Molecular Hyperpolarisabilities

By A. D. Buckingham and B. J. Orr

DEPARTMENT OF THEORETICAL CHEMISTRY, UNIVERSITY OF BRISTOL, BRISTOL 8

1 Introduction

The idea that an atom or molecule may be distorted by a uniform electric field so that a dipole moment is induced in direct proportion to the field strength has long been a basic postulate in physical and chemical theories. This postulate may be expressed algebraically in the form

$$\mathbf{m} = \alpha \mathbf{F} \tag{1}$$

where **m** (a vector) is the dipole moment induced in the system by the uniform electric field F (also a vector), and the proportionality constant α (a second-rank tensor) is known as the *polarisability* of the system. Equation (1) is satisfactory for normal laboratory fields, but fails when the induced moment is comparable with a permanent molecular dipole. In strong fields, eqn. (1) becomes

$$\mathbf{m} = \alpha \mathbf{F} + \tfrac{1}{2}\beta \mathbf{F}^2 + \tfrac{1}{6}\gamma \mathbf{F}^3 + \ . \ . \ . \tag{2}$$

where the coefficients β and γ of the higher powers of F are referred to as the *first* and *second hyperpolarisabilities*, respectively. As shown in Section 2A, β is zero for systems with inversion symmetry, and the term involving γ then represents the initial deviation of **m** from a linear dependence on **F**. Figure 1 illustrates the dependence of **m** on **F**, obtained by substituting typical values of

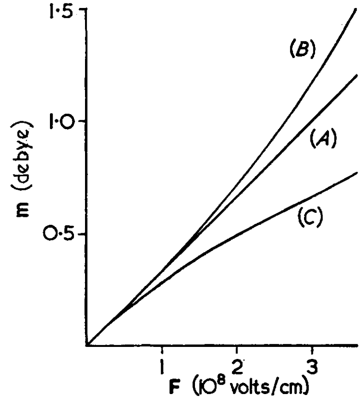

Fig. 1 *Typical dependences of the induced moment* **m** *on electric field strength* **F**. *Values of* α, β, γ (*in e.s.u.*) *are, respectively: curve* (*A*) $+ 10^{-24}$, 0, 0; *curve* (*B*) $+ 10^{-24}$, 0, $+ 10^{-36}$; *curve* (*C*) $+ 10^{-24}$, $- 10^{-30}$, $+ 10^{-36}$.

$\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and $\boldsymbol{\gamma}$ in eqn. (2). Other varieties of hyperpolarisability, describing the distortion of molecules by magnetic fields and electric field-gradients,[1] exist but these are not considered in this Review.

Quantitative calculations of the magnitude of γ were first made by Sewell[2] for atomic hydrogen, and by Coulson, Maccoll, and Sutton,[3] who referred to earlier suggestions that eqn. (1) might fail at high field strengths. Allowances for hyperpolarisabilities have been incorporated in theories of a number of physical effects, including electric birefringence (the Kerr effect),[4,5] dielectric saturation,[6,7] depolarisation of scattered light,[8,9,10] the pressure-dependence of molar refractivity,[11,12] and intermolecular forces.[13] The topic has been surveyed briefly by Le Fèvre.[14]

The development of lasers has recently brought into prominence the subject of 'non-linear optics'. Here hyperpolarisabilities play an important rôle since they are responsible for the phenomenon of optical harmonic generation (frequency doubling and trebling) and other associated effects. There are several reviews of this rapidly expanding subject.[15–18a]

In this Review we discuss the properties and measurement of hyperpolarisabilities and attempt to suggest future lines of research in this field.

2 Properties of Hyperpolarisabilities

A. Symmetry Properties.—Equation (2) can be rewritten in Cartesian tensor notation:

$$m_\alpha = \alpha_{\alpha\beta}F_\beta + \tfrac{1}{2}\beta_{\alpha\beta\gamma}F_\beta F_\gamma + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \ \ldots \tag{3}$$

where m_α is the α-component of $\mathbf{m}$, $\alpha_{\alpha\beta}$ the $\alpha\beta$-component of α, and so on; the Greek suffixes denote Cartesian components, and a repeated suffix implies a summation over the X, Y, and Z components.[19] It may be assumed that the

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[1] A.D. Buckingham, *Quart. Rev.*, 1959, **13**, 183; *Chem. in Britain*, 1965, **1**, 54.

[2] G. L. Sewell, *Proc. Cambridge Phil. Soc.*, 1949, **45**, 678.

[3] C. A. Coulson, A. Maccoll, and L. E. Sutton, *Trans. Faraday Soc.*, 1952, **48**, 106.

[4] A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc.*, 1955, *A*, **68**, 905.

[5] S. Kielich, *Acta Phys. Polon.*, 1958, **17**, 239.

[6] A. D. Buckingham, *J. Chem. Phys.*, 1956, **25**, 428.

[7] S. Kielich and A. Piekara, *J. Chem. Phys.*, 1958, **29**, 1297; *Acta Phys. Polon.*, 1959, **18**, 439.

[8] A. D. Buckingham and M. J. Stephen, *Trans. Faraday Soc.*, 1957, **53**, 884.

[9] A. L. Andrews and A. D. Buckingham, *Mol. Phys.*, 1960, **3**, 183.

[10] S. Kielich, *Acta Phys. Polon.*, 1960, **19**, 149; 1963, **23**, 321, 819.

[11] A. D. Buckingham, *Trans. Faraday Soc.*, 1956, **52**, 747.

[12] S. Kielich, *Acta Phys. Polon.*, 1962, **22**, 477.

[13] A. D. Buckingham, *Discuss. Faraday Soc.*, 1965, no. 40, 232.

[14] R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

[15] P. A. Franken and J. F. Ward, *Rev. Mod. Phys.*, 1963, **35**, 23.

[16] N. Bloembergen, *Proc. I.E.E.E.*, 1963, **51**, 124; 'Nonlinear Optics', Benjamin, New York, 1965.

[17] R. W. Terhune, *Solid State Design*, 1963, **4**, 38; R. W. Terhune and P. D. Maker, in a review entitled 'Nonlinear Optics', *Prog. in Lasers*, vol. II, in the press.

[18] P. S. Pershan, *Progress in Optics*, 1966, **5**, 85.

[18] (*a*) J. A. Giordmaine, *Scientific American*, 1964, **210** (4), 38.

[19] H. Jeffreys, 'Cartesian Tensors', Cambridge Univ. Press, 1931; G. Temple, 'Cartesian Tensors', Methuen, London, 1960.

Table 1 *Symmetry properties of hyperpolarisabilities*

Symmetry group	*Examples*	*Non-zero components of* $\boldsymbol{\beta}$	*Non-zero components of* $\boldsymbol{\gamma}$
Spherical	He, Na^+	None	$\gamma_{1111} = \gamma_{2222} = \gamma_{3333} = 3\gamma_{1122} = 3\gamma_{2233} = 3\gamma_{3311}$
$D_{\infty h}$	H_2, CO_2	None	$\gamma_{1111} = \gamma_{2222} = 3\gamma_{1122}$; $\gamma_{1133} = \gamma_{2233}$; γ_{3333}
$C_{\infty v}$	HCl, N_2O	$\beta_{113} = \beta_{223}$; β_{333}	$\gamma_{1111} = \gamma_{2222} = 3\gamma_{1122}$; $\gamma_{1133} = \gamma_{2233}$; γ_{3333}
D_{3h}	BF_3, cyclopropane	$\beta_{111} = -\beta_{122}$	$\gamma_{1111} = \gamma_{2222} = 3\gamma_{1122}$; $\gamma_{1133} = \gamma_{2233}$; γ_{3333}
C_{3v}	NH_3, CH_3Cl	$\beta_{111} = -\beta_{122}$; $\beta_{113} = \beta_{223}$; β_{333}	$\gamma_{1113} = \gamma_{2222} = 3\gamma_{1122}$; $\gamma_{1113} = -\gamma_{1223}$; $\gamma_{1133} = \gamma_{2233}$; γ_{3333}
C_{2v}	H_2O, CH_2Cl_2	β_{113}; β_{223}; β_{333}	γ_{1111}; γ_{2222}; γ_{1122}; γ_{1133}; γ_{2233}; γ_{3333}
T_d	CH_4	β_{123}	$\gamma_{1111} = \gamma_{2222} = \gamma_{3333}$; $\gamma_{1122} = \gamma_{2233} = \gamma_{3311}$
O_h	SF_6	None	$\gamma_{1111} = \gamma_{2222} = \gamma_{3333}$; $\gamma_{1122} = \gamma_{2233} = \gamma_{3311}$

tensors $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, and $\gamma_{\alpha\beta\gamma\delta}$ are symmetric in all suffixes, that is, $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$, $\beta_{\alpha\beta\gamma} = \beta_{\gamma\beta\alpha} = \beta_{\beta\gamma\alpha} = \beta_{\alpha\gamma\beta} = \beta_{\gamma\alpha\beta} = \beta_{\beta\alpha\gamma}$, and $\gamma_{\alpha\beta\gamma\delta} = \gamma_{\delta\gamma\beta\alpha}$, etc. This is strictly valid for static fields **F**; for optical fields, the influence of dispersion may invalidate the assumption.[15] However it represents a reasonable approximation as long as the frequencies of the optical fields are not close to absorption bands (see Section 5).

The number of independent constants required to specify the tensors $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ for various molecular symmetries has been tabulated,[8] and a group-theoretical study of $\boldsymbol{\beta}$ has recently been reported.[20] The non-zero components of $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ for several symmetries are listed in Table 1, where symmetry groups are described in the Schönflies notation.[21] The subscripts 1, 2, 3 refer to molecular axes, the assignment of which is illustrated in Figure 2. For the groups $D_{\infty h}$, $C_{\infty v}$, D_{3h}, C_{3v}, and C_{2v}, the 3-axis is along the major axis of rotation and the 13-plane coincides with a plane of symmetry. For the group T_d, the axes 1, 2, 3 are the edges of the cube containing the tetrahedron. It can be shown that all components of $\boldsymbol{\beta}$ are zero for molecules possessing a centre of inversion, and that all polar molecules have a non-vanishing $\boldsymbol{\beta}$. The second hyperpolarisability $\boldsymbol{\gamma}$ is not subject to the same symmetry restrictions, and is non-zero for all atoms and molecules.

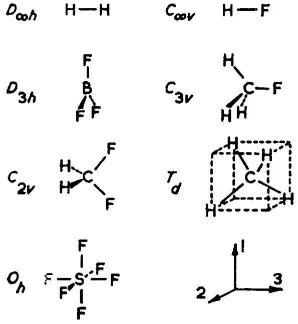

Fig. 2 *Symmetry notation and designation of molecular axes for typical molecules*

For any molecule, the *mean* first hyperpolarisability can be defined as

$$\beta = \frac{3}{5}(\beta_{113} + \beta_{223} + \beta_{333}) \tag{4}$$

and the first hyperpolarisability *anisotropy* as

$$\Delta\beta = \beta_{333} - \frac{3}{2}\beta_{113} - \frac{3}{2}\beta_{223} \tag{5}$$

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[20] S. J. Cyvin, J. E. Rauch, and J. C. Decius, *J. Chem. Phys.*, 1965, **43**, 4083.

[21] A useful tabulation of symmetry symbols and elements is to be found in 'Tables of Interatomic Distances and Configuration in Molecules and Ions', *Chem. Soc. Special Publ.* No. 11, ed. L. E. Sutton *et al.*, 1958, pp. 18-26.

where the 3-axis is that of the permanent dipole. The parameters β and $\Delta\beta$ specify completely the tensor $\boldsymbol{\beta}$ of a molecule with $C_{\infty v}$ symmetry. For C_{3v} symmetry, β_{111} completes the specification of $\boldsymbol{\beta}$, and for C_{2v} an additional parameter is $(\beta_{113} - \beta_{223})$.

The mean second hyperpolarisability can be defined as

$$\gamma = \frac{1}{5}\gamma_{\alpha\alpha\beta\beta} = \frac{1}{5}(\gamma_{1111} + \gamma_{2222} + \gamma_{3333} + 2\gamma_{1122} + 2\gamma_{2233} + 2\gamma_{3311}) \qquad (6)$$

which completely specifies $\boldsymbol{\gamma}$ for a spherical system. For lower symmetries, additional anisotropy parameters would be required.

B. The Bond-additivity Approximation.—The usefulness of a bond-additivity scheme for molecular polarisability $\boldsymbol{\alpha}$ is well established,[14] and it is reasonable to suggest an analogous approximation for hyperpolarisabilities. This approximation should, however, be applied with caution, since the molecular internal field at a particular bond could cause deviations from additivity.

For a molecule with N bonds, the approximation for $\boldsymbol{\beta}$ can be written in the form

$$\beta_{\alpha\beta\gamma} = \sum_{i=1}^{N} \beta^{(i)}_{\alpha\beta\gamma}.$$

If the ith bond is symmetric about its axis, $\beta^{(i)}_{\alpha\beta\gamma}$ can be expressed in terms of its mean and its anisotropy:

$$\beta^{(i)}_{\alpha\beta\gamma} = \left(\frac{1}{3}\beta^{(i)} - \frac{1}{5}\Delta\beta^{(i)}\right)\left(l_\alpha{}^{(i)}\delta_{\beta\gamma} + l_\beta{}^{(i)}\delta_{\gamma\alpha} + l_\gamma{}^{(i)}\delta_{\alpha\beta}\right) + \Delta\beta^{(i)} l_\alpha{}^{(i)} l_\beta{}^{(i)} l_\gamma{}^{(i)} \qquad (7)$$

where $l_\alpha{}^{(i)}$ is the cosine of the angle between the axis of the ith bond and the α-direction. The substitution tensor $\delta_{\alpha\beta}$ equals unity if $\alpha = \beta$ and is zero otherwise.[19]

To illustrate the usefulness of the bond model, consider a series of substituted methanes with tetrahedral bond angles. The only non-zero component of $\boldsymbol{\beta}$ for CX_4 is

$$\beta_{123}(CX_4) = (4/3\sqrt{3})\,\Delta\beta_{C-X} \qquad (8)$$

where $\Delta\beta_{C-X}$ is the anisotropy of $\boldsymbol{\beta}$ for a C–X bond. For CY_3X, which has C_{3v} symmetry

$$\beta(CY_3X) = \beta_{C-X} - \sqrt{3}\beta_{C-Y} \qquad (9)$$

$$\Delta\beta(CY_3X) = \Delta\beta_{C-X} + (2/\sqrt{3})\,\Delta\beta_{C-Y} \qquad (10)$$

$$\beta_{111}(CY_3X) = (1/\sqrt{6})\,\Delta\beta_{C-Y} \qquad (11)$$

The molecule CY_2X_2 has C_{2v} symmetry, and

$$\beta(CY_2X_2) = (2/\sqrt{3})\,(\beta_{C-X} - \beta_{C-Y}) \qquad (12)$$

$$\Delta\beta(\mathrm{CY_2X_2}) = -(4/3\surd 3)\,(\Delta\beta_{\mathrm{C-X}} - \Delta\beta_{\mathrm{C-Y}}) \tag{13}$$

$$(\beta_{113} - \beta_{223})\,(\mathrm{CY_2X_2}) = (4/3\surd 3)\,(\Delta\beta_{\mathrm{C-X}} + \Delta\beta_{\mathrm{C-Y}}) \tag{14}$$

The application of the bond-additivity approximation to γ, defined in eqn. (6), is even more straightforward, since γ is independent of the bond directions. Hence for a substituted methane $\mathrm{CY}_n\mathrm{X}_{4-n}$, where n can take values from 0 to 4

$$\gamma(\mathrm{CY}_n\mathrm{X}_{4-n}) = n\gamma_{\mathrm{C-Y}} + (4-n)\gamma_{\mathrm{C-X}} \tag{15}$$

The parameters $\gamma_{\mathrm{C-Y}}$ and $\gamma_{\mathrm{C-X}}$ can be evaluated from γ for $\mathrm{CY_4}$ and $\mathrm{CX_4}$. Bond-additivity rules could also be stated for the anisotropic components of $\boldsymbol{\gamma}$.

Applications of the bond-additivity approximation are mentioned in subsequent sections.

C. An Electrostatic Model.—It is easy to understand qualitatively why a molecule should have a second hyperpolarisability γ, since each of its component atoms has a non-vanishing γ. In the case of β, however, the isolated atoms do not possess a β,[22] so that, like the dipole moment, it must arise from interactions within the molecule. In order to investigate this, a simple electrostatic model of a polar diatomic molecule such as HCl is now considered.

The model consists of a pair of oppositely charged spheres A (charge $-q$) and B (charge $+q$) with centres separated by the internuclear distance R of the molecule which they represent, as illustrated in Figure 3. It is assumed that the polarisability α^{A} and second hyperpolarisability γ^{A} of A are much greater than those of B, which are negligible. Such a model might represent HCl, but it would be a poor representation of CO, where the two atoms are of comparable size. The charge q of B produces an internal field $F = -qR^{-2}$ along the 3-axis at A. From consideration of the two situations in which a uniform external electric field is applied parallel and perpendicular to the 3-axis, the two com-

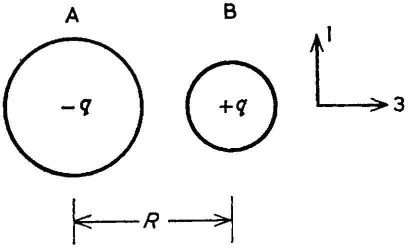

Fig. 3 *Electrostatic model of a polar diatomic molecule*

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[22] The excited H atom is an exception, for spatial degeneracy leads to energy terms in odd powers of the electric field strength; see E. U. Condon and G. H. Shortley, 'Theory of Atomic Spectra', Cambridge University Press, 1935, ch. XVII.

ponents of $\boldsymbol{\beta}$ emerge as $\beta_{333} = \gamma^{A}F$ and $\beta_{311} = \frac{1}{3}\gamma^{A}F$. Hence the first hyperpolarisability of the model arises from the internal field F and the second hyperpolarisabilities of the component atoms. The anisotropy $\Delta\beta$ of the model is zero and, when reasonable numerical parameters (q = *ca.* 10^{-10} e.s.u., R = *ca.* 10^{-8} cm., γ^{A} = *ca.* 10^{-36} e.s.u.) are inserted, the mean hyperpolarisability β of a molecule such as HCl should be *ca.* -10^{-30} e.s.u. A negative sign for β_{333} implies that an external field acting along the dipole (from $-$ to $+$) induces a moment (proportional to the square of its strength) which is *opposed* to the permanent moment. Similarly a negative β_{311} implies that a field perpendicular to the axis induces a dipole component antiparallel to the permanent moment.

3 Determination of First Hyperpolarisabilities

Information concerning the first hyperpolarisability $\boldsymbol{\beta}$ of a number of simple molecules has been obtained by a variety of methods. Mean hyperpolarisabilities and other parameters are listed in Table 2. It should be stressed that some of the values are tentative. The methods by which the results have been obtained are discussed below.

A. Quantum Mechanical Calculations.—Third-order perturbation theory[13] for a molecule in a uniform static electric field gives, for the ground state,

$$\beta_{\alpha\beta\gamma} = S\sum_{i,j\neq 0} \frac{<\psi_0|\mu_\alpha|\psi_i><\psi_i|\mu_\beta|\psi_j><\psi_j|\mu_\gamma|\psi_0>}{(W_i - W_0)\,(W_j - W_0)}$$
$$- S\sum_{i\neq 0} \frac{<\psi_0|\mu_\alpha|\psi_0><\psi_0|\mu_\beta|\psi_i><\psi_i|\mu_\gamma|\psi_0>}{(W_i - W_0)^2} \qquad (16)$$

where S denotes a sum of all permutations of the subsequent vector components, W_0 and W_i are the unperturbed energies of the ground and ith states (ψ_0 and ψ_i) of the system, and μ_α is the α-component of the electric dipole operator. Matrix elements $<\psi_i|\mu_\alpha|\psi_j>$ have been written in the Dirac bracket notation.

Approximate quantum mechanical calculations have been carried out[8] for methane, using eqn. (16), to yield $\beta_{123} = -0{\cdot}21 \times 10^{-30}$ e.s.u. Estimates of β and $\Delta\beta$ for a number of polar diatomic molecules have recently been obtained from Hartree–Fock wave functions.[22a]

B. Second Harmonic Scattering.—When a very intense beam of light, such as that produced by a pulsed ruby laser, passes through a fluid composed of molecules lacking inversion symmetry, a small fraction of the light is scattered at a frequency twice that of the incident radiation. The origin of the scattering may be understood in terms of a simple classical treatment (more rigorous theories have been given by Kielich,[23] Bersohn, Pao, and Frisch,[23a] and others). If the incident radiation, propagating along the X-direction in space, is polarised with

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[22] (*a*) J. M. O'Hare and R. P. Hurst, *J. Phys. Chem.*, 1967, **46**, 2356.
[23] S. Kielich, *Bull. acad. polon. Sci.*, 1964, **12**, 53.
[23] (*a*) R. Bersohn, Y.-H. Pao, and H. L. Frisch, *J. Chem. Phys.*, 1966, **45**, 3184.

Table 2 *Values of first hyperpolarisability parameters*

Molecule	$10^{30}\beta$(*e.s.u.*)[a]	*Other parameters*	*Source*	*Ref.*[b]
CH_4	0	$10^{30}\beta_{123} \simeq -0{\cdot}21$ e.s.u.	Approximate quantum mechanical calculations	8
CH_4	0	$10^{30}\lvert\beta_{123}\rvert \simeq 0{\cdot}01$ e.s.u.	Second harmonic scattering of gas	25
CCl_4	0	$10^{30}\lvert\beta_{123}\rvert < 0{\cdot}03$ e.s.u.	Second harmonic scattering of gas	26
CH_3F	(−2)	—	Refractivity virial data	32
CH_3Cl	(−8)	—	Refractivity virial data	32
NH_3	(−7)	—	Refractivity virial data	32
SO_2	(−12)	—	Refractivity virial data	32
CH_2Cl_2	-7 ± 2	—	Kerr effect of dilute solutions	*R*
CH_2Br_2	-12 ± 2	—	Kerr effect of dilute solutions	*R*
CH_2I_2	-16 ± 4	—	Kerr effect of dilute solutions	*R*
$CH_2(CN)_2$	-8 ± 2	—	Kerr effect of dilute solutions	*R*
$O(CH_3)_2$	(−5)	—	Kerr effect of dilute solutions	*R*
$CHCl_3$	(+26)	$10^{30}\Delta\beta \simeq 0$ (assumed)	Rayleigh scattering of liquid	8, *R*

[a] Values in parentheses are approximate only; [b] Reference numbers refer to those in the text. *R* denotes this Review.

its electric vector in the Z-direction, then eqn. (3) shows that an oscillating dipole moment with frequency 2ω is produced by the electric field $F_0 \cos \omega t$ of the radiation. The amplitude of the α-component of this oscillating dipole is $\frac{1}{4}\beta_{\alpha zz}F_0{}^2$. Now, according to classical radiation theory, the intensity of light scattered from the medium is proportional to the mean square oscillating dipole moment. The depolarisation ratio for second harmonic scattering, defined as the ratio of the intensity S_x of light of frequency 2ω scattered in the Y-direction and polarised in the X-direction to the intensity S_z of that polarised in the Z-direction, is

$$\rho_0(2\omega) = S_x/S_z = \frac{<\beta_{xzz}\beta_{xzz}>}{<\beta_{zzz}\beta_{zzz}>} \tag{17}$$

where the angular brackets denote an average over all orientations in space of a molecule of the scattering medium, provided that there is no correlation between the positions and orientations of the molecules. Evaluation of the average by use of standard methods[9] gives

$$\rho_0(2\omega) = (8\xi^2 + 7)/(12\xi^2 + 63) \tag{18}$$

where $\xi^2 = (5\beta_{\alpha\beta\gamma}\beta_{\alpha\beta\gamma} - 3\beta_{\alpha\beta\beta}\beta_{\alpha\gamma\gamma})/2\beta_{\alpha\beta\beta}\beta_{\alpha\gamma\gamma}$

In the case of molecules with symmetries T_d and D_{3h} it follows that $\rho_0(2\omega)$ equals $\frac{2}{3}$.[20] For molecules with $C_{\infty v}$ symmetry, $\xi^2 = 9(\Delta\beta)^2/25\beta^2$. Corresponding relations can be obtained for molecules of other symmetries. Expressions can also be written for the individual scattered intensities S_x and S_z, which are proportional to $(2\omega)^4$ and to the square of the intensity of the incident radiation.

Few second harmonic scattering results have so far been reported; the experiment was first described in 1965 by Terhune, Maker, and Savage,[24] who examined several liquids. Recent measurements[25] of the total scattered intensity $(S_z + S_x)$ indicate that $|\beta_{123}|$ for gaseous methane is *ca.* 10^{-32} e.s.u., with an estimated experimental uncertainty of a factor of three. This differs considerably from the approximate theoretical estimate[8] of $-2{\cdot}1 \times 10^{-31}$ e.s.u. (Section 3A). Absolute intensity measurements on carbon tetrachloride as a liquid[24] give $|\beta_{123}| = 3{\cdot}5 \times 10^{-31}$, an interaction-free model of the liquid being assumed. However, in recent experiments[26] no second harmonic scattering could be observed from carbon tetrachloride in the vapour phase, from which it has been deduced that $|\beta_{123}|$ is less than 3×10^{-32} e.s.u., and the comparatively strong scattering from the liquid has been attributed to intermolecular interactions. This is supported by the fact that $\rho_0(2\omega)$ observed for liquid CCl_4 is $0{\cdot}34 \pm 0{\cdot}03$, whereas that expected for isolated tetrahedra is 2/3.[23a] The difference between the observed magnitudes of second harmonic scattering from liquid and vapour is surprisingly large; some of the discrepancy may be due to uncertainties in the measured intensities of the scattered beam and of the focused laser. Second harmonic

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[24] R. W. Terhune, P. D. Maker, and C. M. Savage, *Phys. Rev. Letters*, 1965, **14**, 681.

[25] P. D. Maker, to be published.

[26] P. D. Maker, personal communication.

scattering from water and acetonitrile has also been measured,[24] and depolarisation ratios of 0·12 ± 0·01 and 0·10 ± 0·01 obtained. Detailed analysis of these results is not justified, in view of the uncertainties associated with interpreting harmonic scattering by liquids, but the qualitative conclusion that the parameter ξ^2 is *ca.* 10^{-2} or less may be drawn in both cases. This implies that, for H_2O, $|\beta|$ is at least an order of magnitude greater than $|\Delta\beta|$ and $|(\beta_{113} - \beta_{223})|$; likewise for CH_3CN, $|\beta|$ is apparently much greater than $|\Delta\beta|$ and $|\beta_{111}|$.

The bond-additivity approximation (Section 2B) shows that β_{123} for a tetrahedral molecule is proportional to, and of the same order as, $\Delta\beta$ for its bonds. The measurements on gaseous CH_4 and CCl_4 therefore indicate that $|\Delta\beta|$ for C–H and C–Cl bonds is *ca.* 10^{-32} e.s.u., which is orders of magnitude less than $|\beta|$ for typical bonds (see Section 3F). The scattering results for the three liquids are in conformity with this difference, as is the model of Section 2C (for which $\Delta\beta/\beta = 0$).

Apart from scattering at frequency 2ω, inelastic scattering at frequencies $(2\omega \pm \omega_t)$, where ω_t is the frequency of a molecular transition, may also occur. A few observations of this second harmonic analogue of the Raman effect have been reported;[24–26] expressions for the intensities of inelastic scattering have been derived,[25] and selection rules deduced from the symmetry properties of $\boldsymbol{\beta}$.[20]

C. Electric Birefringence (the Kerr Effect).—When a uniform electric field is applied to any material it becomes birefringent, causing a beam of plane-polarised light passing through it to emerge elliptically polarised. Measurement of the ellipticity for gases or for solutes at high dilution in non-polar solvents leads to a molar Kerr constant ${}_{\mathrm{m}}K$, characteristic of the molecules of the gas or solute. It has been shown[4] by classical statistical mechanics that, provided $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and $\boldsymbol{\gamma}$ are symmetric,

$$
{}_{\mathrm{m}}K = (2\pi N/405)\left\{10\gamma + (1/kT)\left[\frac{20}{3}\mu\beta + 3(\alpha_{\alpha\beta}\alpha_{\alpha\beta}{}^{(0)} - 3\alpha\alpha^{(0)})\right] + (3/k^2T^2)\left[\alpha_{\alpha\beta}\mu_\alpha\mu_\beta - \alpha\mu^2\right]\right\} \tag{19}
$$

where $\alpha_{\alpha\beta}{}^{(0)}$ represents the static polarisability, $\alpha_{\alpha\beta}$ the optical (high frequency) polarisability, μ_α the permanent molecular dipole moment, and α ($= \frac{1}{3}\alpha_{\beta\beta}$) the mean polarisability. For isotropically polarisable molecules (*e.g.*, Ar, CH_4, SF_6), only the temperature-independent term survives (Section 4B). For anisotropic molecules with no permanent dipole moment (*e.g.*, N_2, BF_3, C_6H_6), ${}_{\mathrm{m}}K$ is normally dominated by the second term in T^{-1}. If there is a dipole, the final term, which is proportional to the difference between the polarisability in the dipole direction and α, is generally predominant. However, in certain polar molecules the symmetry is such that this difference is small and the term involving β is dominant. The series of substituted methanes CH_2X_2, where C–X is an axially symmetric polar group, represents such a case.

Molar Kerr constants of three methylene dihalides[27] and of malononitrile

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[27] D. Izsak and R. J. W. Le Fèvre, *J. Chem. Soc.* (*B*), 1966, 102.

(dicyanomethane),[28] measured as solutes at infinite dilution in carbon tetrachloride and benzene, are much more negative than expected from the Langevin–Born theory of the Kerr effect, which neglects hyperpolarisability contributions. A number of rather unattractive explanations of the apparent anomalies have been advanced,[27,28] but when the contributions of β and γ are included experimental and calculated results are readily reconciled. The bond-additivity approximation[14] for α, with the assumption that C–H bonds are isotropically polarisable,[29] gives

$$
\begin{aligned}
{}_{\mathrm{m}}K(\mathrm{CH_2X_2}) = (4\pi N/405)\{&5\gamma + (1/kT)\,[10\mu\beta/3 + 4(\alpha_{33} - \alpha_{11})^2_{\mathrm{C\text{-}X}} \\
&(3\cos^4\phi - 3\cos^2\phi + 1)\,] + (1/k^2T^2)\,\mu^2(\alpha_{33} - \alpha_{11})_{\mathrm{C\text{-}X}} \\
&(3\cos^2\phi - 1)\} \qquad (20)
\end{aligned}
$$

where $(\alpha_{33} - \alpha_{11})_{\mathrm{C\text{-}X}}$ is the C–X bond anisotropy and 2ϕ the XCX bond angle. If 2ϕ is tetrahedral, $\cos^2\phi$ equals $\frac{1}{3}$, and the term in T^{-2} vanishes. In practice, when 2ϕ is not exactly tetrahedral, the T^{-2} term is non-zero but still small in comparison to the T^{-1} terms. Values of μ are known[27,28] and estimates of $(\alpha_{33} - \alpha_{11})_{\mathrm{C\text{-}X}}$ for aliphatic C–X bonds have been reported.[14,28,30] From measurements of γ for CH_4, CCl_4, and CBr_4 (Section 4), and with use of eqn. (15), values of $10^{36}\gamma$ emerge as 15 and 40 e.s.u. for CH_2Cl_2 and CH_2Br_2, respectively; for CH_2I_2 and $CH_2(CN)_2$, $10^{36}\gamma$ may be *ca.* 50 and *ca.* 15 e.s.u. With these data, eqn. (20) can be used to calculate β; the results are in Table 3. Variations in β are particularly pronounced in the case of CH_2Cl_2 and may indicate that β is more sensitive than α to changes in state. Despite the uncertainties, these estimates of β are the most accurate now available for any molecule. Unfortunately, the method is limited to polar molecules in which the T^{-2} term happens to be comparatively small. Another molecule in which this occurs is dimethyl ether, and its β, derived from Kerr effect measurements in carbon tetrachloride,[31] is approximately -5×10^{-30} e.s.u. Temperature studies of ${}_{\mathrm{m}}K$ for selected gaseous polar molecules would increase the precision of β, and experiments of this type are currently being organised in Bristol.

D. Refractivity Virial Data.—The earliest concerted effort to evaluate β experimentally involved the measurement of the pressure-dependence of the molar refraction ${}_{\mathrm{m}}R$ of polar gases,[32] which can be written as a virial-type expansion in the molar volume V:

$$
{}_{\mathrm{m}}R = (n^2 - 1)V/(n^2 + 2) = A_R + B_R/V + C_R/V^2 + \;\ldots \qquad (21)
$$

where n is the refractive index and A_R, B_R, C_R, . . . are the first, second, third, . . . refractivity virial coefficients. The coefficient A_R is $4\pi N\alpha/3$ and B_R is related to the mean contribution to the refraction due to an interacting pair of

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[28] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.*, 1965, 2499.
[29] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273.
[30] R. J. W. Le Fèvre and B. J. Orr, *J. Chem. Soc.*, 1965, 5349; *J. Chem. Soc.* (*B*), 1966, 37.
[31] M. J. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, *J. Chem. Soc.*, 1963, 2886.
[32] A. R. Blythe, J. D. Lambert, P. J. Petter, and H. Spoel, *Proc. Roy. Soc.*, 1960, *A*, **255**, 427.

Table 3 *Calculation of* β *from Kerr effects of* CH_2X_2*-type molecules*

Molecule	2ϕ	*State*[a]	*Temp.*	$10^{12}{}_{\mathrm{m}}K$(*e.s.u.*)	$10^{18}\mu$(*e.s.u.*)	$10^{30}\beta$(*e.s.u.*)	
CH_2Cl_2	112°	CT	25°	−12·7	$1{\cdot}59_5$	− 5·5	− 7 ± 2
		B	25°	−21·0	1·59	− 9·0	
		G	83·5°	−12·1	1·58	− 6·6	
CH_2Br_2	112°	CT	25°	−17·6	1·40	−10·6	−12 ± 2
		B	25°	−23·6	1·41	−13·3	
CH_2I_2	114°	CT	25°	−15·2	1·08	−16·0	−16 ± 4
		B	25°	−14·9	1·08	−15·8	
$CH_2(CN)_2$	114°	B	25°	−72	3·56		− 8 ± 2

[a] CT, B, G indicate respectively that measurements were made on solutions in carbon tetrachloride, solutions in benzene, or the gas. The gas measurement is that of H. A. Stuart, 'Die Struktur des Freienmoleküls', Springer-Verlag, Berlin, 1952.

molecules. In a polar gas, B_R can be related approximately to μ, α, β, and γ.[11] Measurement of B_R, however, involves finding the small difference of two large quantities, so the precision obtained is low. Estimates of β obtained in this way are in Table 2, but they may be unreliable to the extent of an order of magnitude. Similar measurements[33] for triethylamine yielded $\beta = ca. + 10^{-26}$ e.s.u., which is inconsistent with the results in Table 2. Much more precise estimates of B_R might be expected from a 'differential' experimental method, rather than one involving absolute measurement of n as a function of pressure.

E. Rayleigh Scattering by Polar Liquids.—When a beam of unpolarised light passes through a fluid, a fraction of the light is scattered with the same frequency as the incident radiation. This is known as Rayleigh scattering, and its depolarisation ratio is $\rho(\omega)$.[34] A theoretical treatment[8] of depolarisation in polar liquids, using the Onsager model, has yielded information about β for chloroform. However the estimates of the anisotropy of $\boldsymbol{\alpha}$ for $CHCl_3$ used in this calculation are wrong because of an error which has since been corrected.[35] Using correct polarisabilities,[36] the depolarisation ratio of liquid $CHCl_3$,[34] and the Onsager model, $(\beta_{333} - 0{\cdot}8\,\beta_{113})$ is $+18 \times 10^{-30}$ e.s.u. If $\Delta\beta$ is vanishingly small, as seems likely from Section 3B and the bond-additivity model, β is approximately $+26 \times 10^{-30}$ e.s.u. It should be noted that β for $CHCl_3$ is positive, whereas for all the other molecules listed in Table 2 it is negative; this difference in sign may be understood in terms of eqn. (9).

A similar theory due to Kielich, combining the depolarisation ratio and Rayleigh ratio of a polar liquid, has yielded[37] for chloroform $\beta = +203 \times 10^{-30}$ e.s.u. and $\Delta\beta = -267 \times 10^{-30}$. This β is an order of magnitude greater than any of the results in Table 2, and the very large $\Delta\beta$ is inconsistent with other estimates (Section 3B).

F. Comparison of Hyperpolarisability Estimates.—The values of β listed in Table 2 for substituted methanes can readily be analysed in terms of the bond-additivity approximation, by use of eqn. (9) and (12). Table 4 displays values of $(\beta_{C-X} - \beta_{C-H})$ deduced in this way. For CH_3X and CHX_3 it has been assumed that β_{C-H} is vanishingly small.

4 Determination of Second Hyperpolarisabilities

The range of sources from which information about γ has been derived is smaller than that for $\boldsymbol{\beta}$. Estimates of the mean second hyperpolarisability γ for a number of atoms and molecules are listed in Table 5, and the methods employed discussed hereunder.

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[33] D. H. Everett and R. J. Munn, *Trans. Faraday Soc.*, 1963, **59,** 2486.
[34] R. C. C. Leite, R. S. Moore, and S. P. S. Porto, *J. Chem. Phys.*, 1964, **30,** 3741.
[35] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041; R. J. W. Le Fèvre and B. P. Rao, *J. Chem. Soc.*, 1957, 3644.
[36] N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc.*, 1966, *A*, **295,** 334.
[37] S. Kielich, *Acta Phys. Polon.*, 1962, **22,** 299.

Table 4 *Values of hyperpolarisabilities for polar bonds in substituted methanes*

Bond	*Source*	$10^{30}\beta(e.s.u.)^a$	$10^{30}(\beta_{C\text{–}X} - \beta_{C\text{–}H})^a$
C–F	CH_3F	(−2)	$(-2)^b$
C–Cl	CH_3Cl	(−8)	$(-8)^b$
	CH_2Cl_2	− 7 ± 2	− 6 ± 2
	$CHCl_3$	(+ 26)	$(-15)^b$
C–Br	CH_2Br_2	−12 ± 2	−10 ± 2
C–I	CH_2I_2	−16 ± 4	−14 ± 3
C–CN	$CH_2(CN)_2$	− 8 ± 2	− 7 ± 2

[a] Values in parentheses are approximate; [b] Calculated on the assumption that $\beta_{C—H} = ca.\ 0$.

A. Quantum Mechanical Calculations.—For the hydrogen atom, γ has been evaluated exactly by Sewell,[2] giving $10^{36}\gamma = 0{\cdot}6714$ e.s.u. Recent calculations[38] employing a perturbation procedure give, for helium, $10^{36}\gamma = 0{\cdot}0157$ e.s.u., which compares with the experimental result of 0·026 e.s.u.;[38] further calculations currently being carried out at Bristol employ a variational method and are expected to yield an improved theoretical result. Langhoff, Lyons, and Hurst[39] have calculated γ for a variety of *S*-state atoms and ions by a Hartree–Fock perturbation procedure; their estimates for helium, neon, and argon are in reasonable agreement with experiment (see Table 5). Further calculations of γ for several *S*-state atoms have been made by Cohen.[40] For an atom in its ground state ψ_0, the static hyperpolarisability γ is given by fourth-order perturbation theory as

$$\gamma_{\alpha\beta\gamma\delta} = S \sum_{i,j,k \neq 0} \frac{<\psi_0|\mu_\alpha|\psi_i><\psi_i|\mu_\beta|\psi_j><\psi_j|\mu_\gamma|\psi_k><\psi_k|\mu_\delta|\psi_0>}{(W_i - W_0)(W_j - W_0)(W_k - W_0)}$$
$$- S \sum_{i,j \neq 0} \frac{<\psi_0|\mu_\alpha|\psi_i><\psi_i|\mu_\beta|\psi_0><\psi_0|\mu_\gamma|\psi_j><\psi_j|\mu_\delta|\psi_0>}{(W_i - W_0)^2(W_j - W_0)} \qquad (22)$$

where notation is as for eqn. (16). For most systems, γ is positive; for two-level systems, however, the first term in eqn. (22) is zero (provided that the excited state is non-dipolar), so that γ is negative. In their early investigation, Coulson, Maccoll, and Sutton[3] determined the effect of field strength on the mean polarisability of an anisotropic two-level model and found two contributions in F^2; these terms are those which determine the Kerr constant. The temperature-independent contribution, corresponding to γ, was found to be negative, as expected for a two-level system. Mention is made in Section 5 of calculations of γ for hydrogenic and alkali-metal atoms at frequencies close to electronic transitions.

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[38] L. L. Boyle, A. D. Buckingham, R. L. Disch, and D. A. Dunmur, *J. Chem. Phys.*, 1966 **45**, 1318.

[39] P. W. Langhoff, J. D. Lyons, and R. P. Hurst, *Phys. Rev.*, 1966, **148**, 18.

[40] H. D. Cohen, *J. Chem. Phys.*, 1965, **43**, 3558; 1966, **45**, 10.

Table 5 *Values of mean second hyperpolarisabilities*

Molecule	$10^{36}\gamma$(*e.s.u.*)[a]	*Source*[b]	*Ref.*	*Molecule*	$10^{36}\gamma$(*e.s.u.*)[a]	*Source*[b]	*Ref.*
H	0·6714	C	2	Xe	(4·0)	G	41
He	0·026	G	38	CH_4	2·6	G	*c*
He	(0·016)	C	38	CCl_4	(12)	L	*d*
He	(0·026)	C	39				
Ne	(0·055)	G	41	CCl_4	(28)	S	*e*
Ne	(0·062)	C	39	CBr_4	(78)	S	*d*
Ar	(0·73)	G	41, *c*	$C(NO_2)_4$	(32)	S	*f*
Ar	(1·16)	C	39	CS_2	(54)	L	42
Kr	(1·6)	G	41	Mesitylene	(85)	L	42

[a] Values in parentheses are approximate or preliminary results; [b] The symbol C indicates that γ was obtained by quantum mechanical calculation; G, L, and S refer to experimental determination in gas, liquid, and solution phases, respectively; [c] E. Kuss and H. A. Stuart, *Phys. Z.*, 1941, **42**, 95; [d] C. G. Le Fèvre, R. J. W. Le Fèvre, and D. A. A. S. N. Rao, *J. Chem. Soc.*, 1956, 708; [e] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041; [f] C. G. Le Fèvre, R. J. W. Le Fèvre, and M. R. Smith, *J. Chem. Soc.*, 1958, 16.

B. Electric Birefringence (the Kerr Effect).—The most important source of information about γ has been the Kerr effect. For non-interacting isotropic molecules, $_{\mathrm{m}}K$ is directly proportional to γ (see eqn. 19):

$$_{\mathrm{m}}K = (4\pi N/81)\,\gamma = (9{\cdot}34 \times 10^{22})\,\gamma \qquad (23)$$

The use of a phase-sensitive detection system and a gas laser light source has recently enabled hyperpolarisabilities as small as that of helium to be determined accurately from the Kerr effect.[38,41] Earlier evaluations of γ from the Kerr effect have been mentioned by Le Fèvre.[14] From eqn. (19), it can be seen that γ for non-spherical systems is determinable, at least in principle, from studies of the temperature-dependence of $_{\mathrm{m}}K$. Approximate values of γ for carbon disulphide and mesitylene have been obtained in this way;[42] the reliability of these estimates has, however, been questioned.[14] Temperature studies of the Kerr effect for a number of non-polar gases and vapours, currently being undertaken in Bristol, should provide additional information about γ. Measurements of the Kerr effect of solids, in which molecules are not free to be oriented by the applied field, might also yield estimates of γ; however, suitable experimental results are not available.

5 Hyperpolarisabilities at Optical Frequencies

A. Frequency-dependence of β and γ.—In the foregoing discussion it has been assumed that hyperpolarisabilities possess symmetry properties and magnitudes which are independent of frequency. Detailed quantum mechanical theory of the frequency-dependence of hyperpolarisabilities has been formulated, with use of time-dependent perturbation theory.[43,15,44] If the frequencies of all the optical fields impinging on the hyperpolarisable system are much smaller than those of the significant absorption bands, β and γ are approximately symmetric in the Cartesian suffixes $\alpha, \beta, \gamma, \ldots$[15] This is supported by second-harmonic generation experiments on piezoelectric solids.[45] The frequency-dependence of γ is further complicated by resonance at the difference frequencies of the optical fields involved.[17]

B. Non-linear Optical Effects.—A number of the experiments which have been performed in the new field of non-linear optics involve hyperpolarisabilities; all the physical effects discussed in Sections 3 and 4 may be classed as non-linear optical effects.[15,17,44] The hyperpolarisability β gives rise to the following non-linear phenomena: second-harmonic generation by solids,[15,17] second harmonic scattering by fluids[24,25] (Section 3B), optical rectification,[15] two-wave mixing,[17] and the linear electro-optic (Pockels) effect.[15] Non-linear effects in which γ is

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[41] D. A. Dunmur, D. Phil. Thesis, Oxford, 1965.

[42] A. D. Buckingham and R. E. Raab, *J. Chem. Soc.*, 1957, 2341.

[43] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, *Phys. Rev.*, 1962, **127**, 1918.

[44] J. F. Ward, *Rev. Mod. Phys.*, 1965, **37**, 1. B. J. Orr and J. F. Ward, to be published.

[45] R. C. Miller, *Phys. Rev.*, 1963, **131**, 95.

involved include third harmonic generation,[17,46] electric-field-induced second harmonic generation,[46] the Kerr effect[4] (Section 3C), intensity-dependent refractive index,[46,47] and three-wave mixing.[46] For a number of these phenomena only macroscopic susceptibilities, characteristic of the bulk medium, have been evaluated; their interpretation in terms of molecular hyperpolarisabilities may be complicated by co-operative effects.

The frequency-dependence of $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ can conveniently be represented in a notation[44,46] in which a dipole oscillating at frequency ω_1 induced by electric fields $\mathbf{F}(\omega_i)$ of frequency ω_i is:

$$m_\alpha(\omega_1) = \alpha_{\alpha\beta}(-\omega_1,\omega_1)\, F_\beta(\omega_1) + \kappa\beta_{\alpha\beta\gamma}(-\omega_1,\omega_2,\omega_3)\, F_\beta(\omega_2)\, F_\gamma(\omega_3) + \lambda\gamma_{\alpha\beta\gamma\delta}(-\omega_1,\omega_2,\omega_3,\omega_4)\, F_\beta(\omega_2)\, F_\gamma(\omega_3)\, F_\delta(\omega_4) \qquad (24)$$

The sign attached to a frequency is positive if the appropriate photon is absorbed and negative if it is emitted. The sums of the frequencies attached in parentheses to the tensors are zero, so in $\boldsymbol{\beta}(-\omega_1,\omega_2,\omega_3)$ and $\boldsymbol{\gamma}(-\omega_1,\omega_2,\omega_3,\omega_4)$ it is necessary that ω_1 equals $(\omega_2 + \omega_3)$ and $(\omega_2 + \omega_3 + \omega_4)$, respectively. The numbers κ and λ take particular values for each non-linear process, according to the number of frequencies which are equal or zero.[44] For example, $\kappa = 1/4$ if $\omega_2 = \omega_3$ and $\lambda = 1/24$ if $\omega_2 = \omega_3 = \omega_4$; $\kappa = 1/2$ and $\lambda = 1/6$ if all frequencies are zero. Thus the tensor for second harmonic generation is $\beta_{\alpha\beta\gamma}(-2\omega,\omega,\omega)$, which is symmetric in the suffixes $\beta\gamma$. Those appropriate to the Kerr effect are $\alpha_{\alpha\beta}(-\omega,\omega)$, $\beta_{\alpha\beta\gamma}(-\omega,\omega,0)$, and $\gamma_{\alpha\beta\gamma\delta}(-\omega,\omega,0,0)$, which are symmetric in $\alpha\beta$; γ is also symmetric in $\gamma\delta$.

Recently, calculations have been made of $\boldsymbol{\gamma}(-\omega,\omega,0,0)$ for hydrogenic atoms[48] and alkali-metal vapours[49,50] at frequencies ω close to electronic absorption bands, using formulae derived by double perturbation theory.[51] The results for sodium vapour in the vicinity of the D-lines are found[50] to be in satisfactory agreement with the early experiments of Kopfermann and Ladenburg.[52]

6 Conclusion

This Review has dealt with two new electronic properties of molecules, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$. As fundamental constants determining the distortion of a molecule by a strong electric field, they are intimately connected with intermolecular forces, electronic interactions within molecules, and chemical reactivity.[3,14] But quite apart from these applications, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are of interest in themselves, for they provide new information about the electronic structure of the molecule; presumably they are particularly sensitive to the precise nature of the outer reaches of electronic wave-functions.

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[46] P. D. Maker and R. W. Terhune, *Phys. Rev.*, 1965, **137**, 801.

[47] A. D. Buckingham, *Proc. Phys. Soc.*, 1956, *B*, **69**, 344; G. Mayer and F. Gires, *Compt. rend.*, 1964, **258**, 2039; M. Paillette, *Compt. rend.*, 1966, **262**, 264.

[48] L. L. Boyle and C. A. Coulson, *Proc. Phys. Soc.*, 1966, **89**, 499.

[49] L. L. Boyle and C. A. Coulson, *Mol. Phys.*, 1966, **11**, 165.

[50] M. P. Bogaard, A. D. Buckingham, and B. J. Orr, *Mol. Phys.*, 1967, in the press.

[51] A. D. Buckingham, *Proc. Roy. Soc.*, 1962, *A*, **267**, 271.

[52] H. Kopfermann and R. Ladenburg, *Ann. Physik*, 1925, **78**, 659.

Much of the information now available about β and γ should find application in assessing hyperpolarisability contributions to the Kerr effect, thereby increasing the reliability of a well-established method of structural analysis.[14] The constants β and γ are also at the heart of some of the important new non-linear optical effects; it has been suggested that optical harmonic generation could be used in characterising macromolecules[53,23a] and in studying molecular interactions in liquids.[23a,24]

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[53] R. Bersohn, *J. Amer. Chem. Soc.*, 1964, **86**, 3505.