Appl. Phys. B 41, 169–172 (1986)

Applied Physics B Photophysics and Laser Chemistry

Theoretical Investigation of Kleinman Symmetry in Molecules

G. Wagnière

Institute of Physical Chemistry, University, Winterthurerstrasse 190,
CH-8057 Zürich, Switzerland

Received 7 July 1986/Accepted 2 August 1986

Abstract. From measurements of the electric-field-induced second-harmonic generation with different polarizations of incident light, direct information should be obtainable on the extent to which Kleinman symmetry is obeyed in single molecules.

PACS: 31.20, 42.65

Kleinman's symmetry rule was originally derived by thermodynamic arguments as a macroscopic property of crystals [1]. It should apply to such quantities as the susceptibility for the Pockels effect $\chi^{(2)}(\omega; 0, -\omega)$, or for second-harmonic generation $\chi^{(2)}(2\omega; -\omega, -\omega)$. It states that, far removed from resonances and in the absence of strong dispersion, the respective tensor components related to each other by the interchange of indices should be equal:

$$\chi^{(2)}_{ijk} = \chi^{(2)}_{jik}, \quad \text{etc.} \tag{1}$$

Kleinman's symmetry rule should also be valid for single molecules, as was pointed out by Franken and Ward [2]. If one looks at the quantum mechanical expression for the susceptibility for sum frequency generation [3] $\chi^{(2)}(\omega_1+\omega_2; -\omega_1, -\omega_2)$, one indeed notices that for $\omega_1=\omega_2=\omega$, and in the limit $\omega \to 0$, the predicted equality is attained.

Many investigations of this topic have been carried out on crystals, particularly inorganic crystals [4, 5]. To obtain information on single molecules, dc electric-field-induced second-harmonic generation in gases or liquids has been often applied. Intermolecular interactions are then, to a large extent, averaged out. Beside experimental difficulties, the drawback of the method is that it does not provide data on particular tensor elements but merely gives an average of the hyperpolarizability tensor. The aim of this note is to point out that by changing the polarization of incident light, one should nevertheless be able to assess the extent to which Kleinman symmetry is fulfilled in single molecules. From this point of view it should be interesting to study the dependence of the efficiency of second-harmonic generation on the frequency of incident light, in particular, the expected deviations from Kleinman symmetry as one approaches two-photon resonances.

1. Polarization Effects

The theoretical foundations of dc electric field-induced second harmonic generation have been worked out some time ago [3, 4, 6–9]. We are here interested in the effect due to anisotropic averaging, arising from the interaction of the permanent electric dipole moment $\boldsymbol{\mu}_0$ of the molecule with the static field. We rederive relevant quantities in a formulation as compact and general as possible and in a manner convenient for our purposes. The corresponding part of the induced electric polarization $\mathbf{p}^{(3)}_-$ in the molecule is written, to first order in the static electric field ${}^0\mathbf{E}$:

$$\begin{aligned} \boldsymbol{p}^{(3)}_- &= \langle \exp(\boldsymbol{\mu}_0 \cdot {}^0\mathbf{E}/kT)\boldsymbol{\mu}(\boldsymbol{\mu}' \cdot {}^1\mathbf{E}_-)(\boldsymbol{\mu}'' \cdot {}^2\mathbf{E}_-)\rangle \\ &= \langle \boldsymbol{\mu}(\boldsymbol{\mu}' \cdot {}^1\mathbf{E}_-)(\boldsymbol{\mu}'' \cdot {}^2\mathbf{E}_-)\rangle \\ &\quad + (kT)^{-1}\langle(\boldsymbol{\mu}_0 \cdot {}^0\mathbf{E})\boldsymbol{\mu}(\boldsymbol{\mu}' \cdot {}^1\mathbf{E}_-)(\boldsymbol{\mu}'' \cdot {}^2\mathbf{E}_-)\rangle + \ldots . \end{aligned} \tag{2}$$

The square brackets signify averaging over all spatial orientations, ${}^1\mathbf{E}_-$ and ${}^2\mathbf{E}_-$ are the radiation field components. The first term in the expansion only fails to vanish in an optically active medium, if $\omega_1 \neq \omega_2$

[10]. The second term, proportional to $(kT)^{-1}$, becomes, after isotropic averaging [Ref. 11, Eq. (A2)].

$$\begin{aligned}\mathbf{p}_{-}^{(3)}=\frac{1}{kT}\{&[\tfrac{2}{15}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu})(\boldsymbol{\mu}'\cdot\boldsymbol{\mu}'')-\tfrac{1}{30}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu}')(\boldsymbol{\mu}\cdot\boldsymbol{\mu}'')\\&-\tfrac{1}{30}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu}'')(\boldsymbol{\mu}\cdot\boldsymbol{\mu}')]{}^0\mathbf{E}({}^1\mathbf{E}_-\cdot{}^2\mathbf{E}_-)\\&+[-\tfrac{1}{30}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu})(\boldsymbol{\mu}'\cdot\boldsymbol{\mu}'')+\tfrac{2}{15}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu}')(\boldsymbol{\mu}\cdot\boldsymbol{\mu}'')\\&-\tfrac{1}{30}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu}'')(\boldsymbol{\mu}\cdot\boldsymbol{\mu}')]({}^0\mathbf{E}\cdot{}^1\mathbf{E}_-){}^2\mathbf{E}_-\\&+[-\tfrac{1}{30}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu})(\boldsymbol{\mu}'\cdot\boldsymbol{\mu}'')-\tfrac{1}{30}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu}')(\boldsymbol{\mu}\cdot\boldsymbol{\mu}'')\\&+\tfrac{2}{15}(\boldsymbol{\mu}_0\cdot\boldsymbol{\mu}'')(\boldsymbol{\mu}\cdot\boldsymbol{\mu}')]({}^0\mathbf{E}\cdot{}^2\mathbf{E}_-){}^1\mathbf{E}_-\}\,.\end{aligned}\tag{3}$$

The quantities $\boldsymbol{\mu},\boldsymbol{\mu}',\boldsymbol{\mu}''$ transform like electric dipoles. $\boldsymbol{\mu}$ is connected to the polarization vector, $\boldsymbol{\mu}'$ to the radiation field vector ${}^1\mathbf{E}_-$ and $\boldsymbol{\mu}''$ to the radiation field vector ${}^2\mathbf{E}_-$. In particular we have:

$$\mu_i\mu_j'\mu_k''\equiv\chi_{ijk}^{(2)}(\omega_1+\omega_2,-\omega_1,-\omega_2)\equiv\beta_{ijk}\,.\tag{4}$$

Expression (3) allows one to deduce easily the influence of the polarization of the incident radiation upon field-induced second-harmonic generation. In what follows, $\mathbf{i},\mathbf{j},\mathbf{k}$ are unit vectors in the laboratory frame X, Y, Z. Quantities defined within the molecular frame of reference carry small indices x, y, z. Furthermore, we assume $\omega_1=\omega_2$. We consider different cases.

I) The polarization of the incident radiation is *parallel* to the direction of the static field

$${}^0\mathbf{E}=\varepsilon_0\mathbf{i}\,,\quad {}^1\mathbf{E}_-=\frac{\varepsilon}{\sqrt{2}}\mathbf{i}\,,\quad {}^2\mathbf{E}_-=\frac{\varepsilon}{\sqrt{2}}\mathbf{i}\,.\tag{5}$$

Introducing (5) into (3), and making use of (4), we obtain

$$\begin{aligned}\boldsymbol{p}_{I-}^{(3)}&=\bar{\gamma}_{XX}\frac{\varepsilon_0\varepsilon^2}{2}\mathbf{i}\\&=\frac{1}{15kT}[3(\mu_{0x}\beta_{xxx}+\mu_{0y}\beta_{yyy}+\mu_{0z}\beta_{zzz})\\&\quad+\mu_{0x}(\beta_{xyy}+2\beta_{yyx}+\beta_{xzz}+2\beta_{zzx})\\&\quad+\mu_{0y}(\beta_{yxx}+2\beta_{xxy}+\beta_{yzz}+2\beta_{zzy})\\&\quad+\mu_{0z}(\beta_{zxx}+2\beta_{xxz}+\beta_{zyy}+2\beta_{yyz})]\frac{\varepsilon_0\varepsilon^2}{2}\mathbf{i}\,.\end{aligned}\tag{6}$$

We have made use of the fact that, because $\omega_1=\omega_2$, $\beta_{yxy}=\beta_{yyx}$, etc.

II) The polarization of the incident radiation is *perpendicular* to the direction of the static field

$${}^1\mathbf{E}_-=\frac{\varepsilon}{\sqrt{2}}\mathbf{j}\,,\quad {}^2\mathbf{E}_-=\frac{\varepsilon}{\sqrt{2}}\mathbf{j}\,,\tag{7}$$

from which follows

$$\begin{aligned}\mathbf{p}_{II-}^{(3)}&=\bar{\gamma}_{YY}\frac{\varepsilon_0\varepsilon^2}{2}\mathbf{i}\\&=\frac{1}{15kT}[\mu_{0x}\beta_{xxx}+\mu_{0y}\beta_{yyy}+\mu_{0z}\beta_{zzz}\\&\quad+\mu_{0x}(2\beta_{xyy}-\beta_{yyx}+2\beta_{xzz}-\beta_{zzx})\\&\quad+\mu_{0y}(2\beta_{yxx}-\beta_{xxy}+2\beta_{yzz}-\beta_{zzy})\\&\quad+\mu_{0z}(2\beta_{zxx}-\beta_{xxz}+2\beta_{zyy}-\beta_{yyz})]\frac{\varepsilon_0\varepsilon^2}{2}\mathbf{i}\,.\end{aligned}\tag{8}$$

Notice that in this case the incident radiation is polarized perpendicularly to the frequency-doubled beam.

III) The direction of propagation of the incident radiation is, as in I) and II), assumed to be perpendicular to the static electric field. The polarization is now left (L) circular (we could for our purposes just as well use right c.p. light)

$${}^1\mathbf{E}_-=\frac{\varepsilon}{2}(\mathbf{i}+i\mathbf{j})\,,\quad {}^2\mathbf{E}_-=\frac{\varepsilon}{2}(\mathbf{i}+i\mathbf{j})\,.\tag{9}$$

We then notice that

$${}^1\mathbf{E}_-\cdot{}^2\mathbf{E}_-=0\,.\tag{10}$$

Consequently, by (3)

$$\begin{aligned}\mathbf{p}_{III-}&=\bar{\gamma}_{LL}\frac{\varepsilon_0\varepsilon^2}{4}(\mathbf{i}+i\mathbf{j})\\&=\frac{1}{15kT}[2(\mu_{0x}\beta_{xxx}+\mu_{0y}\beta_{yyy}+\mu_{0z}\beta_{zzz})\\&\quad+\mu_{0x}(-\beta_{xyy}+3\beta_{yyx}-\beta_{xzz}+3\beta_{zzx})\\&\quad+\mu_{0y}(-\beta_{yxx}+3\beta_{xxy}-\beta_{yzz}+3\beta_{zzy})\\&\quad+\mu_{0z}(-\beta_{zxx}+3\beta_{xxz}-\beta_{zyy}+3\beta_{yyz})]\\&\quad\times\frac{\varepsilon_0\varepsilon^2}{4}(\mathbf{i}+i\mathbf{j})\,.\end{aligned}\tag{11}$$

We immediately find that the susceptibilities $\bar{\gamma}_{XX}$, $\bar{\gamma}_{YY}$, and $\bar{\gamma}_{LL}$, as defined by (6, 8, and 11), fulfill the relation [6]

$$\bar{\gamma}_{XX}=\bar{\gamma}_{YY}+\bar{\gamma}_{LL}\,.\tag{12}$$

The quantity of interest to us here, however, is

$$\begin{aligned}2\bar{\gamma}_{YY}-\bar{\gamma}_{LL}=\frac{1}{3kT}&[\mu_{0x}(\beta_{xyy}-\beta_{yyx}+\beta_{xzz}-\beta_{zzx})\\&+\mu_{0y}(\beta_{yxx}-\beta_{xxy}+\beta_{yzz}-\beta_{zzy})\\&+\mu_{0z}(\beta_{zxx}-\beta_{xxz}+\beta_{zyy}-\beta_{yyz})]\,.\end{aligned}\tag{13}$$

Table 1. Computed hyperpolarizability data. The components of β are in units of $10^{-30}\,g^{-1/2}\,cm^{7/2}\,s$. The quantity $3kT(2\bar{\gamma}_{YY}-\bar{\gamma}_{LL})$ is in units of $10^{-48}\,cm^6$. For computational details, see [12]

Energy [eV]	0.50	0.83	1.17	1.33	1.50	1.66	1.83	2.00	2.17	2.34
Molecure	p-Nitroaniline									
βyxx	-1.446	-1.652	-2.111	-2.522	-3.302	-4.969	-14.138	8.503	1.479	-1.301
βxxy	-1.385	-1.446	-1.535	-1.577	-1.601	-1.551	-1.212	0.915	-20.176	-9.310
$3kT(2\bar{\gamma}_{YY}-\bar{\gamma}_{LL})$	-0.503	-1.70	-4.75	-7.79	-14.03	-28.19	-106.6	62.58	178.6	66.05
Molecule	m-Nitroaniline									
βxyy	2.743	2.678	2.175	1.167	-3.928	34.445	12.788	11.331	-1.330	38.447
βyyx	2.898	3.174	3.522	3.462	1.571	21.653	12.239	13.748	6.597	58.532
βyxx	1.486	1.626	1.742	1.541	-0.452	18.487	9.259	10.636	9.926	44.595
βxxy	1.537	1.822	2.490	3.184	5.339	-5.885	2.193	5.169	22.371	0.084
$3kT(2\bar{\gamma}_{YY}-\bar{\gamma}_{LL})$	-0.682	-2.38	-7.77	-15.46	-48.26	178.14	44.03	27.21	-94.33	220.55
Molecule	o-Nitroaniline									
βxyy	4.896	5.997	9.666	15.890	87.945	-22.769	-9.784	-7.220	-8.838	-21.769
βyyx	4.948	6.186	10.326	17.316	97.623	-25.369	-10.484	-6.739	-20.620	1.876
βyxx	2.817	3.587	6.121	10.365	58.952	-15.416	-6.392	-4.056	-4.395	-1.653
βxxy	2.735	3.332	5.458	9.234	54.178	-15.372	-7.599	-6.594	-7.639	-23.669
$3kT(2\bar{\gamma}_{YY}-\bar{\gamma}_{LL})$	0.176	0.466	0.719	0.347	-9.25	7.44	6.87	8.74	47.46	18.80

Table 2. The units are the same as in Table 1

Energy [eV]	0.50	0.83	1.17	1.33	1.50	1.66	1.83	2.00
Molecule	4-amino-4'-nitrostilbene							
βxyy	-1.498	-1.593	-1.647	-1.473	0.043	-11.461	-6.359	-7.717
βyyx	-1.712	-2.396	-4.578	-7.691	-21.279	57.311	13.999	5.992
βyxx	14.345	19.838	37.483	62.916	175.282	-482.707	-126.824	-89.300
βxxy	13.791	17.770	29.949	46.865	119.636	-299.422	-70.075	-44.664
$3kT(2\bar{\gamma}_{YY}-\bar{\gamma}_{LL})$	-1.749	-6.57	-23.99	-50.85	-173.93	558.29	163.50	105.56
Molecule	Stilbazolium betaine (merocyanine)							
βxyy	-13.554	-16.950	-25.076	-443.962	39.879	15.417	8.786	9.691
βyyx	-12.759	-13.607	-13.395	48.973	-35.745	-38.456	-53.184	-119.660
βyxx	-17.773	-20.444	-38.620	-301.220	47.374	39.567	71.408	335.390
βxxy	-21.663	-36.098	-151.304	-368.762	114.764	65.826	48.113	32.264
$3kT(2\bar{\gamma}_{YY}-\bar{\gamma}_{LL})$	16.52	68.64	306.24	7556.15	-1224.42	-847.43	-913.54	-1615.43

In the case that Kleinman symmetry is exactly obeyed, the right side of (13) vanishes. We then have

$$2\bar{\gamma}_{YY}-\bar{\gamma}_{LL}=0\,, \tag{14}$$

leading to

$$\bar{\gamma}_{XX}:\bar{\gamma}_{LL}:\bar{\gamma}_{YY}=3:2:1\,. \tag{15}$$

The aim of this note is to point out the potential use of different incident polarizations, in particular the quantities $\bar{\gamma}_{YY}$ and $\bar{\gamma}_{LL}$, to study Kleinman symmetry in molecules. With the increasing availability of powerful tunable lasers, it should be instructive to follow $2\bar{\gamma}_{YY}-\bar{\gamma}_{LL}$ as a function of wavelength. As the computed numerical estimates of the next section suggest, the quantity should react very sensitively to the approach of resonances, in particular two-photon resonances, and should provide information of general spectroscopic interest.

2. Computed Numerical Examples

As examples we consider planar molecules in which the long-wavelength susceptibility for second-harmonic generation is due mainly to $\pi-\pi^*$ transitions. We neglect $\sigma-\sigma^*$ transitions, as well as $\pi-\sigma^*$ and $\sigma-\pi^*$ transitions polarized perpendicularly to the molecular plane. The numerical computations have been performed by the PPP SCF-MO-CI procedure. The numbers obtained depend on the choice of semiempirical parameters. This question has been treated in detail in [12]. There is nevertheless good evidence that the results reflect correct trends and orders of magnitude. They illustrate the difference between the long-wavelength behavior of the tensor elements and the situation close to resonances.

We assume the molecules considered to lie in the x, y-plane. The absence of z-polarized dipole moments and transition moments makes all tensor elements of β vanish which contain the index z. Equation (13) simplifies accordingly. In planar molecules of higher symmetry, such as C_{2v} in the case of urea or p-nitroaniline, we may let one axis, y say, coincide with the symmetry axis, leading to the simple relation

$$2\bar{\gamma}_{YY}-\bar{\gamma}_{LL}=\frac{1}{3kT}\,\mu_0(\beta_{yxx}-\beta_{xxy})\,. \tag{16}$$

Tables 1 and 2 show that at low radiation frequency Kleinman symmetry is almost fulfilled. In considering these numbers one must, however, make the reservation that below 0.5 eV vibrational transitions may start to become important, which here have been totally neglected. On the other hand this data shows that close to electronic two-photon resonances the deviations from Kleinman symmetry become very large and that the observable quantity $2\bar{\gamma}_{YY}-\bar{\gamma}_{LL}$ should be particularly sensitive to this situation. It is therefore suggested to measure this quantity as a function of the wavelength of incident light. Evidently, the dissipation of radiation energy inside resonances will have to be taken into account in evaluating the results of such measurements.

Acknowledgements. This research has in parts been supported by the Swiss National Science Foundation.

References

1. D.A. Kleinman: Phys. Rev. **126**, 1777 (1962)
2. P.A. Franken, J.F. Ward: Rev. Mod. Phys. **35**, 23 (1963)
3. J.F. Ward: Rev. Mod. Phys. **37**, 1 (1965)
4. N. Bloemberger: *Nonlinear Optics* (Benjamin, New York 1965)
5. A. Yariv: *Quantum Electronics* (Wiley, New York 1975)
6. G. Mayer: C.R. Acad. Sc. Paris B **267**, 54 (1968)
7. S. Kielich: Chem. Phys. Lett. **2**, 569 (1968)
8. S. Kielich: IEEE J. QE-**5**, 562 (1969)
9. J.F. Ward, I.J. Bigio: Phys. Rev. A **11**, 60 (1975)
10. J.A. Giordmaine: Phys. Rev. **138**, A1599 (1965)
11. G. Wagnière: J. Chem. Phys. **77**, 2786 (1982)
12. C.W. Dirk, R.J. Twieg, G. Wagnière: J. Am. Chem. Soc. (in press)