PHYSICAL REVIEW B VOLUME 30, NUMBER 10 15 NOVEMBER 1984

In-crystal hyperpolarizabilities of F^- and Cl^-

P. W. Fowler
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

P. A. Madden
Royal Signals and Radar Establishment, Saint Andrews Road, Great Malvern, Worcestershire WR14 3PS, England

(Received 11 April 1984)

Ab initio hyperpolarizabilities γ and B are calculated at the self-consistent field level for the ions F^- and Cl^- in lithium halide crystals. Large reductions with respect to free-ion values are found, and the physical factors contributing to the reduction are discussed. Artifacts arise for a point-charge model of the crystal but are removed when a more realistic model of the ionic environment is used. The final calculated values are in good agreement with the limited experimental data available from third-harmonic generation and three-wave-mixing experiments.

I. INTRODUCTION

We have recently used *ab initio* calculations to put the understanding of the polarizabilities of in-crystal ions on a sound footing.[1-3] Calculated polarizabilities were in agreement with those derived from experiment and their systematic differences from free-ion values explained in terms of electrostatic and overlap interactions.

Dipole polarizabilities account for the optical properties of ions in the highly symmetrical environments of the crystal lattice. If we want to describe the properties of ions in less symmetrical environments,[4] e.g., in disordered ionic crystals or melts, we must consider the nonlinear response of ions to strong and nonuniform fields, i.e., the hyperpolarizabilities. For a centrosymmetric system placed in an external field the induced dipole moment $\underline{\mu}$ may be expanded in terms of the field F_α and field gradient $F_{\alpha\beta}$,[5]

$$\mu_\alpha=\alpha_{\alpha\beta}F_\beta+\tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta+\tfrac{1}{3}B_{\alpha\beta,\gamma\delta}F_\beta F_{\gamma\delta}+\cdots, \quad (1)$$

where the tensors $\underline{\gamma}$ and $\underline{B}$ are the dipole and quadrupole hyperpolarizabilities of the system.

The behavior of $\underline{\alpha}$ for the ions we have studied[1-3] (F^-, Cl^-, H^-, O^{2-}, Li^+, Na^+, Mg^{2+}, K^+, and Ca^{2+}) suggests that the hyperpolarizabilities of *anions* drop sharply when the free ion enters a crystalline environment, probably even more so than the polarizability itself. Both electrostatic crystal-field effects and overlap compression are important in this reduction. The hyperpolarizabilities of *cations* such as Li^+ and Na^+ are expected to be small and insensitive to the crystalline environment. Correlation contributions to $\underline{\gamma}$ and $\underline{B}$, though likely to be very large for free anions, are expected to be quenched in the crystal. A self-consistent-field (SCF) calculation on in-crystal F^- and Cl^- is therefore likely to furnish useful information for modeling the properties of molten LiF and LiCl, information not accessible from a study of the free anions.

In this present paper we describe *ab initio* calculations designed to illustrate the ideas outlined above. The plan of the paper is as follows. In Sec. II we describe the method of modeling the anion in a crystal. In Sec. III some preliminary work on the hyperpolarizability of F^- in LiF using our previous basis[1] is described. Section IV is devoted to a discussion of basis-set extension for F^- and its somewhat surprising effects. In Sec. V we give our best-calculated results for the in-crystal hyperpolarizabilities of F^- and Cl^- in their lithium salts, and compare them with experiment.

II. METHOD

The general scheme of the calculations has already been described,[1,2] and only a brief outline is given here. All calculations were carried out at the SCF level using the University of Cambridge and Cray Research versions of HONDO [Ref. 6(a)] and ATMOL 4 [Ref. 6(b)] (the latter is needed for basis sets with *f* functions).

We distinguish three models for the effect of a crystalline environment on an anion. These are labeled FREE, CRYST, and CLUS. FREE is the free anion; CRYST is the anion in a finite fragment of the cubic lattice of point charges, and CLUS is the anion in the point-charge lattice, but with the electrons and basis functions of nearest-neighbor cations included in the calculation. In a CLUS calculation the central anion is represented using a large basis, but the neighboring cations are given small, highly contracted basis sets.[1,2] The overall effect is to describe the response of the central anion to the electrostatic and overlap interactions with its neighbors.

It was found to be important to consider basis-set superposition error (BSSE) in order to interpret CLUS calculations of $\underline{\gamma}$,[1-3] and a method of correcting for BSSE was developed. The basis sets used here give rise to a very small BSSE in $\underline{\gamma}$ and are likely to produce an even smaller error in $\underline{\gamma}$. This is because $\underline{\gamma}(Li^+)$ is so much smaller than $\underline{\gamma}(F^-)$ and $\underline{\gamma}(Cl^-)$. A calculation using a ($10s\,5p\,2d$) basis gave $\gamma_{zzzz}(Li^+)=0.23$ a.u., and, as we shall see, $\gamma_{zzzz}(F^-)$ is 209 a.u. Thus, although the polarizability of the $(Li^+)_6$ cage is about 30% of $\underline{\alpha}(F^-)$, the hyperpolarizability is only about 0.5% of $\underline{\gamma}(F^-)$. Dipole—induced-dipole corrections to $\underline{\gamma}$ are similarly unnecessary. Thus both $\underline{\gamma}$ and $\underline{B}$ were calculated by direct subtraction of the response of the $(\mathrm{Li}^+)_6$ cage from that of the $X^-(\mathrm{Li}^+)_6$ cluster.

Apart from their differences in magnitude, the hyperpolarizabilities of free and in-crystal ions also differ in symmetry. In spherical symmetry, $\underline{\gamma}$ and $\underline{B}$ are each specified by a single constant,[5]

$$\gamma_{\alpha\beta\gamma\delta}=\tfrac{1}{3}\gamma(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}) \tag{2}$$

and

$$B_{\alpha\beta,\gamma\delta}=B[\tfrac{3}{4}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})-\tfrac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}]\ , \tag{3}$$

so that

$$\gamma_{xxxx}=\gamma_{yyyy}=\gamma_{zzzz}=\gamma_1=\gamma\ , \tag{4a}$$

$$\gamma_{xxyy}=\gamma_{xxzz}=\gamma_{yyzz}=\gamma_2=\tfrac{1}{3}\gamma\ , \tag{4b}$$

$$B_{xx,xx}=-2B_{xx,yy}=-2B_{xx,zz}=B_1=B\ , \tag{5a}$$

$$B_{xy,xy}=B_{xz,xz}=B_{yz,yz}=B_2=\tfrac{3}{4}B\ . \tag{5b}$$

However, in a rocksalt-crystal structure the ions occupy sites of O_h symmetry and γ_1 (B_1) is no longer related by symmetry to γ_2 (B_2). Thus for the FREE ion we have to calculate a single component for each hyperpolarizability, but two components for CRYST and CLUS ions.

III. PRELIMINARY CALCULATIONS FOR F$^-$ IN LiF

In Ref. 1 a large *spd* Gaussian-type orbital (GTO) basis was used to calculate $\underline{\alpha}$ for F$^-$ at the FREE, CRYST, and CLUS levels. Table I shows the corresponding $\underline{\gamma}$ and $\underline{B}$ hyperpolarizabilities calculated in the same basis. $\underline{\gamma}$ was obtained from a fit to the dipole (μ_z), and $\underline{B}$ was obtained from a fit to the quadrupole moment (θ_{zz}) in external fields $(0,0,F_z)$. In the CLUS calculation, θ_{zz} was corrected by subtraction of the quadrupole moment of the $(\mathrm{Li}^+)_6$ cage.

Although definitive values of these properties are not to be expected from a basis without *f* functions on F$^-$, the results in Table I are of interest for two reasons. First, they illustrate the dramatic reduction in hyperpolarizability from free to in-crystal F$^-$. Second, the results are useful as intermediate data in calculations of the effect of crystal distortions on the polarizability of in-crystal F$^-$.[7]

Table I also shows that both electrostatic and overlap compression are important in the reduction of $\underline{\alpha}$, $\underline{\gamma}$, and $|\underline{B}|$. At the SCF level α is reduced by ~ 2, γ_1, by ~ 50, and $|B_1|$ by ~ 10 when the ion is placed in a cluster of cations. Significant departure from spherical symmetry is induced by point-charge electrostatic interactions. The effect of overlap compression on anisotropy was not found for this basis because the original CLUS calculation[1] was performed in the highest symmetry allowed for a finite-field calculation with $F=(0,0,F_z)$, i.e., in C_{4v}.

As stated above, the calculation of $\underline{\gamma}$ and $\underline{B}$ in this basis is not definitive, but it clearly demonstrates that models using the properties of the free ion are irrelevant to the ion in a crystal. In the next section we consider extension of the basis by inclusion of *f* functions.

IV. EFFECTS OF BASIS EXTENSION

The polarizability and hyperpolarizability of the free F$^-$ ion arise mainly from the outer p^6 shell. Analysis of the orbital polarizabilities shows that these electrons contribute 92% of α at the SCF level. If we take the external electric field strength as a perturbation parameter, then the first-order wave function arising from a *p* orbital is a mixture of *s* and *d* functions. Thus *s*- and *d*-polarization functions are needed in a calculation of $\alpha(\mathrm{F}^-)$. In second order, *p* and *f* functions are mixed into the wave function. Thus, for an accurate calculation of $\gamma(\mathrm{F}^-)$ and $\mathrm{B}(\mathrm{F}^-)$ the basis should include *s*-, *p*-, *d*-, and *f*-polarization functions.

A fluoride ion in the LiF crystal is in an environment of octahedral symmetry, and, in principle, functions corresponding to *all* values of angular momentum are required for the description of both perturbed and unperturbed ions. In practice, a large *spdf* basis is expected to give a good description of the energy, polarizability, and hyperpolarizability of the in-crystal ion.

Table II shows the effect of *f* basis functions on the calculated hyperpolarizability of the FREE F$^-$ ion. A spherical-harmonic version of a $[12s\,8p\,5d]$ contracted GTO basis[8] was extended by a set of seven *f* functions with exponent ξ_f. Table II shows how γ, derived from a three-field fit to the induced dipole moment, varies with ξ_f. The SCF energy and dipole polarizability remain at their values for the basis without *f* functions, namely $E=-99.457\,777$ a.u. and $\alpha=10.649$ a.u. γ is insensitive to inclusion of *f* sets with large exponents, but increases rapidly for small *f* exponents. No maximum in γ was found. Analogy with the Hylleraas variation principle[9] leads us to suppose that, if the unperturbed and first-order wave functions are sufficiently close to the exact Hartree-Fock solutions, then the calculated γ is a lower bound for the true γ_{SCF}. Numerical difficulties with very diffuse

TABLE I. Polarizability and hyperpolarizabilities (in a.u.) of F$^-$ in different environments. These are preliminary results since the basis in Ref. 1 lacks *f* functions.

	α_{zz}	γ_{zzzz}	γ_{xxzz}	$B_{zz,zz}$	$B_{xz,xz}$
FREE	10.65	8100	$\frac{1}{3}\gamma_{zzzz}$	-433	$\frac{3}{4}B_{zz,zz}$
CRYST(LiF)	7.30	679	141	-96	-56
CLUS(LiF)	5.40	149		-34	

TABLE II. Variation of the free-F$^-$ dipole hyperpolarizability with f exponent.

ξ_f (a.u.)	γ_{zzzz} (a.u.)
	8200
4	8203
2	8204
1	8205
0.5	8216
0.25	8302
0.20	8384
0.15	8560
0.10	8997
0.05	9962

functions may also introduce errors in γ, and so we simply note that γ for the FREE ion increases when f functions are added to the basis and that the estimated γ for free F$^-$ is in excess of 10^4 a.u.

Having checked on the qualitative effect of f functions for the FREE ion, the next step is to consider their effect in CRYST calculation. In the CRYST model an F$^-$ ion is surrounded by bare charges on the lattice sites. Inclusion of the very diffuse f functions indicated by the FREE calculation therefore has an obvious danger. A spuriously high polarizability or hyperpolarizability may be produced because the diffuse polarization functions have sufficient amplitude at the nearest-neighbor distance to allow electrons to flow off the central ion into empty "1s" orbitals of the six neighboring "cations." In octahedral symmetry these cage orbitals span $A_{1g}+T_{1u}+E_g$, and, for instance, a diffuse f set could simulate the T_{1u} cage orbitals. A similar problem was encountered in the calculation of the superposition error in polarizabilities of ion clusters by the conventional counterpoise method.[1] This problem is an artifact of the *point*-charge electrostatics and is not related to the physics of a real crystal where the cations have cores of electrons.

Table III shows the effect of basis extension on the SCF energy, polarizability, and hyperpolarizabilities of the CRYST F$^-$ ion. Inclusion of f functions with an exponent 1.0 a.u. does not change the *spd* values significantly. Lowering the exponent to $\eta=0.206244$ a.u. has a large effect on the hyperpolarizabilities. Although the direction of the changes is what we might expect from the FREE ion calculations, it is also consistent with the spurious effect discussed above. Adding even more diffuse f sets with exponents $\eta/3$ and $\eta/9$ produces large changes in the same direction. As the radial maxima for the three f sets occur at $\sim(0.7R, 1.2R, 2.1R)$, where R is the LiF ionic separation, it is probable that the results for this basis contain large errors due to the localization on the bare point charges of the lattice.

TABLE III. Effect of f functions on the properties of F$^-$ in a point-charge lattice. All properties are in a.u. $\eta=0.206244$ a.u.; ξ_f is an f exponent.

Basis	α	γ_{zzzz}	$B_{zz,zz}$	E_{SCF}
[12s 8p 5d 1f]				
$\xi_f=1.0$	7.29	670	-97	-99.90846
$\xi_f=\eta$	7.50	950	-155	-99.91553
[12s 8p 5d 3f]				
$\xi_f=(\eta,\eta/3,\eta/9)$	7.55	1140	-182	-99.91584

Although this source of error provides good reasons for distrust of CRYST calculations, it is not present in CLUS calculations. In these the cores of the neighboring cations *are* represented. The confined anion suffers overlap compression, and the first- and second-order wave functions are also strongly contracted in extent. Addition of f functions with reasonable exponents will serve a real physical purpose of basis extension. Accordingly, in the final section we present calculations of the hyperpolarizabilities of F$^-$(Li$^+$)$_6$ and Cl$^-$(Li$^+$)$_6$ cluster using f-extended basis sets.

V. RESULTS FOR F$^-$ AND Cl$^-$

This section gives our best estimates of the in-crystal hyperpolarizabilities of F$^-$ and Cl$^-$ in their lithium salts. These were found by CLUS calculations on F$^-$(Li$^+$)$_6$ and Cl$^-$(Li$^+$)$_6$ using the ATMOL 4 SCF routines[6] with a finite-field program (R. Harrison, Cambridge).

The basis sets used are spherical-harmonic extensions of the Cartesian GTO sets used in our previous studies of the polarizability of these clusters.[1,2] For F$^-$ the original [12s 8p 5d] set[8] is augmented by a d set with an exponent $\eta=0.022916$ a.u. and three f sets with exponents $(9\eta, 3\eta, \eta)$. For Cl$^-$ the original [13s 11p 5d] set[10] is augmented by three f sets with exponents $(9\eta, 3\eta, \eta)$ where $\eta=0.0366339$ a.u. The surrounding cage of six lithium ions is described by $(10s\,5p)\rightarrow[1s\,1p]$ contractions which give fully polarizable Li$^+$ (Ref. 1) and lead to only very small basis-set—superposition effects.

In our highly contracted basis sets the two-electron integral evaluation took $\sim$2.5 hours of central-processing-unit time (IBM 3081) per cluster and exponent optimization was not feasible. The dipole hyperpolarizabilities γ_1 and γ_2 are found by fitting the dipole moment in three external fields $\vec{F}=\lambda(0,1,2)$. For B_1 and B_2 a field gradient is imposed by two distant charges q in addition to the point-charge crystal lattice and an external field $\vec{F}=\lambda(0,1,2)$; B_1 and B_2 emerge as the changes in cluster dipole moment that are first order in λ and q. The small response of the cage is subtracted, and thus γ_1, γ_2, B_1, and B_2 for the central in-crystal anion are calculated. Table IV shows our results. Because of the symmetry of the fields, each component of the dipole moment leads to an independent estimate of the $\underline{B}$ hyperpolarizability, giving the spread of values shown in Table IV, and, in turn, reflecting the accuracy of the numerical differentiation of the dipole moment.

The dipole polarizabilities α are obtained from the same fitting process as the $\underline{\gamma}$ hyperpolarizabilities. The values of α obtained are increased by less than 1% (for F$^-$) and less than 0.02% (for Cl$^-$) over the results for basis sets without f functions.[2] This supports our statement in Sec. IV that the dangers inherent in the use of diffuse polariza-

TABLE IV. *Ab initio* in-crystal hyperpolarizabilities of F^- and Cl^- (in a.u.).

	γ_1	γ_2	B_1	B_2
F^- in LiF	209	119	-48 ± 6	-45 ± 1
Cl^- in LiCl	2090	815	-317 ± 1	-275 ± 10

tion functions in CRYST calculations do not affect CLUS calculations. Overlap compression confines the anion charge density and prevents spurious "charge transfer" upon addition of diffuse f functions. Lack of any significant change in α shows that our calculation is behaving in a physically reasonable way.

The results in Table IV are our best predictions of the in-crystal hyperpolarizabilities of F^- and Cl^- in lithium halides. It is clear that the crystalline environment reduces the anionic hyperpolarizabilities by an order of magnitude and introduces significant hyperpolarizability anisotropy. The ratio $\gamma_1/3\gamma_2$, unity for a spherical ion, is reduced to 0.59 for F^- in LiF and to 0.85 for Cl^- in LiCl. B is less anisotropic as $3B_1/4B_2$, which is unity for a spherical ion, falls to ~ 0.8 for F^- in LiF and to ~ 0.9 for Cl^- in LiCl.

As the lithium cation has an insignificant $\underline{\gamma}$ hyperpolarizability, we might hope to compare our calculated $\underline{\gamma}$ value for the in-crystal anions with experimental values for the hyperpolarizability of the lithium halide crystal. Maker and Terhune[11] were able to observe third-harmonic generation (THG) in a lithium fluoride crystal despite the fact that index matching is not possible. They give the following values for the components of the material susceptibility: $C_{1111}(-3\omega,\omega,\omega,\omega)$ and $C_{1122}(-3\omega,\omega,\omega,\omega)$, where ω is the frequency of the pump beam (ruby laser, $\lambda = 694.3$ nm), and

$$C_{1111} + 3C_{1122} = 3 \times 10^{-15}\ \mathrm{cm^3\,erg^{-1}} \tag{6}$$

and

$$C_{1111}/3C_{1122} = 0.64\ . \tag{7}$$

If we neglect the lithium contribution to C_{ijkl} and follow the analysis of Ward and New,[12] we identify

$$C_{1111}(-3\omega,\omega,\omega,\omega) = (\mathscr{L}^3\rho/24)\gamma_1^{\mathrm{THG}}\ , \tag{8a}$$

$$C_{1122}(-3\omega,\omega,\omega,\omega) = (\mathscr{L}^3\rho/24)\gamma_2^{\mathrm{THG}}\ , \tag{8b}$$

where ρ is the number density of F^- ions in LiF ($\rho = 6.118 \times 10^{22}\ \mathrm{cm^{-3}}$) and $\mathscr{L}$ is a local-field factor,[12]

$$\mathscr{L} = (n^2+2)/3\ , \tag{9}$$

where n is the refractive index at the laser frequency ($n = 1.391$). This gives

$$(\gamma_1^{\mathrm{THG}} + 3\gamma_2^{\mathrm{THG}}) = 5.2 \times 10^{-37}\ \mathrm{cm^6\,erg^{-1}}$$

$$= 1030\ \text{a.u.}\ , \tag{10a}$$

whereas we calculate

$$\gamma_1 + 3\gamma_2 = 566\ \text{a.u.} \tag{10b}$$

and

$$\gamma_1^{\mathrm{THG}}/3\gamma_2^{\mathrm{THG}} = 0.64\ , \tag{11a}$$

and also

$$\gamma_1/3\gamma_2 = 0.59\ . \tag{11b}$$

The agreement between the calculated and experimental values is good since the γ^{THG} values include some near-resonant enhancement. Ward and New suggest the following relationship between γ^{THG} and γ:[12]

$$\gamma = \gamma^{\mathrm{THG}}/(1+15\omega^2/\Omega^2)\ ,$$

where Ω is the excitation of the material; if this were chosen to correspond to the reasonable value of an absorption at ~ 150 nm, the calculated and experimental values would agree closely.

This level of agreement is almost certainly fortuitous as the analysis of Maker and Terhune did not account for the effects of focusing the pump beam.[12] Moreover, the calculated values neglected the effect of electron correlation, which is likely to enhance the γ values.

Maker and Terhune[11] also gave results for

$$C_{ijkl}(-(\omega+\delta),\omega,\omega,-(\omega-\delta))$$

values obtained from a three-wave-mixing experiment [nonresonant coherent anti-Stokes Raman spectroscopy (CARS)], when δ is a benzene Raman shift. These results were normalized relative to the value obtained for benzene, for which an absolute value was calculated from the spontaneous Raman intensity, assuming that only a resonant CARS signal would be obtained in this case; the normalization increased the directly measured susceptibility values by a factor of $8^{1/2}$. Using the values of C_{1111} obtained in this way, we obtain the three-wave-mixing results given in Table V. It is clear that these results are much larger than our calculated ones, although the dispersion correction for the three-wave-mixing hyperpolarizabilities should be much smaller than for third-harmonic generation. The agreement would be much better with "unnormalized" experimental values; Maker and Terhune note some inconsistencies in their absolute values.[11]

If we accept that they are internally consistent, the results quoted in Table V show two things. Firstly, they show a strong environmental effect on the in-crystal hyperpolarizability of Cl^-; this effect is much more pronounced than the corresponding effect on the in-crystal polarizability.[2] Secondly, they show that the factor-of-10 difference between the hyperpolarizability of F^- in LiF and of Cl^- in LiCl, predicted by our calculations, is a reasonable result.

The values of the nonlinear susceptibilities found by Maker and Terhune have been critically discussed by

TABLE V. Values for γ_1 (in a.u.) and $\gamma_1/3\gamma_2$ obtained from the three-wave-mixing results of Maker and Terhune (Ref. 11).

	γ_1	$\gamma_1/3\gamma_2$
F^- in LiF	690	0.74 ± 0.1
Cl^- in NaCl	11 600	0.78
Cl^- in KCl	20 300	1.10

Hellwarth[13] in light of further experimental and theoretical work. It was concluded that the THG results on LiF are consistent with improved three-wave-mixing data,[14] but that the original three-wave-mixing results are not. The more recent work therefore supports our calculation of the $\underline{\gamma}$ hyperpolarizability of F$^-$.

ACKNOWLEDGMENTS

The authors thank the University of Cambridge Computer Syndicate for provision of computing resources, and members of the Theoretical Chemistry group at the University of Cambridge for helpful discussions.

---

[1] P. W. Fowler, and P. A. Madden, Mol. Phys. **49**, 913 (1983).

[2] P. W. Fowler and P. A. Madden, Phys. Rev. B **29**, 1035 (1984).

[3] P. W. Fowler and P. A. Madden, J. Phys. Chem. (to be published).

[4] See, e.g., E. Cazzanelli, A. Fontana, G. Mariotto, V. Mazzacurati, G. Ruocco, and G. Signorelli, Phys. Rev. B **28**, 7269 (1983).

[5] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[6] (a) The basic program is described in M. Dupuis, J. Rys and H. T. King, Quant. Chem. Prog. Exch. **13**, 403 (1981); (b) N. R. Saunders, SERC Davesbury Laboratory (U.K.) report (unpublished).

[7] P. W. Fowler and P. A. Madden (unpublished).

[8] G. H. F. Diercksen and A. J. Sadlej, Mol. Phys. **47**, 33 (1982).

[9] J. O. Hirschfelder and P. R. Certain, J. Chem. Phys. **60**, 1118 (1973).

[10] G. H. F. Diercksen and A. J. Sadlej, J. Chem. Phys. Lett. **84**, 390 (1981).

[11] P. D. Maker and R. W. Terhune, Phys. Rev. **137**, A801 (1965).

[12] J. F. Ward and G. H. C. New, Phys. Rev. **185**, 57–72 (1969); see also D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics* (Springer, New York, 1979).

[13] R. W. Hellwarth, Prog. Quant. Electron. **5**, 1 (1977).

[14] M. D. Levenson, IEEE J. Quant. Electron. **QE-10**, 110 (1974).