

TABLE II. Energy levels and quantum numbers for  $S = \frac{1}{2}$  and  $I = \frac{1}{2}$ .

	Low-field quantum numbers		High-field quantum numbers	
	$F$	$m_F$	$M_S$	$m_I$
$E_1 = \frac{1}{2}g\beta H + \frac{1}{4}A$	1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$
$E_2 = -\frac{1}{4}A + \frac{1}{2} \times [(g\beta H)^2 + A^2]^{1/2}$	1	0	$+\frac{1}{2}$	$-\frac{1}{2}$
$E_3 = -\frac{1}{2}g\beta H + \frac{1}{4}A$	1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$
$E_4 = -\frac{1}{4}A - \frac{1}{2} \times [(g\beta H)^2 + A^2]^{1/2}$	0	0	$-\frac{1}{2}$	$+\frac{1}{2}$

$$A = \frac{(2h\nu)(h\nu - g\beta H_1)}{(g\beta H_1 - 2h\nu)} \text{ or } g\beta H_1 = \frac{2h\nu(h\nu + A)}{(2h\nu + A)} \quad (\text{A1})$$

Another high-field transition should be observed for the

$$|F = 1, m_F = 1\rangle \rightarrow |F = 1, m_F = 0\rangle \text{ transition:}$$

$$h\nu = E_1 - E_2 = \frac{1}{2}g\beta H_2 + \frac{1}{2}A - \frac{1}{2} \{ [(g\beta H_2)^2 + A^2] \}^{1/2},$$

$$(2h\nu - g\beta H_2 - A)^2 = (g\beta H_2)^2 + A^2, \quad (\text{A2})$$

$$g\beta H_2 = 2h\nu(h\nu - A)/(2h\nu - A).$$

Taking formulas (A1) and (A2) and setting

$$g = \frac{2h^2\nu^2 - 2h\nu A}{(2h\nu - A)\beta H_2} = \frac{2h^2\nu^2 + 2h\nu A}{(2h\nu + A)\beta H_1},$$

we may cross multiply and solve for  $A$ ,

$$A = [h\nu/2(H_2 - H_1)] \{ (H_2 + H_1) \pm [(H_2 + H_1)^2 + 8(H_2 - H_1)^2]^{1/2} \}. \quad (\text{A3})$$

The transition probabilities for the two lines show that the line at  $H_2$  for  $\nu \approx 9$  GHz, which should appear at  $\sim 10450$  G, is lower in intensity by a factor of  $\sim 3.5$  from the line at  $H_1$  ( $\sim 5700$  G). If the hyperfine interaction has axial symmetry, then the final expressions for  $A_{\parallel}$  and  $A_{\perp}$ , in terms of  $H_1$ , are

$$A_{\parallel} = \frac{(2h\nu)[h\nu - g_{\parallel}\beta H_1] + \frac{1}{2}(A_{\parallel}^2 - A_{\perp}^2)}{[g_{\parallel}\beta H_1 - 2h\nu]}, \quad (\text{A4})$$

$$A_{\perp} = \frac{(2h\nu)[h\nu - g_{\perp}\beta H_1] + \{ \frac{1}{2}A_{\perp}^2 - \frac{1}{2}[\frac{1}{2}(A_{\parallel} + A_{\perp})]^2 \}}{[g_{\perp}\beta H_1 - 2h\nu]}.$$

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## Empirical Relation between the Linear and the Third-Order Nonlinear Optical Susceptibilities

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A simple empirical relation is found to exist between the linear and the third-order nonlinear optical susceptibilities. This empirical relation holds within the available experimental accuracy for gases at low pressures. The applicability of this empirical relation to crystalline solids, and its bearing on the generalized Miller's rule for these solids, are discussed.

In this article we wish to report on an empirical relation between the linear and the third-order non-

linear optical susceptibilities of gases at low pressures. This empirical relation makes use of the

expression

$$\chi^{(1)} = (e^2/m)N_{\text{eff}}/(\omega_0^2 - \omega^2) \quad (1)$$

for the linear susceptibility and relates the corresponding third-order nonlinear susceptibility to it as follows:

$$\chi^{(3)}(\omega \rightarrow 0) = 1.2(\chi^{(1)})^2/(N_{\text{eff}} \hbar \omega_0). \quad (2)$$

Here,  $\chi^{(3)}(\omega \rightarrow 0)$  is the value of the third-order susceptibility at frequencies which are low compared to the electronic absorption frequencies, but are still high compared to the vibrational frequencies;  $N_{\text{eff}}$  and  $\omega_0$  are, respectively, the oscillator strength and the mean absorption frequency. Whereas Eq. (1) is strictly valid for a linear harmonic oscillator, it will be shown later that Eq. (2) follows from a perturbation calculation for the hydrogen atom.

The values of  $N_{\text{eff}}$  and  $\omega_0$  have since long been known for inert gases and other gases.<sup>1</sup> At these low frequencies, the third-order susceptibility constants describing optical third harmonic generation (THG) and optical four-wave mixing (FWM) are the same. For inert gases, this same third-order susceptibility constant also describes the electro-optic Kerr effect. Comparison of  $\chi^{(3)}$  cal-

culated from Eq. (2) with the experimental values extrapolated to zero frequency<sup>2</sup> shows that these values agree within the available experimental accuracy for inert gases<sup>2-3</sup> and other gases<sup>2</sup> reported to date. The existence of this empirical relation, which has never been pointed out before, is important on at least two accounts; it complements the generalized Miller's rule<sup>4</sup> for ionic crystals and sheds light on the many previous attempts<sup>5-10</sup> to calculate  $\chi^{(3)}$  and/or correlate it with other material parameters. These attempts have met with only limited success.

Table I summarizes the values of  $\chi^{(3)}$  calculated from Eq. (2) and those deduced from various experiments and extrapolated to zero frequency. Of particular interest is the agreement within 12% for the inert gases, for which the experimental value of  $\chi^{(3)}$  deduced from measurements of the Kerr effect is believed to be accurate to within that limit. The agreement for other gases is within the available experimental accuracy. It is clear that the empirical relation of Eq. (2) generally holds for gases at low pressures.

To derive Eq. (2), one uses the following expressions for the linear and the third-order nonlinear optical susceptibilities of isolated atoms or molecules<sup>11</sup>:

$$\chi^{(1)}(\omega) = \frac{2e^2}{\hbar} \sum_i' \frac{\omega_i}{\omega_i^2 - \omega^2} \langle 0|x|l \rangle \langle l|x|0 \rangle, \quad (3)$$

$$\begin{aligned} \chi^{(3)}(-\omega_4, \omega_1, \omega_2, \omega_3) &= \frac{e^4}{24\hbar^3} \sum' \langle 0|x|l \rangle \langle l|x|k \rangle \langle k|x|n \rangle \langle n|x|0 \rangle \\ &\times \left( \frac{1}{(\omega_l - \omega_1 - \omega_2 - \omega_3)(\omega_k - \omega_2 - \omega_3)(\omega_n - \omega_3)} \right. \\ &+ \frac{1}{(\omega_l + \omega_1)(\omega_k - \omega_2 - \omega_3)(\omega_n - \omega_3)} \\ &+ \frac{1}{(\omega_l + \omega_1 + \omega_2 + \omega_3)(\omega_k + \omega_2 + \omega_3)(\omega_n + \omega_3)} \\ &\left. + \frac{1}{(\omega_l - \omega_1)(\omega_k + \omega_2 + \omega_3)(\omega_n + \omega_3)} + (\omega_1 \neq \omega_2 \neq \omega_3) \right), \quad (4) \end{aligned}$$

where  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are the incident frequencies and  $\omega_4 = \omega_1 + \omega_2 + \omega_3$ . At low frequencies, Eq. (3) reduces to Eq. (1) in the approximation where a single oscillator with absorption frequency  $\omega_0$  and oscillator strength  $N_{\text{eff}}$  replaces the series of oscillators with different absorption frequencies  $\omega_i$ . Using Eq. (3) and the parameters  $\omega_0$  and  $N_{\text{eff}}$  determined from linear dispersion, Eq. (4) becomes

$$\chi^{(3)}(\omega \rightarrow 0) = g(\chi^{(1)})^2/N_{\text{eff}} \hbar \omega_0 \quad (5)$$

in the limit of zero frequencies. Here,

$$\begin{aligned} g &= \frac{1}{4}\omega_0 \left( \sum_{lkn}' (\omega_l \omega_k \omega_n)^{-1} \langle 0|x|l \rangle \langle l|x|k \rangle \langle k|x|n \rangle \langle n|x|0 \rangle - \sum_i' \omega_i^{-1} \langle 0|x|l \rangle \langle l|x|0 \rangle \right) \\ &\times \sum_n' \omega_n^{-2} \langle 0|x|n \rangle \langle n|x|0 \rangle \left( \sum_i' \omega_i^{-1} \langle 0|x|l \rangle \langle l|x|0 \rangle \right)^{-2} \quad (6) \end{aligned}$$

TABLE I. Comparison of the values of  $\chi^{(3)}$  calculated from Eq. (2) with those deduced from measurements of the Kerr effect, optical third harmonic generation (THG), and four-wave mixing (FWM), extrapolated to zero frequency.

Material	$N_{\text{eff}}$	$\nu_0 (10^{15} \text{ cps})$	$\chi^{(3)} (10^{-39} \text{ cm}^6/\text{atom erg})$			
			Calculated		Experimental	
He	1.22	6.435	1.0 <sup>a</sup>	b	1.1 <sup>c</sup>	1.0 <sup>d</sup>
Ne	2.44	6.26	1.9 <sup>a</sup>	b	2.1 <sup>c</sup>	1.9 <sup>d</sup>
Ar	4.35	4.12	28 <sup>a</sup>	b	27 <sup>c</sup>	27 <sup>d</sup>
Kr	4.95	3.57	65 <sup>a</sup>	b	59 <sup>c</sup>	71 <sup>d</sup>
Xe	5.55	3.0	186 <sup>a</sup>	b	163 <sup>c</sup>	166 <sup>d</sup>
H <sub>2</sub>	1.67	3.52	20 <sup>a</sup>	b		18 <sup>d</sup>
N <sub>2</sub>	4.68	4.14	29 <sup>a</sup>	b		25 <sup>d</sup>
CO <sub>2</sub>	5.70	3.76	60 <sup>a</sup>	b		39 <sup>d</sup>

  

	$N_{\text{eff}}$ ( $10^{22} \text{ cm}^{-3}$ )		$\chi^{(3)} (10^{-14} \text{ cm}^3/\text{erg})$			
			Calculated		Experimental	
Lif	18.25	4.12	0.3 <sup>e</sup>	0.28 <sup>f</sup>	0.25 <sup>g</sup>	0.36 <sup>h</sup>
NaF	12.15	3.62	0.3 <sup>e</sup>	0.13 <sup>f</sup>		0.32 <sup>h</sup>
CaF <sub>2</sub>	17.8	3.79	0.4 <sup>e</sup>	0.4 <sup>f</sup>	0.47 <sup>g</sup>	
SiO <sub>2</sub>	17.8	3.28	1.1 <sup>e</sup>	1.4 <sup>f</sup>	1.0 <sup>g</sup>	
NaCl	10.1	2.49	2.0 <sup>e</sup>	0.8 <sup>f</sup>	1.6 <sup>g</sup>	1.6 <sup>h</sup>
KCl	9.22	2.53	1.9 <sup>e</sup>	0.9 <sup>f</sup>	1.8 <sup>g</sup>	1.6 <sup>h</sup>
KBr	8.15	2.22	3.7 <sup>e</sup>	1.3 <sup>f</sup>	3.2 <sup>g</sup>	3.2 <sup>h</sup>
MgO	17.8	2.73	4.0 <sup>e</sup>	5.7 <sup>f</sup>	2.2 <sup>g</sup>	3.0 <sup>h</sup>
KI	7.08	1.86	9.0 <sup>e</sup>	3.1 <sup>f</sup>	7.2 <sup>g</sup>	
CdS	7.08	1.19	300 <sup>e</sup>	120 <sup>f</sup>	160 <sup>g</sup>	

  

			$\chi^{(3)} (10^{10} \text{ cm}^3/\text{erg})$			
			Calculated		Experimental	
Si	12.7	0.97	0.096 <sup>i</sup>	0.6 <sup>f</sup>	0.08 <sup>j</sup>	
GaAs	8.5	0.86	0.11 <sup>i</sup>	0.3 <sup>f</sup>	0.1 <sup>j</sup>	
Ge	7.87	0.64	0.41 <sup>i</sup>	2.1 <sup>f</sup>	1.3 <sup>j</sup>	

<sup>a</sup> Calculated from Eq. (2).<sup>b</sup> See text.<sup>c</sup> Deduced from measurements of Kerr effect, Ref. 3.<sup>d</sup> Deduced from measurements of THG, Ref. 2.<sup>e</sup> Calculated from Eq. (2').<sup>f</sup> Calculated from the generalized Miller's rule  $\chi^{(3)} = (\chi^{(1)})^4 \times 10^{-10}$ .<sup>g</sup> Deduced from measurements of FWM, Ref. 17. The symmetrical combination  $\frac{1}{3}(\chi_{1111}^{(3)} + 4\chi_{1122}^{(3)} + 2\chi_{1221}^{(3)})$  is taken.<sup>h</sup> The values in this column are 1.4 times those deduced from measurements of THG in Ref. 12. This normalization factor of 1.4 is applied so that the coefficient for air ( $\chi_a^{(3)} = 4.1 \times 10^{-19}$  esu) deduced from these measurements is equal to that normalized to He in Ref. 2.<sup>i</sup> Calculated from Eq. (2'), assuming  $f=2$ .<sup>j</sup> Deduced from measurements of FWM, Ref. 4.

is a dimensionless quantity involving the properties of the ground state as well as the excited states of the system; except for a few cases such as the hydrogen atom and harmonic oscillators, this factor  $g$  is not amenable to calculation. For an anharmonic oscillator,  $g = \eta$ , where  $\eta \ll 1$  is the anharmonicity coefficient defined previously.<sup>12</sup> For the hydrogen atom, use of results from perturbation calculations<sup>13,14</sup> shows that  $\omega_0 = 0.41 e^2/a_0$  with a corresponding value of  $g = 1.2$ , where  $a_0 = \hbar^2/me^2$ . The existence of the empirical relation of Eq. (2) thus suggests that the model of anharmonic oscillator<sup>15</sup> with small anharmonicity coefficient  $\eta$  is not applicable to actual atomic systems.

When modified to include the local-field effects,

the empirical relation of Eq. (2) is also found to hold for ionic crystals. This is seen by rewriting Eq. (2) as follows:

$$\chi^{(3)}(\omega \rightarrow 0) = 1.2(\chi^{(1)})^2 f^3 / (N_{\text{eff}} \hbar \omega_0). \quad (2')$$

Here  $f$  is the local-field correction factor;  $f = 1$  for gases at low pressures and  $f = \frac{1}{3}(\epsilon + 2)$  for ionic crystals with cubic symmetry,<sup>15</sup>  $\epsilon$  being the electronic dielectric constant. To compare with the values of  $\chi^{(3)}$  calculated from Eq. (2'), the experimental values for the symmetrical combination<sup>7</sup>  $\chi^{(3)} = \frac{1}{3}(\chi_{1111}^{(3)} + 4\chi_{1122}^{(3)} + 2\chi_{1221}^{(3)})$  are taken for cubic crystals. Using the values of  $N_{\text{eff}}$  and  $\omega_0$  recently deduced for crystalline solids,<sup>16</sup> the calculated values of  $\chi^{(3)}$  for ionic crystals are found to be in

agreement with those deduced from various experiments<sup>12,17</sup> and extrapolated to zero frequency.

For semiconductors with tetrahedral coordination, the local-field factor  $f$  is usually much smaller than the Lorentz value of  $\frac{1}{3}(\epsilon + 2)$  because of the extended nature of the valence-electron wave functions.<sup>7</sup> The exact value of  $f$  is not known, but is generally believed to be about 2 for most of these semiconductors.<sup>18</sup> Assuming  $f=2$  for Si and Ge as well as GaAs, it is found that the values of  $\chi^{(3)}$  calculated from Eq. (2') are in good order-of-magnitude agreement with the corresponding experimental values deduced from the four-wave mixing experiments.<sup>4</sup> It is to be noted, however, that in addition to the uncertainty in the  $f$  values, the experimental values of  $\chi^{(3)}$  are also uncertain by about a factor of 2 because of the lack of reliable absolute calibration and because of the mixing of the various  $R$ - and  $P$ -branch frequency components of the laser used in these experiments.<sup>4</sup> The value of  $\chi^{(3)}$  for Si may also be influenced by the presence of an impurity absorption band near the laser frequencies.<sup>19</sup> A close check on the applicability of this empirical relation to semiconductors must thus await improved measurements of  $\chi^{(3)}$

using single-frequency lasers.

It is of interest to note that the values of  $\chi^{(3)}$  for ionic crystals can also be predicted from the generalized Miller's rule.<sup>4</sup> According to this rule, one predicts that  $\chi^{(3)} = A(\chi^{(1)})^4$ , where  $A$  is a constant. With  $A = 10^{-10}$ , the predicted values for ionic crystals (Table I) agree with the experimental values within about a factor of 2. It is observed, however, that the generalized Miller's rule predicts a dependence on  $\chi^{(1)}$  different from that prescribed by Eq. (2'). This apparent difference may be reconciled by noting that Eq. (2') can be recast into the form  $\chi^{(3)} = A'(\chi^{(1)})^4$ , where

$$A' = 1.2 \left( \frac{4}{3} \pi + 1 \right) \chi^{(1)3} / N_{\text{eff}} \bar{n} \omega_0$$

ranges from  $0.6 \times 10^{-10}$  to  $2.5 \times 10^{-10}$  for the ionic crystals included in Table I, and thus can be taken to be approximately constant. For gases at low pressures,  $A'$  assumes a much different value and varies over a wide range ( $A' \approx 0.01-10$ ) for different gases; in this case, the generalized Miller's rule is not applicable.

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