

An *ab initio* study of the molecular electric polarizabilities of N₂, HCN, acetylene, and diacetylene

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The independent components of the α , β , γ , **A**, and **B** tensors were computed for the ground states of N₂, HCN, acetylene, and diacetylene molecules from electric moments induced in a perturbing static electric field. The results are used to comment on trends in nonlinear susceptibilities of polyacetylenes and polydiacetylenes.

INTRODUCTION

Third-order nonlinear optical properties of organic materials offer great promise for various applications. Electromagnetic fields can be altered in phase, frequency, amplitude, or other propagation characteristics by passage through such media.¹ The polarization induced in a medium by an external electric field is given by

$$P = \chi^{(1)}F + \chi^{(2)}FF + \chi^{(3)}FFF + \dots,$$

where $\chi^{(n)}$ defines the n th order susceptibility tensor of the medium. The third-order nonlinear susceptibility $\chi^{(3)}$ of materials in which these effects occur is of interest since high values of $\chi^{(3)}$ are desirable in applications involving degenerate four-wave mixing.² Device operating conditions place additional severe demands on the stability, ease of preparation, and mechanical properties of the materials. Therefore, although a large number of substances have been tested, there is a need to extend the list of candidates for various applications. Theory can help here by providing a description that relates $\chi^{(3)}$ to the electronic structure, thus enabling the design of materials with high $\chi^{(3)}$.

The macroscopic susceptibility $\chi^{(3)}$ is related to the second hyperpolarizability of a molecule $\gamma_{\alpha\beta\gamma\delta}$ ($-\omega_4$; $\omega_1, \omega_2, \omega_3$), where ω_1, ω_2 , and ω_3 are the frequencies of the incident optical fields and ω_4 is the frequency of the induced dipole moment.³ The molecular contributions to $\chi^{(3)}$ are weighted by a frequency-dependent factor that takes into account the effects of internal fields.

Organic molecules with delocalized π systems have anomalously large $\chi^{(3)}$ susceptibilities, which can exceed the best values for inorganic dielectrics and semiconductors.⁴ It has been observed⁵ that in linear conjugated molecules $\chi^{(3)}$ increases dramatically with chain length, much faster than for the isoelectronic saturated molecules. This is attributed to the mobility of the π electrons in the delocalized molecular orbitals extending along the chain, giving rise to large components of γ in this direction.

For a molecule in an external electric field the induced electric dipole moment is⁶

$$\begin{aligned} \mu_\alpha &= \mu_\alpha^{(0)} + \alpha_{\alpha\beta}F_\beta + \frac{1}{2}\beta_{\alpha\beta\gamma}F_\beta F_\gamma \\ &+ \frac{1}{6}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta \\ &+ \frac{1}{3}A_{\alpha,\beta\gamma}F_\beta F_\gamma + \frac{1}{3}B_{\alpha\beta,\gamma\delta}F_\beta F_\gamma F_\delta + \dots, \end{aligned}$$

where α is the dipole polarizability, β and γ are first and second hyperpolarizabilities, **A** is the dipole-quadrupole polarizability, and **B** is a mixed dipole-quadrupole hyperpolarizability. Greek subscripts denote vector or tensor components in the molecular axis system and take values x, y , or z ; a repeated subscript denotes summation over all three Cartesian directions. The quadrupole moment may likewise be expanded in terms of the electric field⁶:

$$\begin{aligned} \Theta_{\alpha\beta} &= \Theta_{\alpha\beta}^{(0)} + A_{\gamma,\alpha\beta}F_\gamma + \frac{1}{2}B_{\gamma\delta,\alpha\beta}F_\gamma F_\delta \\ &+ C_{\alpha\beta,\gamma\delta}F_\gamma F_\delta + \dots, \end{aligned}$$

where **C** is the quadrupole polarizability. α , β , and γ are independent of origin for any molecule whereas **A** and **C** depend on origin. **B** is independent of origin for a neutral, nonpolar molecule.⁶ For centrosymmetric molecules (with origin at that center) $\mu^{(0)}$, β , and **A** vanish by symmetry. In general, the nonvanishing tensor components are linear combinations of a smaller set of independent quantities; the relations between nonvanishing components may be determined by group theory.⁷

For $D_{\infty h}$ molecules α has two independent components, γ has three and **B** has four⁷:

$$\begin{aligned} \alpha_{zz}; \quad \alpha_{xx} &= \alpha_{yy}, \\ \gamma_{zzz}; \quad \gamma_{xxx} &= \gamma_{yyy}; \quad \gamma_{xxx} = \gamma_{yyy} = 3\gamma_{xxyy}, \\ B_{zz,zz} &= -2B_{zz,xx} = -2B_{zz,yy}; \quad B_{xz,xz} = B_{yz,yz}; \\ B_{xx,zz} &= B_{yy,zz} = -(B_{xx,xx} + B_{xx,yy}); \\ B_{xy,xy} &= \frac{1}{2}(B_{xx,xx} - B_{xx,yy}). \end{aligned}$$

$C_{\infty v}$ molecules have in addition two independent components of β and two of **A**:

$$\begin{aligned} \beta_{zzz}; \quad \beta_{xxx} &= \beta_{yyy}, \\ A_{z,zz} &= -2A_{z,xx} = -2A_{z,yy}; \quad A_{x,xz} = A_{y,yz}. \end{aligned}$$

The present paper is concerned only with the *static* polarizabilities and hyperpolarizabilities ($\omega_i = 0$). The frequency-dependent properties generally have a larger number of non-zero components.

γ is sensitive to the details of the outer regions of the electron cloud and therefore calculations of γ require large basis sets. *Ab initio* values of γ have been reported for atoms,^{8,9} diatomic molecules,¹⁰⁻¹⁴ and a very few polyatomics.¹⁵ On the other hand, the materials of interest for their

values of $\chi^{(3)}$ are generally large aromatic molecules or quasi-one-dimensional polyacetylenes and polydiacetylenes.⁴ For these cases parametrized models rather than *ab initio* calculations are appropriate. Models should, however, be based on a correct physical description and thus need to be calibrated against high quality *ab initio* results. In this paper we report *ab initio* SCF calculations of γ for molecules which are small enough for accurate treatment but which retain some physical features of the typical large organic molecules of practical interest. It has been observed that: (a) components of γ along the chain (γ_{zzzz}) are much larger than the cross components γ_{xxxx} and γ_{zzzz} ; (b) γ_{zzzz} is about three orders of magnitude larger for the polymer than for the monomer; (c) in polyphenylacetylene polymers where the side groups attached to the carbon backbone are not identical, carbon atoms in the chain acquire heteroatomic character. The values of the susceptibility components depend on the degree of "heteroatomicity" (i.e., the presence of different atoms on the chain or of different side groups on the chain reduces γ).¹⁶ We investigate some of these aspects with a set of small molecules with triple bonds: $\text{N}\equiv\text{N}$, $\text{HC}\equiv\text{N}$, $\text{HC}\equiv\text{CH}$, and $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$. This is the first *ab initio* calculation of γ for these molecules. The first three members of the set are related by progressive substitution of a heteroatom with a CH group. Comparison of acetylene and diacetylene will show the effect of increasing chain length. Furthermore, diacetylene is itself of interest as a monomeric unit of the polydiacetylene which has one of the largest known values of $\chi^{(3)}$.⁴

CALCULATIONS AND RESULTS

The properties of interest in this paper describe the response of a molecule in its electronic ground state to perturbation by an electric field. In calculating them it is necessary to represent both the unperturbed wave function (ψ^0) and the changes induced in it to first [$\psi^1(F_\alpha)$] and second order [$\psi^2(F_\alpha F_\beta)$]. For π systems consisting of first-row atoms a large *spdf* basis is expected to achieve this, thereby giving accurate energies, polarizabilities, and hyperpolarizabilities at the SCF level. In the case of diacetylene it was not feasible to include *f* functions in the basis; this deficiency is assessed later in the present section.

All calculations used contracted Gaussian basis sets and were carried out using the CADPAC program.¹⁷ Each first row atom carries a [5s4p2d 1f] set of GTOs: for N this consisted of a Dunning [5s3p] set¹⁸ plus an STO-2G 3d function (Slater exponent $\zeta = 2.33a_0^{-1}$) and *p*, *d*, and *f* GTO primitives (exponents 0.08, 0.11, and $0.10a_0^{-2}$, respectively); for C a Dunning [5s4p] set¹⁸ was used with an STO-3G 3d function ($\zeta = 2.15a_0^{-1}$) and uncontracted *d* and *f* GTOs (exponent 0.08 and $0.10a_0^{-2}$, respectively). The H basis was a [3s2p] set consisting of the Dunning [3s] set¹⁸ ($\zeta = 1.25a_0^{-1}$), an STO-2G 2p set ($\zeta = 1.5a_0^{-1}$) and a *p* set with exponent $0.08a_0^{-2}$. Cartesian *d* and *f* sets were used. In the calculations on C_4H_2 the *f* functions on carbon were deleted.

Bond lengths were taken from experiment. They are: for N_2 $r(\text{NN}) = 1.0976 \text{ \AA}$;¹⁹ for HCN $r(\text{HC}) = 1.0655 \text{ \AA}$, $r(\text{CN}) = 1.1532 \text{ \AA}$;²⁰ for C_2H_2 $r(\text{HC}) = 1.0606 \text{ \AA}$, $r(\text{CC}) = 1.2032 \text{ \AA}$;²¹ for C_4H_2 $r(\text{HC}) = 1.0935 \text{ \AA}$, $r(\text{C}\equiv\text{C}) = 1.2176 \text{ \AA}$, $r(\text{C}-\text{C}) = 1.3831 \text{ \AA}$.²²

There are three well-established methods for calculation of polarizability and hyperpolarizability from an SCF wave function. The most elegant is by analytical differentiation of the wave function with respect to the field, the coupled Hartree-Fock (CHF) method. The most widely used is the finite field method, in which the interaction with a uniform static electric field is added directly to the Hamiltonian in an SCF calculation. Useful for properties involving field gradients is the point charge method, in which arrays of distant point charges are used as sources of field, field gradient, etc., at the molecule. The CHF procedure is now routine for α , and programs capable of CHF calculation of \mathbf{A} , $\mathbf{\beta}$, \mathbf{C} ,¹⁷ and \mathbf{B}^{23} exist, but for γ one of the finite perturbation methods is generally used. Results from all three methods are exactly equivalent. In this work the finite field method was used throughout.

In finite field calculations the property tensors are obtained by numerical differentiation of the energy, dipole, and quadrupole moments with respect to the perturbing electric field. The magnitude of the applied field is chosen as a compromise between numerical accuracy and contamination from higher order polarizabilities. Bishop and Solunac²⁴ have pointed out the dangers inherent in using very large perturbing fields. We used fields of magnitude 0.0005 to

TABLE I. Dipole polarizabilities and hyperpolarizabilities of triple-bonded systems. All quantities are in atomic units. For α $1 \text{ a.u.} \equiv e^2 a_0^2 E_h^{-1} = 0.16488 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$, for β $1 \text{ a.u.} \equiv e^3 a_0^3 E_h^{-2} = 0.32063 \times 10^{-52} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$, for γ $1 \text{ a.u.} \equiv e^4 a_0^4 E_h^{-3} = 0.62360 \times 10^{-64} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. The best results for HCCH are given in the third row. The results in the fourth row are for a test calculation to assess the effect of *f* functions in the basis (see the text).

	α_{zz}	α_{xx}	$\bar{\alpha}$	γ_{zzzz}	γ_{xxxx}	γ_{zzzz}	$\bar{\gamma}$	β_{zzz}	β_{xxx}
N_2	14.944 ^a	9.648 ^a	11.413	775	662	240	700
HCN	22.389 ^b	13.736 ^b	16.620	1533	1840	564	1740	-6.386	-3.434
HCCH	31.341 ^c	19.000 ^c	23.114	2917	5100	1460	4471
HCCH (without <i>f</i>)	31.295	18.891	23.026	2786	3360	1439	3500
$\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$	86.042	30.534	49.037	19486	5539	3616	9744
	$\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$								
	$\bar{\gamma} = \frac{1}{3}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$								

^a Experimental $\alpha(-\omega; \omega)$ at 632.8 nm = 15.09 and 10.34 a.u. (Ref. 39). Many theoretical calculations have been reported (Refs. 23, 25, 40, and 41).

^b For other calculations see Ref. 26.

^c Experimental $\alpha(-\omega; \omega)$ at 632.8 nm = 31.91 and 19.34 a.u. (Ref. 39), other calculations (Refs. 23, 27, and 28).

TABLE II. Mixed dipole-quadrupole polarizabilities of triple-bonded systems. All quantities are in atomic units: for A $1 \text{ a.u.} \equiv e^2 a_0^3 E_h^{-1} = 0.872 49 10^{-51} \text{ C}^2 \text{ m}^3 \text{ J}^{-1}$, for B $1 \text{ a.u.} \equiv e^3 a_0^4 E_h^{-2} = 1.696 71 \times 10^{-63} \text{ C}^3 \text{ m}^4 \text{ J}^{-2}$. The best results for C_2H_2 are given in the third row. Those in the fourth row are for a test calculation to assess the effect of f functions in the basis (see the text).

	$B_{zz,zz}$	$B_{xx,zz}$	$B_{xz,xz}$	$B_{xy,xy}$
N_2	-174	67	-102	-86
HCN	-319	162	-204	-182
HCCH	-497	406	-416	-399
HCCH (without f)	-496	365	-411	-292
$\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$	-2122	504	-1272	-442
HCN		$A_{z,zz}$ 10.96	$A_{z,xz}$ 1.90	

0.0025 a.u. along and perpendicular to the internuclear axis. Crossed fields are needed for some components such as γ_{xxxx} . α and γ (and β for HCN) are derived by a fit to the induced dipole moment. \mathbf{B} (and \mathbf{A} for HCN) is derived by a fit to the induced quadrupole moment. Fitting to the induction energy gives a useful check on these values but is less accurate [γ occurs in the dipole expansion as $(1/6)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta$ but as $(1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta$ in the energy].

In all four molecules the occupied orbitals are of σ or π symmetry, i.e., the component of angular momentum about the figure axis is $m = 0$ (σ) or $m = \pm 1$ (π) for each MO. The ground state wave function can therefore be described by atomic s and p functions, and a sufficiently large sp basis can recover the Hartree-Fock limiting energy. Now a perturbation by an axial field conserves m , so that $\psi^1(F_z)$ is still a mixture of σ and π . On the other hand, a field perpendicular to the axis mixes in other symmetries according to the selection rule $\Delta m = \pm 1$. Therefore $\psi^1(F_x)$ is a mixture of σ , π , and δ functions, requiring d atomic orbitals. The Hartree-Fock limit for α_{zz} can be achieved in an sp basis but α_{xx} requires an spd basis. Similar reasoning based on the perturbation theory expression⁶ for γ shows that γ_{zzzz} requires sp functions, γ_{xxxx} needs d in addition, and γ_{xxxx} needs the ϕ symmetry introduced by f polarization functions. Some components of \mathbf{B} , e.g., $B_{xy,xy}$ also require f functions.

Tables I and II show the results for all four molecules and these are now discussed in turn. For N_2 the calculated SCF energy is $-108.983 65 E_h$ and the permanent quadrupole moment is $\Theta_{zz}^{(0)} = -0.8763ea_0^2$. The results for E , $\Theta^{(0)}$, and α are all close to those found by Amos²⁵ using the present basis minus f functions. The polarizability α is anisotropic, with the molecule being more polarizable along its length than across the bonds. By contrast γ is nearly isotropic [recall that for an atom $\gamma_{zzzz} = \gamma_{xxxx} = 3\gamma_{xxxx}$ and $B_{zz,zz} = -2B_{xx,zz} = (4/3)B_{xz,xz}$].

For HCN the calculated SCF energy is $-92.908 00 E_h$, the dipole is $1.2966ea_0$ (HCN), and the quadrupole moment with respect to the center of mass is $2.1273ea_0^2$. α is anisotropic with $\alpha_{zz} > \alpha_{xx}$ as for N_2 . Our values for E and α are a little better than those reported by Gready *et al.*²⁶ for a basis without f functions. γ is still nearly isotropic but now with $\gamma_{xxxx} > \gamma_{zzzz}$. Note that β is negative with this choice of axis

TABLE III. Mixed second moment-dipole hyperpolarizabilities \mathcal{B} for N_2 and $\text{HC}\equiv\text{CH}$. \mathcal{B} has the same units as \mathbf{B} but is a traced quantity. See the text for a description of the relationship between \mathbf{B} and \mathcal{B} . The values in Table VI of Ref. 23 for C_2H_2 are inconsistent in sign with those for N_2 , but have been given our sign convention.

	N_2		HCCH	
	This work	Dykstra ^a	This work	Dykstra ^a
$\mathcal{B}_{zz,zz}$	-215.0	-212.61	-655.7	-665.73
$\mathcal{B}_{zz,xx}$	-43.1	-42.06	-156.9	-173.28
$\mathcal{B}_{xx,xx}$	-149.5	-134.32	-692.9	-648.32
$\mathcal{B}_{xx,zz}$	-23.7	-28.33	-22.5	-38.24
$\mathcal{B}_{xx,yy}$	-34.1	-44.79	-161.4	-239.16
$\mathcal{B}_{xz,xz}$	-68.2	-70.23	-277.5	-275.71
$\mathcal{B}_{xy,xy}$	-57.7	-44.76	-265.8	-204.58

^a Reference 23.

system (H at positive z) and thus acts to reduce the dipole when the field is parallel to the permanent moment.

For C_2H_2 the calculated SCF energy is $-76.848 57 E_h$ and the permanent quadrupole moment is $\Theta_{zz}^{(0)} = 5.4666ea_0^2$. Our results for α are comparable with those obtained using electric-field-dependent basis functions by Sadlej,²⁷ and by Amos and Williams²⁸ in a basis without f functions. As for N_2 and HCN, the polarizability is anisotropic with α_{zz} about 50% larger than α_{xx} . γ_{xxxx} is now significantly larger than γ_{zzzz} .

For N_2 and HCCH the present results for \mathbf{B} may be compared with a CHF-type calculation by Dykstra.²³ We have used a definition of \mathbf{B} in which the change in the quadrupole moment

$$\Theta_{\alpha\beta} = \langle \psi | \sum_i q_i (\frac{3}{2} r_{i\alpha} r_{i\beta} - \frac{1}{2} \delta_{\alpha\beta} r_{i\gamma} r_{i\gamma}) | \psi \rangle$$

induced by a uniform field has a leading term⁶:

$$\Delta\Theta_{\alpha\beta} = \frac{1}{2} B_{\gamma\delta,\alpha\beta} F_\gamma F_\delta.$$

\mathbf{B} is then traceless, $B_{\alpha\beta,\gamma\gamma} = 0$. Dykstra adopts a definition of a tensor \mathcal{B} for which the change of the second moment

$$Q_{\alpha\beta} = \langle \psi | \sum_i q_i r_{i\alpha} r_{i\beta} | \psi \rangle$$

induced by a uniform field has a leading term:

$$\Delta Q_{\alpha\beta} = \frac{1}{2} \mathcal{B}_{\gamma\delta,\alpha\beta} F_\gamma F_\delta.$$

\mathcal{B} has a trace related to the spherically averaged expansion of the electron cloud in a uniform field. Since

$$\Theta_{\alpha\beta} = \frac{3}{2} Q_{\alpha\beta} - \frac{1}{2} \delta_{\alpha\beta} Q_{\gamma\gamma}.$$

We can recover \mathbf{B} from \mathcal{B} by

$$B_{\alpha\beta,\gamma\delta} = \frac{3}{2} \mathcal{B}_{\alpha\beta,\gamma\delta} - \frac{1}{2} \mathcal{B}_{\alpha\beta,\epsilon\epsilon} \delta_{\gamma\delta}.$$

By fitting the second moments rather than quadrupoles we have derived values of \mathcal{B} for N_2 and HCCH. In Table III these are compared with Dykstra's results. The two sets are broadly similar, the main differences probably being due to the lack of f functions in Dykstra's basis.

As noted above, the full basis with f functions is not feasible for an SCF calculation of the properties of C_4H_2 in a field. The effects of this deficiency have been discussed in general terms and Tables I and II give a concrete example for C_2H_2 . Removal of f functions has a very small effect on the

SCF energy ($+0.0008 E_h$), quadrupole moment (-0.2% in Θ_{zz}), and polarizability (-0.2% in α_{zz} , $+0.6\%$ in α_{xx}). The major change in γ is the drop of 34% in γ_{xxxx} , as expected from the total loss of $m = \pm 3$ functions from the basis. Smaller changes in γ_{zzzz} (4.5%) and γ_{xxzz} (1.4%) indicate that the *spd* basis is not quite saturated and is improved by the σ , π , and δ functions in a set of ten Cartesian *f* functions. Note that γ_{xxxx} remains larger than γ_{zzzz} . The major effect on **B** occurs for the *xy,xy* component as expected.

With these results in mind it is possible to assess the diacetylene results. The calculated SCF energy for C_4H_2 is $-152.54287 E_h$ and the permanent quadrupole moment is $\Theta_{zz}^{(0)} = 11.1859ea_0^2$. The polarizability shows a much more marked anisotropy with α_{zz} about three times larger than α_{xx} . In γ the anisotropy is reversed with respect to $HC\equiv CH$, with γ_{zzzz} now about four times larger than γ_{xxxx} . Even allowing for the underestimation of γ_{xxxx} by perhaps 40% due to omission of *f* functions, γ_{zzzz} is clearly dominant. In **B** the B_{zzzz} component is much larger in magnitude than B_{xxxx} , reversing the situation found in C_2H_2 .

From this admittedly limited comparison it appears that anisotropy of a single $C\equiv C$ bond is in the direction $\gamma_{xxxx} > \gamma_{zzzz}$ but that on conjugation the highly nonlinear increase in γ_{zzzz} for the delocalized π cloud reverses this anisotropy to give $\gamma_{zzzz} \gg \gamma_{xxxx}$.

CONCLUSIONS

For the acetylenes with $2N$ carbon atoms, both α and γ along the molecular axis show a more than linear increase with N but γ increases much faster than α . For an idealized chain of $2N$ carbon atoms separated by equal bond lengths, the Hückel approximation gives $\gamma \sim N^5/\beta^3$, where β is the "resonance integral" parameter.²⁹ The same behavior is also obtained within the free electron model.³⁰ The two models are designed only for very long chains and neglect electron repulsion. We have in $HC\equiv CH$ and $HC\equiv C-C\equiv CH$ a real $N = 1,2$ system. It is interesting to see how closely the ratio approaches the idealized limit of 2⁵. Actually the ratio we find is only about 2³.

Model calculations of γ which include only π electrons attribute the other components (γ_{xxxx} , γ_{xxzz}) to the σ electrons, and assume that the contributions to γ from σ electrons are negligible or in any case may be represented by means of bond additivity schemes.^{5,31} Sum-over-states calculations of γ_{xxxx} and γ_{xxzz} for conjugated hydrocarbon chains give nonsensical negative results,²⁹ γ_{xxzz} increasing in magnitude nearly as fast as γ_{zzzz} with increasing chain length. In this work we note that γ_{xxxx} in acetylene and its dimer is roughly additive, i.e., 3360 a.u. vs 5539 a.u., respectively, and so is γ_{xxzz} , with 1439 a.u. vs 3616 a.u. The dramatic nonadditive increase of γ_{zzzz} over the other components (γ_{xxzz} and γ_{xxxx}) in going from acetylene to diacetylene is particularly striking and supports the known close relationship between π -electron delocalization and high values of $\chi^{(3)}$.

The static value calculated here is related to γ for various processes as

$$\gamma^e(0; 0,0,0) = \lim_{\text{all } \omega_i \rightarrow 0} \gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3).$$

The following measurements have been reported for N_2 :

Third harmonic generation:

$$\gamma(-3\omega; \omega, \omega, \omega) = 1300 \pm 200 \text{ a.u.}^{32}$$

Four-wave mixing:

$$\gamma(-\omega_3; \omega_1, \omega_1, -\omega_2) = 1250 \pm 170 \text{ a.u.}^{33}$$

Three-wave mixing:

$$\gamma(-\omega - \Delta; \omega, \omega, -\omega + \Delta) = 1240 \text{ a.u.}^{34,35}$$

dc Field-induced second harmonic generation:

$$\gamma(-2\omega; 0, \omega, -\omega) = 1030 \pm 10 \text{ a.u.}^{35}$$

Kerr effect: $\gamma(-\omega; 0, 0, \omega) = 1440 \pm 160 \text{ a.u.}^{36}$

The values for the three-wave mixing and the third harmonic generation measurements have been normalized to γ (dcSHG) for Ar and the theoretical value for He, respectively. Measurement of the Kerr effect in $HC\equiv CH$ yields $\gamma(-\omega; 0, 0, \omega) = (2.04 \pm 0.5) \times 10^4 \text{ a.u.}^{36}$

Our calculated electronic static values of $\bar{\gamma}$ are, respectively, 60% and 20% of the experimental dynamic values reported for N_2 and $HC\equiv CH$. The difference between the measured third-order nonlinear susceptibilities and the static electronic γ includes the following:

(a) Cooperative effects. The experimental values cited above have been obtained by measurements of the macroscopic susceptibilities characteristic of the bulk medium. However, cooperative effects are expected to be small in the gas phase.

(b) Frequency dispersion and vibrational contributions. Experimental third-order polarizabilities for different processes in the same molecule differ due to a combination of dispersion and vibrational contributions, roughly in the order

$$\gamma(\text{THG}) > \gamma(\text{FWM}) > \gamma(\text{dcSHG}) > \gamma(\text{Kerr}) > \gamma(\text{static}).$$

While vibrational contributions have been estimated to be insignificant ($\sim 4\%$) for some processes for some molecules, the vibrational contribution to $\gamma(\text{Kerr})$ for some molecules is estimated to be comparable with the experimental values.³⁷ Vibrational contributions to $\gamma(\text{FWM})$ have been estimated to be 35 a.u. for N_2 and 350 a.u. for $HC\equiv CH$.³³ The Ω_v^{-2} dependence in the Kerr effect³⁷ could lead to significantly larger vibrational contributions to $\gamma(\text{Kerr})$ for $HC\equiv CH$ which has some low frequency vibrations.

(c) Vibrational corrections to the static γ . We have calculated γ for the fixed equilibrium configuration only. Reliable estimates of the vibrational correction due to the dependence of γ on the internuclear separation can only be obtained by calculations of derivatives of γ .

(d) Experimental errors. The first Kerr virial coefficient is measured as a function of temperature in the range 250–350 K and the extrapolation of these to $T^{-1} = 0$ yields an intercept which is reported as γ^K .³⁶ Since the extrapolation extends to 2.5 times the range of T^{-1} values at which measurements are carried out, relatively small errors in the data can lead to large uncertainties in γ . Absolute determination from dcSHG and THG measurements are thought to be good only to a factor of 3 or so although the relative uncertainties are much smaller. Thus, Ward and co-workers

have scaled their relative measurements to theoretical He values.³⁸ The reasonably good agreement between independent experimental measurements of γ for N_2 (1200 ± 200 a.u.) suggests that the experimental errors are not worse than 20% for this molecule.

Finally, we should comment on the expected reliability of the present results. They are calculated entirely within the SCF framework and thus neglect electron correlation. The correlation effects on γ and α for H_2 at or near the equilibrium bond distance are fairly small: 4% for γ , 1%–2% for α .¹¹ However, they may be much larger for molecules with triple bonds, and therefore diffuse π clouds. In the extreme case of the diffuse electron cloud of the F^- anion, correlation increases γ by about 100%.⁴² For neutral molecules the effects of correlation are less drastic.

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