PHYSICAL REVIEW A **67**, 055801 (2003)

Polarizability and the resonance scattering of light: Damping sign issues

D. L. Andrews,[1,*] L. C. Dávila Romero,[1] and G. E. Stedman[2]
[1]*School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, NR4 7TJ, United Kingdom*
[2]*Department of Physics and Astronomy, University of Canterbury, Christchurch 8020, New Zealand*

(Received 14 October 2002; published 21 May 2003)

In the theory of molecular light scattering and nonlinear optics, excited state damping is a significant consideration at frequencies near to resonance. Despite attempts to resolve a long-standing controversy over the propriety of such methods, there remains a dispute over the correct sign for the damping of *antiresonant* terms. Most established theory of Raman and associated light scattering employs a constant-sign rule at odds with a variable sign commonly used in nonlinear optics. However, by focusing on the polarizability it is demonstrated that arguments for the constant-sign convention vindicate standard Raman theory; flaws in the counterpropositions undermine the case for variable signing. It is also shown that a polarizability sum rule is valid only with constant-sign damping.

DOI: 10.1103/PhysRevA.67.055801 PACS number(s): 42.65.An, 33.80.−b, 42.50.Ct

I. INTRODUCTION

In the theory of molecular light scattering and nonlinear optics, the issue of damping the frequency response in linear and nonlinear electronic polarizabilities is a significant consideration primarily when operating at frequencies near to resonance. This condition generally applies to any optical process when there exist states of the matter differing in energy from the initial state by an amount approaching the energy of one or more of the photons involved. Technical difficulties arise because at any exact resonance the results directly delivered by time-dependent perturbation theory exhibit divergences; *ad hoc* phenomenological methods are usually employed to secure well-behaved results associated with proper lineshape. Attempts have recently been made to resolve a long-standing controversy over the propriety of such methods employed to account for resonance damping [1–4]. As references cited in these works reveal, despite unanimity over the implementation of damping for positive frequency resonances in the polarizability—and in other quantum mechanical expressions for nonlinear optical response—there remains a dispute over the correct sign for the damping of *antiresonant* terms. In particular, most of the established theory of Raman and associated light scattering [5,6] is associated with a (constant-sign) rule that is at odds with the (variable-sign) rule commonly used in nonlinear optics. However, the impression that resolution of this issue requires a rewriting of conventional Raman theory [7] is incorrect. This paper aims to clarify the outstanding issues.

In the following we first present consistent and compelling arguments for the constant-sign convention—results that vindicate standard Raman theory. The two approaches are introduced and contrasted in Sec. II, then in Sec. III it is shown that flaws in the counterpropositions undermine the case for variable signing. In Sec. IV, focusing on the electronic polarizability (Rayleigh scattering) for simplicity, we present a sum rule that is manifestly valid only with constant-sign damping. In the final section it is emphasized that the principles validated by this analysis operate with equal force not only to Rayleigh and Raman scattering, but across the whole field of nonlinear optics and electro-optics. It is made clear that experimental verification of the correct formalism is not an easily tractable option; the signing controversy is principally significant for its exposure of fundamental issues.

II. TWO APPROACHES TO PHENOMENOLOGICAL DAMPING

The term ‘‘damping’’ alludes to the classical concept of a resonant response tempered by dissipation—here, coupling into decay channels for the molecular excited states. In the implementation of phenomenological damping, energy denominators in quantum mechanical expressions for molecular polarizability and other optical response tensors are modified to incorporate imaginary corrections, whose magnitudes $\hbar\gamma_r$ represent damping consistent with an exponential decay factor $\exp(-\gamma_r t)$ for each excited state $|r\rangle$. Close to resonance, damping accordingly delivers a physically broadened, Lorentzian lineshape to the optical response. Generally, each $\hbar\gamma_r$ is several orders of magnitude smaller than the molecular energies, and available intramolecular and intermolecular decay channels determine the precise values. In solid-state systems, local field effects generate additional, heterogeneous line broadening; other forms of phenomenological damping can also appear in connection with modeling a slow ‘‘adiabatic’’ switching on of the interaction from $t=-\infty$ with a growth factor $\exp(\Gamma t)$. In the following, we focus on molecular state damping, assuming that the interaction proceeds from a suitably prepared initial state of the system.

Take the specific case of Rayleigh scattering by a system of molecules, for which theory is developed in terms of a molecular electronic polarizability. This case serves the purpose not only for its simplicity; through a Born-Oppenheimer development based on Placzek's original theory [8], vibrational Raman scattering is also representable in terms of variations in the electronic polarizability. From calculations based on either tradition the scattering amplitude is cast in components of the polarizability tensor α^{ss}. For

---

*Corresponding author.

generality here, and with a view to the theory to be developed in Sec. III, we employ superscripts to designate the electronic polarizability for a molecule in an arbitrary initial state $|s\rangle$. Introducing a signing parameter σ to highlight the issues we address, the components of this tensor are expressible as follows:

$$\alpha_{ij}^{ss}(\sigma)=\sum_r \left[\frac{\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle}{E_r-E_s-\hbar\omega-i\hbar\gamma_{rs}} + \frac{\langle s|\mu_j|r\rangle\langle r|\mu_i|s\rangle}{E_r-E_s+\hbar\omega-i\sigma\hbar\gamma_{rs}}\right], \qquad (1)$$

where the circular frequency of the input radiation (implicit on the left) is ω, $\gamma_{rs}=\gamma_r-\gamma_s$ and other symbols have their usual meaning. For the constant-sign convention $\sigma=+1$, while under the variable-sign convention $\sigma=-1$. Note that the terms "constant sign convention" (CSC) and "variable sign convention" (VSC) signify a similarity or difference of sign for the damping correction in the two energy denominators. Constancy or variability is manifested in the sign of $i\hbar\gamma_r$ with respect to the energy E_r. The CSC approach signifies consistent modification of the energy $\tilde{E}_r=E_r-i\hbar\gamma_r$; there is a unique relationship between a particular energy level E_r and its corresponding damping constant γ_r [9]. On the other hand, with VSC [10–12], the sign of the damping factor follows the sign of the radiation frequency. It is notable that, whatever the sign of σ, the result of Eq. (1) is never a real quantity. This is neither a surprise nor a problem; in quantum mechanics the tensor is not a measurable. However, the complex character of the tensor serves as an alert to the fact that there are limitations to the conditions that can be imposed upon it, or expressions such as signal amplitudes in which it is linearly cast.

III. PROBLEMS WITH VARIABLE SIGNING

In earlier work the inconsistency of VSC with the fundamental principles of time-reversal symmetry has been thoroughly enunciated [1,3,9]. In the following we resolve further issues connected with applications of the molecular polarizability, and processes in general involving static electric fields. It is evident that VSC logically requires that for any electro-optical (or magneto-optical) process, interactions with which static fields are associated should carry no damping. This follows from the premise that the damping factor follows the sign of the radiation frequency.[1] However, from a quantum field viewpoint, static perturbations must induce damping. In the multipolar gauge all electromagnetic interactions are mediated through the exchange of virtual photons [13], and a static field is no different from a time-varying field, except that, while causality is of course satisfied, explicit retardation features disappear in the limit of zero frequency. The damping associated with any molecular excited state is not frequency dependent; it has a characteristic magnitude, regardless of the frequency of the perturbation with which it is associated.

Next we correct an argument in defense of VSC, based on the case of an electric dipole induced by a static electric field **F** [4]. The argument concerns the correct form of polarizability to use in the defining formula for the induced moment, expressed as follows:

$$\mu_\alpha=\alpha_{\alpha\beta}^{ss}F_\beta, \qquad (2)$$

where the salient polarizability is given by Eq. (1) with $\omega=0$ (here we generalize to the static polarizability of a molecule in any state, not necessarily the ground state):

$$\alpha_{ij}^{ss}(\sigma)=\sum_r \left[\frac{\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle}{E_r-E_s-i\hbar\gamma_{rs}}+\frac{\langle s|\mu_j|r\rangle\langle r|\mu_i|s\rangle}{E_r-E_s-i\sigma\hbar\gamma_{rs}}\right]$$

$$\equiv\sum_r \frac{2(E_r-E_s)\mathrm{Re}[\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle]+(-i\hbar\gamma_{rs})[\sigma\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle+\langle s|\mu_j|r\rangle\langle r|\mu_i|s\rangle]}{(E_r-E_s-i\hbar\gamma_{rs})(E_r-E_s-i\sigma\hbar\gamma_{rs})}. \qquad (3)$$

Care must be taken with Eq. (2), expressed on the right-hand side, using the usual Einstein summation convention for repeated indices. To be clear, each term in the given expression for μ_α (one hanging index α, applicable to any of three Cartesian directions) correctly features the subscript index α once only, as befits a hanging index; each also features a repeated subscript β, a dummy index whose repetition signifies implied summation over all Cartesian directions, as in a scalar product. No physical inferences can be drawn from interchanging α and β; in the context of Eq. (2) where it is used, the result of doing so is in fact meaningless.

It is also to be noted that in the case for VSC damping, then with $\sigma=-1$, we have

---

[1] In the susceptibility $\chi(-\omega_1,f\omega_0,\omega_0)$ associated with a signal frequency $\omega_1=(1+f)\omega_0$, VSC gives a discontinuity at $f=0$. Here positive f denotes sum-frequency generation; negative f, difference-frequency generation; $f=0$, a linear electro-optical effect. No discontinuity arises with CSC.

$$\alpha_{ij}^{ss}(\sigma=-1)=2\sum_{r}\frac{(E_r-E_s)\mathrm{Re}[\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle]-\hbar\gamma_{rs}\mathrm{Im}[\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle]}{(E_r-E_s-i\hbar\gamma_{rs})(E_r-E_s+i\hbar\gamma_{rs})}, \tag{4}$$

with imaginary contributions from the Dirac brackets, which denote transition moments; some ensuing difficulties have been identified in Ref. [4]. However, in the case we endorse, $\sigma=+1$ and

$$\alpha_{ij}^{ss}(\sigma=+1)=2\sum_{r}\frac{\mathrm{Re}[\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle]}{(E_r-E_s-i\hbar\gamma_{rs})}, \tag{5}$$

revealing that any imaginary parts of the transition moment product disappear. Moreover, if the molecular states involved are degenerate, such that the numerator of each term in the polarizability (1) is complex, it is always possible to find an alternative basis where the transition dipole moments are real. Any measurable result is independent of the basis used. It is clear that for a spherical atom, a static electric field in a particular direction, say x, induces a dipole moment in the same direction; this statement is independent of the sign of the damping, involving only the numerators of the polarizability.

IV. POLARIZABILITY SUM RULE

The electronic polarizability tensor satisfies a particular sum rule

$$\sum_{s}\alpha_{ij}^{ss}=0, \tag{6}$$

signifying the character of the polarizability operator as traceless in the Hilbert space. By interchange of the dummy state labels r and s (where it is legitimate to interchange because both are summed) the polarizability as given in expression (1) can be seen to satisfy the summation rule when the damping factors are null, or more generally when $\sigma=+1$ CSC. Specifically, the sum given by Eq. (6) is

$$\sum_{s}\alpha_{ij}^{ss}(\sigma)=\sum_{sr}\left[\frac{\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle}{E_{rs}-\hbar\omega-i\hbar\gamma_{rs}}+\frac{\langle s|\mu_j|r\rangle\langle r|\mu_i|s\rangle}{E_{rs}+\hbar\omega-i\sigma\hbar\gamma_{rs}}\right]. \tag{7}$$

By interchanging the dummy variables $r\leftrightarrow s$ in the second term it follows that

$$\sum_{s}\alpha_{ij}^{ss}=(\sigma-1)\sum_{sr}\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle\times\frac{i\hbar\gamma_{rs}}{(E_{rs}-\hbar\omega-i\hbar\gamma_{rs})(E_{sr}+\hbar\omega-i\sigma\hbar\gamma_{sr})}. \tag{8}$$

If $\sigma=-1$ VSC, then

$$\sum_{s}\alpha_{ij}^{ss}=2\sum_{sr}\langle s|\mu_i|r\rangle\langle r|\mu_j|s\rangle\frac{i\hbar\gamma_{rs}}{((E_{rs}-\hbar\omega)^2+(\hbar\gamma_{rs})^2)}$$

and the sum rule (6) is violated. However, Eq. (6) retains validity with $\sigma=+1$; the only rule consistent with the sum rule is constant-sign damping.

V. THE PROVINCE OF LEGITIMACY FOR PHENOMENOLOGICAL DAMPING

The principles validated by the analysis in Secs. III and IV operate with equal force across the whole of nonlinear optics and electro-optics, Rayleigh scattering only being used as a simple and well-known example. However, it is clear that experimental verification of one or other approach to the inclusion of phenomenological damping is not an easy option.

In considering possible avenues for possible experimental verification (of either damping convention) it is to be borne in mind that, for any linear, nonlinear optical or electro-optical process, differences between predictions of the two theories are apparent only through “anti resonant” terms. In connection with the Rayleigh and Raman scattering, and also most nonlinear optical processes, such terms cannot dominate the optical response; they become, at most, marginally significant in the regions very far removed from resonance. Optimally one might look for a system with optical properties dominated by one very low-lying excited state, well below the energy of photons involved. From lengthy but straightforward calculations it emerges that the order of magnitude of fractional rate corrections lies in the region of $\gamma^2/E_{\mathrm{mol}}^2$. Even then, only if all other electronic states were very significantly higher in energy than the photons involved could an antiresonant feature be considered amenable to experimental identification. No such truly two-level systems exist; always higher energy states play a part in the summation over states entailed in the polarizability. Moreover, whereas attempts to determine an absolute damping sign might be expedited in a system with large damping constants, these parameters are largest for molecules with a high density of vibrational levels—and any vibrational structure would certainly obscure the sought features through its role in the sum over states. In practice it could only be in atomic species with comparatively small damping constants that one could attempt the necessary measurements.

In connection with other optical processes, where the allowedness of a signal is consistent with only one sign rule, experimental verification might more realistically be sought. Indeed there are certain processes where the two conventions lead to very significant different results; for example, the constant-signing rule is necessary to uphold the principle that linear electro-optical response cannot occur in any isotropic liquid [14]. Much of the recent interest and attention to these issues resulted from previous analysis of this effect, which strikingly exposes differences between proponents of semiclassical and quantum electrodynamical methods to accommodate damping [14,15].

A pragmatic solution to the whole controversy might be to neglect damping in antiresonant terms and only include it in potentially resonant terms—where it does have significant impact and there is agreement over the correct sign. Indeed, recent work by Agarwal and Boyd [16] has concluded that it is only close to resonance that such damping has legitimacy. A proper perspective on the subject comes with recollection that phenomenological damping is at best only an approximate device designed to model a Lorentzian lineshape, and that, whereas there is always a leading order or perturbation theory contributing to the signal, other higher orders exist and also contribute marginally to observations. Ultimately the signing controversy we have addressed is significant primarily for its exposure of fundamental issues.

ACKNOWLEDGMENTS

We gratefully acknowledge stimulating correspondence with B. Dick. We also thank G. S. Agarwal and R. W. Boyd for sending us a preprint of their paper. This was work completed during a visit to the University of East Anglia by G.E.S., financed by the Erskine Fund. L.C.D.R. is funded by the Engineering and Physical Sciences Research Council.

---

[1] D. L. Andrews, S. Naguleswaran and G. E. Stedman, Phys. Rev. A **57**, 4925 (1998).
[2] A. D. Buckingham and P. Fischer, Phys. Rev. A **61**, 035801 (2000).
[3] G. E. Stedman, S. Naguleswaran, D. L. Andrews and L. C. Dávila Romero, Phys. Rev. A **63**, 047801 (2001).
[4] A. D. Buckingham and P. Fischer, Phys. Rev. A **63**, 047802 (2001).
[5] J. A. Koningstein, *Introduction to the Theory of the Raman Effect* (Reidel, Dordrecht, 1972).
[6] C. Shmuttenmaer, *Encyclopedia of Chemical Physics and Physical Chemistry*, edited by J. H. Moore and N. D. Spencer (Institute of Physics Publishing, Philadelphia 2001), Vol. 2, pp. 991–1015.
[7] D. A. Long, *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules* (Wiley, Chichester, 2002).
[8] G. Placzek, *Handbuch der Radiologie*, edited by E. Marx (Akademische Verlag, Leipzig, Germany, 1934), Vol. 6, pt. 2, pp. 205–374.
[9] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Atom-Photon Interactions. Basic Processes and Applications* (Wiley, New York, 1992).
[10] N. Bloembergen, *Nonlinear Optics: A Lecture Note and Reprint Volume* (Benjamin, New York, 1965).
[11] D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules* (Springer-Verlag, Berlin, 1979).
[12] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[13] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics: An Introduction to Radiation-Molecule Interactions* (Dover, New York, 1998).
[14] L. C. Dávila Romero, S. Naguleswaran, G. E. Stedman, and D. L. Andrews, Nonlinear Optics **23**, 191 (2000).
[15] D. Beljonne, Z. Shuai, J. L. Bredas, M. Kauranen, T. Verbiest, and A. Persoons, J. Chem. Phys. **108**, 1301 (1998).
[16] G. S. Agarwal and R. W. Boyd (unpublished).