Nuclear relaxation contribution to static and dynamic (infinite frequency approximation) nonlinear optical properties by means of electrical property expansions: Application to HF, CH_4, CF_4, and SF_6

Josep M. Luis, Josep Martí, Miquel Duran, and José L. Andrés
*Institute of Computational Chemistry and Department of Chemistry, University of Girona,
17017 Girona (Catalonia), Spain*

Bernard Kirtman
Department of Chemistry, University of California, Santa Barbara, California 93106

Electrical property derivative expressions are presented for the nuclear relaxation contribution to static and dynamic (infinite frequency approximation) nonlinear optical properties. For CF_4 and SF_6, as opposed to HF and CH_4, 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 CF_4 and SF_6. 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 CH_4, CF_4, SF_6) 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 established[1–3] 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 limit[4] but at optical frequencies[5] as well.

In recent articles (to which the reader is directed for references) Bishop and Dalskov[6] 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 energy[7] 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:

vibrational hyperpolarizability+ZPVA

$$=\text{nuclear relaxation contribution}$$
$$+\text{curvature contribution}, \quad (1)$$

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 interesting[7,12] 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

$$a_{nm}^{i1\cdots in,j1\cdots jm}$$

$$=\frac{1}{n!m!}\left(\frac{\partial^{(n+m)}V(Q_1,\ldots,Q_{3N-6},F_x,F_y,F_z)}{\partial Q_{i1}\ldots\partial Q_{in}\partial F_{j1}\ldots\partial F_{jm}}\right)_{Q=0,F=0}, \quad (2)$$

where Q are the normal coordinates; F_x, F_y, F_z are the Cartesian components of the electric field; and $n+m \leqslant 2$ for linear polarizability (α), 3 for first hyperpolarizability (β), and 4 for second hyperpolarizability (γ). 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

© 1998 American Institute of Physics

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 β and the sixth derivatives a_{24} for γ (in both cases $Q_i = Q_j$).

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 ≤ 4 for γ. 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[6] 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 $Q = (Q_1, Q_2, \ldots, Q_{3N-6(5)})$ 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:

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

$$
\alpha_{ab} = -\left(\frac{\partial^2 V(\mathbf{Q},\mathbf{F})}{\partial F_a \partial F_b} \right)_{Q=0,F=0},
\tag{3}
$$

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 $\mathbf{F}$. After subtraction of the pure electronic terms, i.e., those terms that do not contain nuclear derivatives, the expansion of μ gives the nuclear relaxation contribution to the static polarizability, $\alpha_{ab}^{\mathrm{nr}}(0;0)$, hyperpolarizabilities, $\beta_{abc}^{\mathrm{nr}}(0;0,0)$, and $\gamma_{abcd}^{\mathrm{nr}}(0;0,0,0)$, according to the Taylor series definition:[20]

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

Here the prime in μ_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 $(-\omega_\sigma; \omega_1, \ldots)$ where the frequencies $\omega_1, \ldots$ correspond to the fields $F_b, \ldots$ (in order) and ω_σ corresponds to F_a. In terms of the derivatives in Eq. (2),

$$
\alpha_{ab}^{\mathrm{nr}}(0;0) = \frac{1}{2}\sum_{i=1}^{3N-6} P_{ab} a_{11}^{i,a} q_1^{i,b},
\tag{5}
$$

$$\beta_{abc}^{\mathrm{nr}}(0;0,0) = \sum_{i=1}^{3N-6} P_{abc} a_{12}^{i,ab} q_1^{i,c} - \sum_{ij}^{3N-6} P_{abc} a_{21}^{ij,a} q_1^{i,b} q_1^{j,c} + \sum_{ijk}^{3N-6} P_{abc} a_{30}^{ijk} q_1^{i,a} q_1^{j,b} q_1^{k,c}, \tag{6}$$

and

$$\gamma_{abcd}^{\mathrm{nr}}(0;0,0,0) = \sum_{i}^{3N-6} P_{abcd}\left(a_{13}^{i,abc} q_1^{i,d} + \frac{a_{12}^{i,ab}}{2} q_2^{i,cd} \right) - \sum_{i,j}^{3N-6} P_{abcd}(a_{22}^{ij,ab} q_1^{i,c} q_1^{j,d} + 2 a_{21}^{ij,a} q_1^{i,b} q_2^{j,cd})$$

$$+ \sum_{i,j,k}^{3N-6} P_{abcd}\left(a_{31}^{ijk,a} q_1^{i,b} q_1^{j,c} q_1^{k,d} + 3 a_{30}^{ijk} q_1^{i,a} q_1^{j,b} q_2^{k,cd} + \frac{a_{21}^{ij,a} a_{21}^{jk,b}}{a_{20}^{j}} q_1^{i,c} q_1^{k,d} \right)$$

$$- \sum_{i,j,k,l}^{3N-6} P_{abcd}\left(a_{40}^{ijkl} q_1^{i,a} q_1^{j,b} q_1^{k,c} q_1^{l,d} + \frac{3 a_{30}^{ijk} a_{21}^{kl,a}}{a_{20}^{k}} q_1^{i,c} q_1^{j,d} q_1^{l,b} \right) + \sum_{i,j,k,l,m}^{3N-6} P_{abcd} \frac{9 a_{30}^{ijk} a_{30}^{klm}}{4 a_{20}^{k}} q_1^{i,a} q_1^{j,b} q_1^{l,c} q_1^{m,d}, \tag{7}$$

where the notation

$$q_1^{\lambda,a} = \frac{a_{11}^{\lambda,a}}{2 a_{20}^{\lambda}}, \quad q_2^{\lambda,ab} = \frac{a_{12}^{\lambda,ab}}{2 a_{20}^{\lambda}} \tag{8}$$

has been introduced and $P_{ab\ldots}$ indicates a sum over all the perturbations of the indices $ab\cdots$.

As BHK[18] have demonstrated the corresponding expansions for $\Delta\alpha'_{ab}$ and $\Delta\beta'_{abc}$ yield the nuclear relaxation contributions to several nonlinear optical (NLO) processes in the infinite frequency approximation [see BHK Eqs. (7), (8), (10), and (11)]:

$$\Delta\alpha'_{ab}(0;0) = \sum_{c}^{x,y,z} \beta_{abc}^{\mathrm{nr}}(-\omega;\omega,0)_{\omega\to\infty} F_c$$

$$+ \frac{1}{2}\sum_{c,d}^{x,y,z} \gamma_{abcd}^{\mathrm{nr}}(-\omega;\omega,0,0)_{\omega\to\infty} F_c F_d \tag{9}$$

and

$$\Delta\beta'_{abc}(0;0,0) = \sum_{d}^{x,y,z} \gamma_{abcd}^{\mathrm{nr}}(-2\omega;\omega,\omega,0)_{\omega\to\infty} F_d. \tag{10}$$

Following exactly the same procedure that was used for $\Delta\mu'$ [i.e., steps (i) and (ii) above followed by expansion of α or β] we find

$$\beta_{abc}^{\mathrm{nr}}(-\omega;\omega,0) = \sum_{i=1}^{3N-6} 2 a_{12}^{i,ab} q_1^{i,c}, \tag{11}$$

$$\gamma_{abcd}^{\mathrm{nr}}(-\omega;\omega,0,0)_{\omega\to\infty}$$

$$= \sum_{i}^{3N-6} P_{cd}(6 a_{13}^{i,abc} q_1^{i,d} + 2 a_{12}^{i,ab} q_2^{i,cd})$$

$$- \sum_{i,j}^{3N-6} P_{cd}(2 a_{22}^{ij,ab} q_1^{i,c} q_1^{j,d} + 4 a_{21}^{ij,c} q_1^{i,d} q_2^{j,ab})$$

$$+ \sum_{i,j,k}^{3N-6} P_{cd} 6 a_{30}^{ijk} q_1^{i,c} q_1^{j,d} q_2^{k,ab}, \tag{12}$$

and

$$\gamma_{abcd}^{\mathrm{nr}}(-2\omega;\omega,\omega,0)_{\omega\to\infty} = \sum_{i}^{3N-6} (6 a_{13}^{i,abc} q_1^{i,d}) \tag{13}$$

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 $\omega\to\infty$ limit of the terms listed in Table I of BHK.[18]

We note that $\alpha^{\mathrm{nr}}(-\omega;\omega)$, $\beta^{\mathrm{nr}}(-2\omega;\omega,\omega)$, and $\gamma^{\mathrm{nr}}(-3\omega;\omega,\omega,\omega)$ 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[1] have the form $[\alpha^2]$ or, in derivative notation, they contain the products $\alpha_{12}^{i,ab} q_2^{i,cd}$. Extracting these products from the formula for IDRI given in BHK we find

$$\gamma_{abcd}^{\mathrm{nr}}(-\omega;\omega,-\omega,\omega)_{\omega\to\infty} = 8 \sum_{i}^{3N-6} (a_{12}^{i,aa} q_2^{i,aa}) \tag{14a}$$

with an analogous expression for the average value (see later). More generally, for an arbitrary component it can be demonstrated[21] that

$$\gamma_{abcd}^{\mathrm{nr}}(-\omega;\omega,-\omega,\omega) = 4 \sum_{i}^{3N-6} (a_{12}^{i,ab} q_2^{i,cd} + a_{12}^{i,ad} q_2^{i,bc}). \tag{14b}$$

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.[7,9] However, the terms in $[\mu^4]^{0,2}$, i.e.,

$$\sum_{i,j,k,l}^{3N-6} P_{abcd} a_{40}^{ijkl} q_1^{i,a} q_1^{j,b} q_1^{k,c} q_1^{l,d},$$

$$\sum_{i,j,k,l,m}^{3N-6} P_{abcd} \frac{9 a_{30}^{ijk} a_{30}^{klm}}{4 a_{20}^{k}} q_1^{i,a} q_1^{j,b} q_1^{l,c} q_1^{m,d} \tag{15}$$

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

Property expansion term[a]	BK treatment	Hyperpolarizability
β^{nr}		
$a_{12}^{iab} q_1^{i,c}$	$[\mu\alpha]^{0,0}$	$\beta^{nr}(0;0,0); \beta^{nr}(-\omega;\omega,0)$
$-a_{21}^{ij,a} q_1^{i,b} q_1^{j,c}$	$[\mu^3]^{1,0}$	$\beta^{nr}(0;0,0)$
$a_{30}^{ijk} q_1^{i,a} q_1^{i,b} q_1^{k,c}$	$[\mu^3]^{0,1}$	$\beta^{nr}(0;0,0)$
γ^{nr}		
$\dfrac{a_{12}^{i,ab}}{2} q_2^{i,cd}$	$[\alpha^2]^{0,0}$	$\gamma^{nr}(0;0,0,0); \gamma^{nr}(-\omega;\omega,0,0); \gamma^{nr}(-\omega;\omega,\omega,-\omega)$
$a_{13}^{i,abc} q_1^{i,d}$	$[\mu\beta]^{0,0}$	$\gamma^{nr}(0;0,0,0); \gamma^{nr}(-\omega;\omega,0,0); \gamma^{nr}(-2\omega;\omega,\omega,0)$
$3a_{30}^{ijk} q_1^{i,a} q_1^{i,b} q_2^{k,cd}$	$[\mu^2\alpha]^{0,1}$	$\gamma^{nr}(0;0,0,0); \gamma^{nr}(-\omega;\omega,0,0)$
$-2a_{21}^{ij,a} q_1^{i,b} q_2^{j,cd} - a_{22}^{ij,ab} q_1^{i,c} q_1^{j,d}$	$[\mu^2\alpha]^{1,0}$	$\gamma^{nr}(0;0,0,0); \gamma^{nr}(-\omega;\omega,0,0)$
$-\dfrac{3a_{30}^{ijk} a_{21}^{kl,a}}{a_{20}^k} q_1^{i,b} q_1^{j,c} q_1^{l,d}$	$[\mu^4]^{1,1}$	$\gamma^{nr}(0;0,0,0)$
$\dfrac{a_{21}^{ij,a} a_{21}^{jk,b}}{a_{20}^j} q_1^{i,c} q_1^{k,d} + a_{31}^{ijk,a} q_1^{i,b} q_1^{j,c} q_1^{k,d}$	$[\mu^4]^{2,0}$	$\gamma^{nr}(0;0,0,0)$
$\dfrac{9a_{30}^{ijk} a_{30}^{klm}}{4a_{20}^k} q_1^{j,a} q_1^{i,b} q_1^{i,c} q_1^{m,d} - a_{40}^{ijkl} q_1^{i,a} q_1^{i,b} q_1^{k,c} q_1^{l,d}$	$[\mu^4]^{0,2}$	$\gamma^{nr}(0;0,0,0)$

[a]A sum over normal coordinates and permutation over field indices $a,b,\ldots$, as in Eq. (7), is understood. For $\beta^{nr}(-\omega;\omega,0)$, $\gamma^{nr}(-\omega;\omega,0,0)$, and $\gamma^{nr}(-2\omega;\omega,\omega,0)$ the permutation over the field indices is limited to the static fields [see Eqs. (11), (12), and (13) respectively]. For $\gamma^{nr}(-\omega;\omega,\omega,-\omega)$ see Eqs. (14a) and (14b).

have been presented just recently[7] 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,[6,22] 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, CH_4, CF_4, and SF_6 were carried out at the *ab initio* self-consistent field molecular-orbital level of theory using the Dunning–Huzinaga[23] basis set with $(9s5p/4s)/[4s2p/2s]$ and $(9s5p/4s)/[5s3p/3s]$ 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 analyti-

cally. The GAUSSIAN94 suite of programs[24] that we use gives analytical results for a_{20}, a_{01}, a_{11}, a_{02}, a_{12}, and a_{03}. Then, numerical differentiation of a_{20}, a_{11}, a_{12}, and a_{03} with respect to the normal coordinates yields a_{30}, a_{21}, a_{22}, and a_{13}, respectively. By inspection of Eqs. (9)–(13) it is evident that these derivatives are sufficient to determine all of the dynamic (infinite frequency) contributions. However, for the static second hyperpolarizability a_{40} and a_{31} are needed as well. They were computed by double numerical differentiation of a_{20} and a_{11}. For CF_4 and SF_6, the derivatives a_{40}^{ijkl} and $a_{31}^{ijk,a}$ with all normal coordinates different were not computed. In several other molecules that were tested[25] this turns out to be an excellent approximation. The a_{40} and a_{31} terms that were computed here make only a small contribution to the static second hyperpolarizability. This suggests that the omitted terms are likely to be small as well. However, that has not been proved.

In this paper our focus will be on the static and dynamic second hyperpolarizability. We report mean values of γ^{nr} defined as

$$\bar{\gamma}^{nr} = \frac{1}{15} \sum_{a,b}^{x,y,z} (\gamma_{aabb}^{nr} + \gamma_{abab}^{nr} + \gamma_{abba}^{nr}) \qquad (16)$$

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

$$\bar{\gamma}_k^{nr} = \frac{1}{10} \sum_{a,b}^{x,y,z} (3\gamma_{abab}^{nr} - \gamma_{aabb}^{nr}), \qquad (17)$$

which is the experimentally measured quantity.

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.$=6.235\,38\times10^{-65}$ C^4 m^4 J^{-3}).

Property expansion term[a]	BK treatment	HF			CH_4		
		DZP	VTZ2P	Ref. 26[b]	DZP	VTZ2P	Ref. 27[c]
$\dfrac{a_{12}^{i,ab}}{2}\,q_2^{i,cd}$	$=[\alpha^2]_{\omega=0}^{0,0}$	25.6	29.8	31.9	862.1	679.5	750.5
$a_{13}^{i,abc}q_1^{i,d}$	$=[\mu\beta]_{\omega=0}^{0,0}$	-15.2	-12.0	-9.9	59.1	16.4	37.2
$3a_{30}^{ijk}q_1^{i,a}q_1^{j,b}q_2^{k,cd}$	$=[\mu^2\alpha]_{\omega=0}^{0,1}$	7.9	8.2		18.6	15.5	
$\left.\begin{array}{l}-2a_{21}^{ij,a}q_1^{i,b}q_2^{j,cd}\\-a_{22}^{ij,ab}q_1^{i,c}q_1^{j,d}\end{array}\right\}$	$=[\mu^2\alpha]_{\omega=0}^{1,0}$	-0.2 2.6	1.2 2.4		-98.9 43.9	-34.8 18.6	
	$[\mu^2\alpha]_{\omega=0}^{0,1}+[\mu^2\alpha]_{\omega=0}^{1,0}$	10.3	11.8	12.2	-36.4	-0.7	6.6
$-\dfrac{3a_{30}^{ijk}a_{21}^{kl,a}}{a_{20}^{k}}\,q_1^{i,b}q_1^{j,c}q_1^{l,d}$	$=[\mu^4]_{\omega=0}^{1,1}$	0.0	0.2		-0.6	-0.5	
$\left.\begin{array}{l}+\dfrac{a_{21}^{ij,a}a_{21}^{jk,b}}{a_{20}^{j}}\,q_1^{i,c}q_1^{k,d}\\+a_{31}^{ijk,a}q_1^{i,b}q_1^{j,c}q_1^{k,d}\end{array}\right\}$	$=[\mu^4]_{\omega=0}^{2,0}$	0.0 0.0	0.1 0.0		10.1 -0.4	5.8 0.3	
	$[\mu^4]_{\omega=0}^{1,1}+[\mu^4]_{\omega=0}^{2,0}$	0.0	0.3	0.2	9.1	5.6	5.8
$\dfrac{9a_{30}^{ijk}a_{30}^{klm}}{4a_{20}^{k}}\,q_1^{i,a}q_1^{j,b}q_1^{l,c}q_1^{m,d}$		0.6	0.6		0.3	0.2	
$+a_{40}^{ijkl}q_1^{i,a}q_1^{j,b}q_1^{k,c}q_1^{i,d}$		-0.2	-0.2		0.6	0.0	
	$=[\mu^4]_{\omega=0}^{0,2}$	0.4	0.4	c	0.9	0.2	c
Total		21.1	30.1	34.4	894.8	701.1	800.1

[a]A sum over normal coordinates and permutation over field indices $a,b,\dots$, as in Eq. (7), is understood.
[b]From results reported in Ref. 6.
[c]Not calculated.

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 $[\mu^4]^{0,2}$ 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. A comparison with larger basis set calculations carried out by Bishop and co-workers[26,27] is also included. For HF the VTZ2P results are in good agreement with the modified McDowell[28] basis employed in Ref. 26. The DZP basis does not agree as well but, for significant terms, gives values within 35% in the worst case.

For CH_4 the $(a_{12}^{i,ab}/2)q_2^{i,cd}=[\alpha^2]^{0,0}$ term is dominant. The difference between the value obtained with the augmented Sadlej[29] basis in Ref. 27 and the VTZ2P basis is about 10% and rises to about 15% for the DZP basis. For the next most important term, i.e., $a_{13}^{i,abc}q_1^{i,d}=[\mu\beta]^{0,0}$ the *percent* disagreement is much larger. This is probably due to the effect of an inadequate hydrogen atom basis in calculating the first hyperpolarizability derivative. In this connection we 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 $[\mu^2\alpha]^{0,1}+[\mu^2\alpha]^{1,0}$ 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.

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 $[\alpha^2]^{0,0}$ 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 $[\mu^4]^{0,2}$ 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 mechanical and/or electrical anharmonicity

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.$=6.235\ 38\times10^{-65}$ C^4 m^4 J^{-3}).

Property expansion term[a]	BK treatment	CF$_4$		SF$_6$	
		DZP	VTZ2P	DZP	VTZ2P
$\dfrac{a_{12}^{i,ab}}{2}\,q_2^{i,cd}$	$=[\alpha^2]_{\omega=0}^{0,0}$	239.1	254.7	745.8	
$a_{13}^{i,abc}q_1^{i,d}$	$=[\mu\beta]_{\omega=0}^{0,0}$	-199.1	-66.5	-485.6	-306.2
$3a_{30}^{ijk}q_1^{i,a}q_1^{j,b}q_2^{k,cd}$	$=[\mu^2\alpha]_{\omega=0}^{0,1}$	480.3	510.5	1624.6	
$-2a_{21}^{ij,a}q_1^{i,b}q_2^{j,cd}$ $-a_{22}^{ij,ab}q_1^{i,c}q_1^{j,d}$	$=[\mu^2\alpha]_{\omega=0}^{1,0}$	100.9 618.7	84.8 625.1	-26.9 794.0	
	$[\mu^2\alpha]_{\omega=0}^{0,1}+[\mu^2\alpha]_{\omega=0}^{1,0}$	1199.9	1220.4	2391.7	
$-\dfrac{3a_{30}^{ijk}a_{21}^{kl,a}}{a_{20}^{k}}\,q_1^{i,b}q_1^{j,c}q_1^{l,d}$	$=[\mu^4]_{\omega=0}^{1,1}$	-166.9	-105.6	-36.4	
$+\dfrac{a_{21}^{ij,a}a_{21}^{jk,b}}{a_{20}^{j}}\,q_1^{i,c}q_1^{k,d}$ $+a_{31}^{ijk,a}q_1^{i,b}q_1^{j,c}q_1^{k,d}$	$=[\mu^4]_{\omega=0}^{2,0}$	74.4 202.8	68.5 199.0	90.1 247.5	
	$[\mu^4]_{\omega=0}^{1,1}+[\mu^4]_{\omega=0}^{2,0}$	110.3	161.9	301.2	
$\dfrac{9a_{30}^{ijk}a_{30}^{klm}}{4a_{20}^{k}}\,q_1^{i,a}q_1^{j,b}q_1^{l,c}q_1^{m,d}$		694.7	653.3	1493.4	
$+a_{40}^{ijkl}q_1^{i,a}q_1^{j,b}q_1^{k,c}q_1^{l,d}$ [b]		-35.2	-31.7	-55.1	
	$=[\mu^4]_{\omega=0}^{0,2}$	659.5	621.6	1438.1	
Total		2009.8	2192.1	4391.1	4570.5[c]

[a]A sum over normal coordinates and permutation over field indices $a,b,\ldots$, as in Eq. (7), is understood.
[b]For CF_4 and SF_6 the derivatives a_{40}^{ijkl} and $a_{31}^{ijk,a}$ 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.

are quite important for CF_4. In particular, the $(9a_{30}^{ijk}a_{30}^{klm}/4a_{20}^{k})q_1^{i,a}q_1^{j,b}q_1^{l,c}q_1^{m,d}$ 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 IV. Nuclear relaxation contributions to the mean dynamic isotropic Kerr effect $\bar{\gamma}^{nr}(-\omega;\omega,0,0)$ for HF, CH_4, CF_4, and SF_6. All values are given in atomic units (1 a.u.$=6.235\ 38\times10^{-65}$ C^4 m^4 J^{-3}).

property expansion term[a]	BK treatment	HF		CH$_4$		CF$_4$		SF$_6$	
		DZP	VTZ2P	DZP	VTZ2P	DZP	VTZ2P	DZP	VTZ2P
$2a_{12}^{i,ab}q_2^{i,cd}$	$=[\alpha^2]_{\omega\to\infty}^{0,0}$	8.5	9.9	287.4	226.5	79.7	84.9	248.6	
$6a_{13}^{i,abc}q_1^{i,d}$	$=[\mu\beta]_{\omega\to\infty}^{0,0}$	-7.6	-6.0	29.6	8.2	-99.5	-33.2	-242.8	-153.1
$6a_{30}^{ijk}q_1^{i,a}q_1^{j,b}q_2^{k,cd}$	$=[\mu^2\alpha]_{\omega\to\infty}^{0,1}$	1.3	1.4	3.1	2.6	80.0	85.1	270.8	
$-4a_{21}^{ij,a}q_1^{i,b}q_2^{j,cd}$ $-2a_{22}^{ij,ab}q_1^{i,c}q_1^{j,d}$	$=[\mu^2\alpha]_{\omega\to\infty}^{1,0}$	0.0 0.4	0.2 0.4	-16.5 7.3	-5.8 3.1	16.8 103.1	14.1 104.2	-4.5 132.3	
	$[\mu^2\alpha]_{\omega\to\infty}^{0,1}+[\mu^2\alpha]_{\omega\to\infty}^{1,0}$	1.7	2.0	-6.1	-0.1	199.9	203.4	398.6	
Total		2.6	5.9	310.9	234.6	180.2	255.1	404.4	494.1[b]

[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.

TABLE V. Nuclear relaxation contributions to the mean dynamic anisotropic Kerr effect $\bar{\gamma}_K^{nr}(-\omega;\omega,0,0)$, IDRI $\bar{\gamma}^{nr}(-\omega;\omega,\omega,-\omega)$ and ESHG $\bar{\gamma}^{nr}(-2\omega;\omega,\omega,0)$ for HF, CH_4, CF_4, and SF_6. All values are given in atomic units (1 a.u.$=6.235\ 38\times10^{-65}$ C^4 m^4 J^{-3}).

property expansion term[a]	BK treatment	HF DZP	HF VTZ2P	CH_4 DZP	CH_4 VTZ2P	CF_4 DZP	CF_4 VTZ2P	SF_6 DZP	SF_6 VTZ2P
$\bar{\gamma}_K^{nr}(-\omega;\omega,0,0)$									
$2a_{12}^{i,ab}q_2^{i,cd}$	$=[\alpha^2]_{\omega\to\infty}^{0,0}$	8.3	5.2	384.9	157.7	105.5	89.4	259.5	
$6a_{13}^{i,abc}q_1^{i,d}$	$=[\mu\beta]_{\omega\to\infty}^{0,0}$	−7.6	−6.0	29.6	8.2	−99.5	−33.2	−242.8	−153.1
$6a_{30}^{ijk}q_1^{i,a}q_1^{j,b}q_2^{k,cd}$	$=[\mu^2\alpha]_{\omega\to\infty}^{0,1}$	1.3	1.0	6.7	4.0	76.6	72.0	260.5	
$-4a_{21}^{ij,a}q_1^{i,b}q_2^{j,cd}$	$=[\mu^2\alpha]_{\omega\to\infty}^{1,0}$	0.0	0.4	−25.2	−5.6	54.4	52.4	91.9	
$-2a_{22}^{ij,ab}q_1^{i,c}q_1^{j,d}$		0.4	1.0	3.8	−3.6	107.6	85.2	85.5	
	$[\mu^2\alpha]_{\omega\to\infty}^{0,1}+[\mu^2\alpha]_{\omega\to\infty}^{1,0}$	1.7	2.4	−14.7	−5.2	238.6	209.6	437.2	
Total		2.4	1.6	399.8	160.7	244.6	265.8	454.6	544.3[b]
$\bar{\gamma}^{nr}(-\omega;\omega,\omega,-\omega)$									
$4a_{12}^{i,ab}q_2^{i,cd}+4a_{12}^{i,ad}q_2^{i,bc}$	$=[\alpha^2]_{\omega\to\infty}^{0,0}$	17.1	19.8	574.7	453.0	159.4	169.8	497.2	
$\bar{\gamma}^{nr}(-2\omega;\omega,\omega,0)$									
$6a_{13}^{i,abc}q_1^{i,d}$	$=[\mu\beta]_{\omega\to\infty}^{0,0}$	−3.8	−3.0	14.8	4.1	−49.8	−16.6	−121.4	−76.5[b]

[a]A sum over normal coordinates and permutation over field indices c,d, as in Eq. (12), is understood for $\bar{\gamma}_K^{nr}(-\omega;\omega,0,0)$. A sum over normal coordinates is understood for $\bar{\gamma}^{nr}(-\omega;\omega,\omega,-\omega)$ and $\bar{\gamma}^{nr}(-2\omega;\omega,\omega,0)$.

[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, $[\alpha^2]^{0,0}$ and $[\mu\beta]^{0,0}$, 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 (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 $[\mu\beta]^{0,0}$ 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 im-

portant 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.[6] 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 (VTZ2P 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.

For CF_4 it was noted above that the primary difference in

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.$=6.235\ 38\times10^{-65}$ C^4 m^4 J^{-3}).

Molecule	Experiment[a]	Calculated nuclear relaxation DZP	Calculated nuclear relaxation VTZ2P
CH_4	289	385	157
CF_4	497	294	282
SF_6	818	576	621[b]

[a]Reference 19.

[b]The $[\mu\beta]^{0,0}$ 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 $[\mu\beta]^{0,0}$ term. Since $[\mu\beta]^{0,0}$ 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

[1] D. M. Bishop, Adv. Chem. Phys. (to be published).

[2] B. Kirtman and B. Champagne, Int. Rev. Phys. Chem. (to be published).

[3] M. del Zoppo, C. Castiglioni, G. Zerbi, M. Rui, and M. Gussoni, Synth. Met. **51**, 135 (1992).

[4] See, for example, E. A. Perpete, B. Champagne, and B. Kirtman, J. Chem. Phys. **107**, 2463 (1997).

[5] See, for example, B. Kirtman and M. Hasan, J. Chem. Phys. **96**, 470 (1992).

[6] D. M. Bishop and E. K. Dalskov, J. Chem. Phys. **104**, 1004 (1996).

[7] J. M. Luis, M. Duran, and J. L. Andrés, J. Chem. Phys. **107**, 1501 (1997).

[8] D. M. Bishop and B. Kirtman, J. Chem. Phys. **95**, 2646 (1991).

[9] D. M. Bishop and B. Kirtman, J. Chem. Phys. **97**, 5255 (1992).

[10] J. Martí and D. M. Bishop, J. Chem. Phys. **99**, 3860 (1993).

[11] J. Martí, J. L. Andrés, J. Bertrán, and M. Duran, Mol. Phys. **80**, 625 (1993).

[12] J. M. Luis, J. Martí, M. Duran, and J. L. Andrés, J. Chem. Phys. **102**, 7573 (1995).

[13] J. L. Andrés, J. Bertrán, M. Duran, and J. Martí, J. Phys. Chem. **98**, 2803 (1994).

[14] J. M. Luis, J. Martí, M. Duran, and J. L. Andrés, Chem. Phys. **217**, 29 (1997).

[15] M. J. Cohen, A. Willets, R. D. Amos, and N. C. Handy, J. Chem. Phys. **100**, 4467 (1994).

[16] G. Papadopolous, A. Willets, N. C. Handy, and A. E. Underhill, Mol. Phys. **88**, 1063 (1996).

[17] B. Champagne, H. Vanderheoven, E. A. Perpète, and J. M. André, Chem. Phys. Lett. **248**, 301 (1996).

[18] D. M. Bishop, M. Hasan, and B. Kirtman, J. Chem. Phys. **103**, 4157 (1995).

[19] D. P. Shelton and J. J. Palubinskas, J. Chem. Phys. **104**, 2482 (1996).

[20] A. Willetts, J. E. Rice, D. M. Burland, and D. P. Shelton, J. Chem. Phys. **97**, 7590 (1992).

[21] D. M. Bishop (private communication).

[22] B. Kirtman, B. Champagne, and J.-M. Andre. J. Chem. Phys. **104**, 4125 (1996).

[23] T. H. Dunning, Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schæfer, III (Plenum, New York, 1976), pp. 1–28.

[24] GAUSSIAN 94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andrés, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. González, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, (1995).

[25] Unpublished calculations on ammonia, ethylene, acetylene, and water.

[26] D. M. Bishop, J. Pipin, and B. Kirtman, J. Chem. Phys. **102**, 6778 (1995).

[27] D. M. Bishop and J. Pipin, J. Chem. Phys. **103**, 4980 (1995).

[28] S. A. C. McDowell, C. R. Le Sueur, A. D. Buckingham, and A. J. Stone, Mol. Phys. **77**, 823 (1992).

[29] A. J. Sadlej, Coll. Czech. Chem. Commun. **53**, 1995 (1988); Theor. Chim. Acta **79**, 123 (1992).

[30] D. S. Elliott and J. F. Ward, Mol. Phys. **51**, 45 (1984).