactly how the individual terms in the property expansion formulas given here connect with the BK perturbation treatment. All of the terms in the static hyperpolarizability have already appeared in one place or another.\textsuperscript{17,9} However, the terms in \( \left[ \mu^4 \right]^{0,2} \), i.e.,

\[ \sum_{i,j,k,l} P_{abcd}^{ijkl} q_1^{i,a} q_1^{j,b} q_1^{k,c} q_1^{l,d} \] (15)

\[ \sum_{i,j,k,l,m} P_{abcd}^{ijkl} q_1^{i,a} q_1^{j,b} q_1^{k,c} q_1^{l,d} \]
have been presented just recently and have not yet been evaluated for any molecule. Each dynamic hyperpolarizability expression contains a subset of the derivative terms included in the static hyperpolarizability, but with different coefficients. In particular, the terms in Eq. (15) are present only in the static hyperpolarizability. As observed previously, for the diagonal tensor components and for the mean (isotropic) value each type of perturbation term that appears in the dynamic nuclear relaxation formula also occurs in the corresponding static formula, the only difference being a change in the multiplicative factor.

### III. COMPUTATIONAL DETAILS

Calculations on HF, CH₄, CF₄, and SF₆ were carried out at the ab initio self-consistent field molecular-orbital level of theory using the Dunning–Huzinaga basis set with (9s5p4d)/(4s2p2s) and (9s5p4d)/(5s3p3s) contractions for C, F, and H and (11s7p)/(6s4p) and (11s7p)/(7s5p) contractions for S. One set of polarization functions was included with exponents 0.532 for S, 0.75 for C, 0.90 for F, and 0.75 for H in the first contraction to yield the DZP basis; and two sets of polarization functions with exponents 0.532 and 0.133 for S, 0.75 and 0.15 for C, 0.90 and 0.15 for F, and 0.75 and 0.15 for H in the second contraction to yield the VTZ2P basis. Six Gaussians were used for each set of d orbitals.

Energy derivatives up to fourth order with respect to either normal coordinates, field strength, or a combination of the two are needed for the complete nuclear relaxation treatment. There is no commonly available computer program, as yet, from which all the derivatives can be obtained analytically. The GAUSSIAN94 suite of programs that we use gives analytical results for the second hyperpolarizability. We report mean values of from numerical differentiation of the static second hyperpolarizability. This suggests that the omitted terms are likely to be small as well. Howbeit, for the static second hyperpolarizability we also report the anisotropic values given by

\[
\gamma_{ab}^{0} = 3 \sum_{a,b,c,d} \gamma_{a,b,c,d}^{0}
\]

for the Kerr effect, we also present the anisotropic values given by

\[
\gamma_{ab}^{0} = 3 \sum_{a,b,c,d} \gamma_{a,b,c,d}^{0}
\]

\[
\gamma_{ab}^{0} = 3 \sum_{a,b,c,d} \gamma_{a,b,c,d}^{0}
\]

### TABLE I. Contribution of individual nuclear relaxation terms in the property expansion formulas for static and dynamic hyperpolarizabilities and connection with BK perturbation treatment.

<table>
<thead>
<tr>
<th>Property expansion term</th>
<th>BK treatment</th>
<th>Hyperpolarizability</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{12}^{i,j} q_{1}^{i} q_{1}^{j} )</td>
<td>([\mu a]^{0} )</td>
<td>( \beta_{40}^{0} )</td>
</tr>
<tr>
<td>(- a_{12}^{i,j} q_{1}^{i} q_{1}^{j} )</td>
<td>([\mu]^{0} )</td>
<td>( \beta_{40}^{0} )</td>
</tr>
<tr>
<td>( a_{0}^{i,j} q_{1}^{i} q_{1}^{j} )</td>
<td>([\mu]^{0} )</td>
<td>( \beta_{40}^{0} )</td>
</tr>
<tr>
<td>( a_{20}^{i,j} q_{1}^{i} q_{1}^{j} )</td>
<td>([\mu]^{0} )</td>
<td>( \beta_{40}^{0} )</td>
</tr>
<tr>
<td>( a_{20}^{i,j} q_{1}^{i} q_{1}^{j} )</td>
<td>([\mu]^{0} )</td>
<td>( \beta_{40}^{0} )</td>
</tr>
</tbody>
</table>

The quantities \( \gamma_{ab}^{0} \) for C, F, and H and \( \gamma_{ab}^{0} \) for S, C, and H are included in the static hyperpolarizability, but with different values. As observed previously, for the diagonal tensor components and for the mean (isotropic) value each type of perturbation term that appears in the dynamic nuclear relaxation formula also occurs in the corresponding static formula, the only difference being a change in the multiplicative factor.

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IV. RESULTS AND DISCUSSION

The first molecules that we considered were HF and CH$_4$. There are good recent treatments of both in the literature; see Ref. 26 for HF and Refs. 6 and 27 for CH$_4$ (in both cases earlier papers are cited therein). However, we had a dual purpose for doing these calculations. One reason was to determine the importance of the static $\alpha$ term [see Eq. (15)], which has not previously been examined, and the other was to test our basis sets.

In Table II we give the contribution of each term in Eq. (7) to the mean static second hyperpolarizability of HF and CH$_4$. All values are given in atomic units (1 a.u. = 6.235 38 10$^{-3}$. 

![Table II](image)

TABLE II. Nuclear relaxation contributions to the mean static second hyperpolarizability for HF and CH$_4$. All values are given in atomic units (1 a.u. = 6.235 38 10$^{-3}$.

For HF the $(a_{12}^{12})/2 q_{i}^{ld}$ term is dominant. The difference between the value obtained with the augmented Sadlej basis in Ref. 27 and the VTZ2P basis is about 10% and rises to about 15% for the DZP basis. For CH$_4$ all terms where the total order in electrical and mechanical anharmonicity is 1 are negligible. In particular, the two terms that contribute to $\alpha$ term are very small in both molecules. These conclusions are independent of the basis set.

Next we turn to CF$_4$ and SF$_6$. Our results for the static second hyperpolarizability are presented in Table III. In contrast to HF and CH$_4$, static nuclear relaxation terms of order 1 in both molecules. These conclusions are independent of the basis set.

All things considered we conclude that, for carbon and fluorine, the VTZ2P basis is satisfactory whereas results obtained with the DZP basis must be used more cautiously. No tests of the sulfur basis could be carried out because there are no calculations available for the quantities of interest.

As noted above, for CH$_4$ the $[\alpha]_{12}^{12}$ term is dominant. The VTZ2P basis is satisfactory whereas results obtained with the DZP basis must be used more cautiously. No tests of the sulfur basis could be carried out because there are no calculations available for the quantities of interest.

As noted above, for CH$_4$ the $[\alpha]_{12}^{12}$ term is dominant. For HF all terms where the total order in electrical and mechanical anharmonicity is 1 are negligible. In particular, the two terms that contribute to $[\mu^4]_{12}^{12}$ are very small in both molecules. These conclusions are independent of the basis set.

Next we turn to CF$_4$ and SF$_6$. Our results for the static second hyperpolarizability are presented in Table III. In contrast to HF and CH$_4$, static nuclear relaxation terms of order 1 in both molecules. These conclusions are independent of the basis set.

![Table III](image)

TABLE III. Nuclear relaxation contributions to the mean static second hyperpolarizability for CF$_4$ and SF$_6$. All values are given in atomic units (1 a.u. = 6.235 38 10$^{-3}$.

Note that the major difference between the augmented Sadlej and the VTZ2P basis set is the presence, in the former, of two sets of d polarization functions on hydrogen. Since the other two molecules that we will consider do not contain hydrogen atoms this is not a significant disadvantage in those cases. There is also a sizable discrepancy (in percentage terms) for the $[\mu^2]_{12}^{12}_{12} + [\mu^2]_{12}^{12}_{12}$ term. This is due to a near cancellation of positive and negative contributions; in our opinion it probably does not reflect large errors in the individual terms calculated with the VTZ2P basis.
are quite important for CF$_4$. In particular, the $\left(9a_{30}^{ijkl}a_{30}^{ijkl}\right)$ contribution to $[\mu^4]^{0.2}$ is about 1/3 of the total value. We note that this term can be evaluated without having to calculate fourth derivatives. Its importance is clear in either basis. In fact, the differences between the DZP and the VTZ2P basis sets are small except for $[\mu\beta]^{0.0}$ and, to a lesser extent, $[\mu^4]^{1.1}$. For SF$_6$ all the calculations except for $[\mu\beta]^{0.0}$ (see later) were done only in the DZP basis. In this case our conclusions are the same as for CF$_4$ and, from the comparison between basis sets made for the latter, we

<table>
<thead>
<tr>
<th>Property expansion term$^a$</th>
<th>BK treatment</th>
<th>CF$_4$</th>
<th>SF$_6$</th>
</tr>
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<tbody>
<tr>
<td>$\frac{a_{12}^{ijkl}}{2}q_i^{c,d}$</td>
<td>= $[\alpha^2]^{0.0}_{\omega=0}$</td>
<td>239.1</td>
<td>745.8</td>
</tr>
<tr>
<td>$a_{13}^{ijkl}q_i^{c,d}$</td>
<td>= $[\mu\beta]^{0.0}_{\omega=0}$</td>
<td>-199.1</td>
<td>-66.5</td>
</tr>
<tr>
<td>$3a_{30}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^2\alpha]^{0.1}_{\omega=0}$</td>
<td>480.3</td>
<td>1624.6</td>
</tr>
<tr>
<td>$-2a_{30}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^2\alpha]^{1.0}_{\omega=0}$</td>
<td>100.9</td>
<td>84.8</td>
</tr>
<tr>
<td>$-a_{12}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td></td>
<td>618.7</td>
<td>794.0</td>
</tr>
<tr>
<td>$[\mu^2\alpha]^{0.1}<em>{\omega=0}+[\mu^2\alpha]^{0.0}</em>{\omega=0}$</td>
<td></td>
<td>1199.9</td>
<td>2204.0</td>
</tr>
<tr>
<td>$\mu^4]^{0.0}_{\omega=0}$</td>
<td></td>
<td>2391.7</td>
<td></td>
</tr>
<tr>
<td>$\frac{3a_{30}^{ijkl}a_{20}^{ijkl}}{a_{30}^{ijkl}}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^4]^{1.0}_{\omega=0}$</td>
<td>-166.9</td>
<td>-105.6</td>
</tr>
<tr>
<td>$\frac{4a_{30}^{ijkl}a_{30}^{ijkl}}{a_{30}^{ijkl}}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^4]^{2.0}_{\omega=0}$</td>
<td>74.4</td>
<td>68.5</td>
</tr>
<tr>
<td>$a_{30}^{ijkl}a_{20}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td></td>
<td>202.8</td>
<td>247.5</td>
</tr>
<tr>
<td>$[\mu^4]^{1.0}<em>{\omega=0}+[\mu^4]^{2.0}</em>{\omega=0}$</td>
<td></td>
<td>110.3</td>
<td>301.2</td>
</tr>
<tr>
<td>$\frac{9a_{30}^{ijkl}a_{30}^{ijkl}}{4a_{30}^{ijkl}}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^4]^{0.0}_{\omega=0}$</td>
<td>694.7</td>
<td>1493.4</td>
</tr>
<tr>
<td>$\frac{9a_{30}^{ijkl}a_{30}^{ijkl}}{4a_{30}^{ijkl}}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^4]^{0.1}_{\omega=0}$</td>
<td>-35.2</td>
<td>-55.1</td>
</tr>
<tr>
<td>$\mu^4]^{0.0}_{\omega=0}$</td>
<td></td>
<td>659.5</td>
<td>1438.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>2099.8</td>
<td>4570.5$^c$</td>
</tr>
</tbody>
</table>

$^a$A sum over normal coordinates and permutation over field indices $i,j,k,l$, as in Eq. (7), is understood.

$^b$For CF$_4$ and SF$_6$ the derivatives $a_{40}^{ijkl}$ and $a_{30}^{ijkl}$ with all the normal coordinates different were not computed.

$^c$The $[\mu\beta]^{0.0}$ contribution was calculated with the VTZ2P basis; the DZP basis was used for all other terms.

| TABLE III. Nuclear relaxation contributions to the mean static second hyperpolarizability for CF$_4$ and SF$_6$. All values are given in atomic units ($1$ a.u. = $6.235\times10^{-65}$ C$^4$m$^4$J$^{-1}$).

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<tr>
<td>$2a_{12}^{ijkl}q_i^{c,d}$</td>
<td>= $[\alpha^2]^{0.0}_{\omega=0}$</td>
<td>8.5</td>
<td>9.9</td>
</tr>
<tr>
<td>$6a_{12}^{ijkl}q_i^{c,d}$</td>
<td>= $[\mu\beta]^{0.0}_{\omega=0}$</td>
<td>-7.6</td>
<td>-6.0</td>
</tr>
<tr>
<td>$6a_{30}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^2\alpha]^{0.1}_{\omega=0}$</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>$-4a_{30}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td>= $[\mu^2\alpha]^{1.0}_{\omega=0}$</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>$-2a_{12}^{ijkl}q_i^{c,d}q_j^{c,d}$</td>
<td></td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$[\mu^2\alpha]^{0.1}<em>{\omega=0}+[\mu^2\alpha]^{0.0}</em>{\omega=0}$</td>
<td></td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>2.6</td>
<td>5.9</td>
</tr>
</tbody>
</table>

$^a$A sum over normal coordinates and permutation over field indices $c,d$, as in Eq. (12), is understood.

$^b$The $[\mu\beta]^{0.0}$ contribution was calculated with the VTZ2P basis; the DZP basis was used for all other terms.
expect this to be true for the larger basis as well. For all four molecules the terms arising from the derivatives $a_{40}$ and $a_{31}$ are relatively small, as indicated above.

Table IV gives our results for the mean isotropic Kerr effect, while Table V gives the mean anisotropic Kerr effect as well as the IDRI and ESHG. There now appears a second key difference between CF$_4$ and SF$_6$ on the one hand, and CH$_4$ on the other. For the former pair of molecules the two doubly harmonic terms, $\alpha_{0,0}$ and $\beta_{0,0}$, are of opposite sign and tend to cancel one another. This cancellation is even more pronounced for the Kerr effect (isotropic and anisotropic) than it is for the static hyperpolarizability $\gamma_{\text{cf}}$ (cf. Table III). As a result, the often-used doubly harmonic approximation is very poor. HF is similar to CF$_4$ and SF$_6$ but the effect is not as striking because the first-order anharmonicity terms are so small. However, even if the sign of $\beta_{0,0}$ were positive, rather than negative, the first-order anharmonicity terms would play a major role for CF$_4$ and SF$_6$. For the latter two molecules the dominance of first-order anharmonicity terms in the nuclear relaxation contribution to the Kerr effect suggests that higher-order anharmonicity effects arising from curvature could be important.

It is known$^{27,30}$ that the difference between the anisotropic Kerr effect and the ESHG dispersion curves is due to contributions from nuclear motions. Recently, Shelton and Palubinskas$^{19}$ have made anisotropic Kerr effect measurements on CH$_4$, CF$_4$, and SF$_6$ from which they extracted the vibrational hyperpolarizability. For CH$_4$ the experimental high frequency limiting value of 289 a.u. turns out to be 45% higher than the value (200 a.u.) calculated by Bishop and Pipin.$^{27}$ The latter calculations were done at the Hartree–Fock level, which could account for the discrepancy. There is also the possibility that basis set limitations could be important and that a significant contribution could arise from higher-order curvature terms that were neglected. The curvature terms that were included increase the vibrational hyperpolarizability by about 22 a.u., as estimated from approximations B and C in Bishop and Dalskov.$^5$ This gives an estimated nuclear relaxation/infinite frequency value of 178 a.u. from the calculations of Ref. 6, which may be compared with our value of 157 a.u. reported in Table VI. The agreement is reasonable.

According to the discussion earlier in this paper our estimate for the nuclear relaxation/infinite frequency hyperpolarizability of CH$_4$ probably suffers from deficiencies in the atomic hydrogen basis. On the other hand, the CF$_4$ calculations do not have this difficulty. However, our best approximation (VT2ZP basis) for the vibrational hyperpolarizability of CF$_4$ is still substantially less than the measured value (see Table VI) just as Bishop and Dalskov found for CH$_4$.

**TABLE VI.** Comparison of experimental differences between the anisotropic Kerr effect and ESHG with the calculated nuclear relaxation approximation in the infinite frequency limit. All values are given in atomic units (1 a.u. = 6.235 38 $\times 10^{-26}$ C$^4$ m$^2$ J$^{-1}$).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Experimenta</th>
<th>DZP</th>
<th>VTZ2P</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>239</td>
<td>385</td>
<td>157</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>497</td>
<td>294</td>
<td>282</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>818</td>
<td>576</td>
<td>621</td>
</tr>
</tbody>
</table>

*a Reference 19.

*b The $\beta_{0,0}$ contribution was calculated with the VTZ2P basis; the DZP basis was used for all other terms.
the results obtained with the two different basis sets lies in the $[\mu\beta]^{0\times0}$ term. Since $[\mu\beta]^{0\times0}$ makes a very substantial contribution to the difference between the anisotropic Kerr effect and ESHG (see Table V) it was decided, for SF$_6$, to compute just this one term in the VTZ2P basis. The result is given in Tables IV–VI. Again, the calculated difference between the anisotropic Kerr effect and ESHG is considerably smaller than the experimental value, although the agreement is much better than for CH$_4$ or CF$_4$. From our experience it is feasible that the disagreement could largely disappear when correlation effects are included. However, that remains to be seen. Of course, as observed above, basis set limitations and curvature contributions could also be significant.

V. CONCLUSIONS

Based on the treatment of BHK$^{18}$ we have used electrical property expansions to obtain derivative expressions for the nuclear relaxation contribution to the most important NLO processes in the infinite (optical) frequency limit. These expressions, as well as the corresponding formulas for the static limit, were evaluated for HF, CH$_4$, CF$_4$, and SF$_6$ at the Hartree–Fock level. For CF$_4$ and SF$_6$ it was found that one particular higher-order static hyperpolarizability term, not previously calculated for any molecule, is quite important. For CH$_4$, CF$_4$, and SF$_6$ we were able to compare with experimental measurements of the difference between the anisotropic Kerr effect and ESHG. The nuclear relaxation values reproduce the experimental trend but are too small by a factor of 1.32–1.75. We hope to extend the treatment presented here to include the curvature contribution to the various NLO processes in the infinite frequency limit.

ACKNOWLEDGMENTS

The authors are indebted to Dr. J. Mestres and Professor D. M. Bishop for their fruitful comments. We also thank Benoît Champagne for sharing results prior to publication. Some of the calculations for this project were carried out at the Maui High Performance Computing Center. This work has been funded though the DGICYT Project No. PB95-0706. One of us (J.M.L.) acknowledges the financial help provided by the Generalitat de Catalunya through the CIRIT Project No. FI95-5101.

21D. M. Bishop (private communication).
25Unpublished calculations on ammonia, ethylene, acetylene, and water.