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Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Rotational hyperpolarizability of a homonuclear diatomic molecule"

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The disagreement between Shelton's result [Phys. Rev. A **36**, 3461 (1987)] for the rotational hyperpolarizability in the dc Kerr effect and that of previous workers [A. D. Buckingham and B. J. Orr, Proc. R. Soc. London, Ser. A **305**, 259 (1968); A. D. Buckingham, Proc. R. Soc. London, Ser. A **267**, 271 (1962)] is resolved in favor of the latter.

Equations (9) and (10) of the paper by Shelton,[1] which offer formulas for the rotational contribution to the dc Kerr hyperpolarizability γ, are in error in as much as they do not take account of the fact that the static electric field will perturb the population distribution function $\rho(J,M)$. When this is done there is an additional term to be included in Eq. (9) which is, for $\omega \neq 0$,

$$\gamma^{\mathrm{rot}} = \sum_J \frac{(\alpha_{\parallel}-\alpha_{\perp})^2_{J,J}}{5kT} \frac{J(J+1)}{(J-1)(2J+3)} \rho(J) \tag{1}$$

and to Eq. (10) which is, for $\omega \neq 0$,

$$\gamma^{\mathrm{rot}} = (\alpha_{\parallel}-\alpha_{\perp})^2/20kT \; . \tag{2}$$

In the case of a single static field, the correction is $\frac{4}{3}$ of that in Eq. (1) or Eq. (2). Thus for $\omega \gg 0$ the dc Kerr contribution in the classical limit, Eq. (10), becomes $(\alpha_{\parallel}-\alpha_{\perp})^2/5kT$ and this agrees with the known classical dc Kerr result as well as the previously calculated quantum result.[2] For a single static field we have $4(\alpha_{\parallel}-\alpha_{\perp})^2/15kT$ which also agrees with the known classical result. There is therefore no basis to question the validity of Buckingham's ansatz for calculating the dc Kerr birefringence in terms of a perturbed refractive index.[2,3] Note, however, that there are two physically distinct contributions to the dc Kerr effect. The existence of the additional contributions given in Eqs. (1) and (2) requires that the molecules interact with a thermal reservoir in order that the M sublevel populations may relax to their perturbed equilibrium values, whereas the rotational hyperpolarizabilities of Eqs. (9) and (10) of Ref. 1 apply even for noninteracting molecules. Real transitions are involved in the first case and the time scale for establishing the macroscopic anisotropy is set by the interactions of the molecules with the bath. In the second case only virtual transitions are involved and the response is determined by just the interaction of the molecule with the applied fields.

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[1] D. P. Shelton, Phys. Rev. A **36**, 3461 (1987).

[2] A. D. Buckingham and B. J. Orr, Proc. R. Soc. London, Ser. A **305**, 259 (1968).

[3] A. D. Buckingham, Proc. R. Soc. London, Ser. A **267**, 271 (1962).