

Scaling law for molecular hyperpolarizabilities

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Received August 25, 1988; accepted December 2, 1988

A scaling law for molecular hyperpolarizabilities is derived and is shown to describe accurately the measured hyperpolarizabilities for an assortment of small atoms and molecules.

Scaling laws for third-order susceptibilities are important in guiding efforts to develop better nonlinear-optical materials. Usually these scaling laws are derived by consideration of simplified model systems chosen for analytic or computational tractability, and they are mostly untested by experiment.¹⁻³ Here we derive a scaling law based on an essentially exact solution for the hyperpolarizability of a real system, the hydrogen atom.⁴ Then we test this scaling law with measurements for a range of atoms and molecules.

For the hydrogen atom the dispersion of the hyperpolarizability $\gamma(-\nu_\sigma; \nu_1, \nu_2, \nu_3)$ frequencies well below resonance is accurately represented by a power series in $\nu_L^2 = \nu_\sigma^2 + \nu_1^2 + \nu_2^2 + \nu_3^2$:

$$\gamma = \gamma_0 [1 + (\nu_L/\Omega)^2 + B(\nu_L/\Omega)^4 + \dots], \quad (1)$$

where γ_0 is the value of γ in the static limit, and the value of the frequency parameter Ω describing the dispersion is the same for all third-order processes.⁴ One may easily determine scaling laws for various properties of the hydrogen atom and hydrogenic ions. In particular, one finds that $V \propto R^3 \propto Z^{-3}m^{-3}$, $\Omega \propto Z^2m$, and $\gamma_0 \propto Z^{-10}m^{-7}$, where Z is the nuclear charge and m is the reduced mass of the system. Combining these relations for volume, frequency, and hyperpolarizability of the hydrogenic ions, one has

$$\Omega^3 \gamma_0 \propto V^{4/3}. \quad (2)$$

Although relation (2) is strictly valid only for one-electron atoms, we intend to apply it to many-electron atoms and molecules. This is not entirely unreasonable because the Z^{-10} scaling for γ_0 makes the contribution of the core electrons of a multielectron system negligible. The contribution of the few outermost electrons, well screened from the bare nuclear charge and possibly delocalized over the molecular volume, will be dominant.

To test relation (2) we draw on measurements, shown in Fig. 1, of the frequency dependence of γ over the visible spectrum for a range of small atoms and molecules.⁵⁻¹⁴ These data were obtained by the technique of gas-phase electric-field-induced second-harmonic generation (ESHG) with periodic phase matching, using cw argon-ion and dye lasers, and yielding a typical absolute accuracy of 1%.^{10,15} The experiment measures the XXXX component of the

isotropic average of γ . The theoretical results for γ of the H and He atoms, accurate at the 0.1% level, are shown as the dotted curves in Fig. 1.^{4,16} The value of γ varies by 3 orders of magnitude for this sample of 18 atoms and molecules.

There are several technical points to consider in applying these data to test the scaling law of relation (2). First, relation (2) refers to the scaling of the electronic hyperpolarizability γ^e , while the experimental data for molecules will also have a vibrational contribution γ^v . In the present case it is adequate to ignore this distinction, since calculations show that γ^v for ESHG at optical frequencies has only weak frequency dependence and makes less than a 10% contribution to γ , even for polyatomic molecules.⁵ Second, the higher dispersion terms of Eq. (1) can be significant, but the frequency range of the dispersion measurements is too small to permit accurate determination of the higher dispersion coefficients. We have used the results of the calculations for H and He for guidance in extracting γ_0^e and Ω . For H and He the coefficients of Eq. (1) increase only slightly faster than the coefficients of the power-series expansion of $\exp(\nu_L/\Omega)^2$. A straight-line fit to a plot of $\log \gamma$ versus ν_L^2 has been used as a convenient way of approximately accounting for the higher dispersion terms when determining γ_0^e and Ω . Third, the molecular volume is not uniquely defined. We have determined V from the density of the liquid or solid phase and assumed that V for the H atom falls between V for He and for H₂. For comparison, molecular volumes estimated from the van der Waals constants for gases are typically 20% larger than the values that we have used. The uncertainty of our estimates of $\Omega^3 \gamma_0^e$ and V is $\sim 20\%$.

The results for $\Omega^3 \gamma_0^e$ versus V have been plotted in Fig. 2. The solid straight line represents the scaling law for hydrogenic atoms and ions (there are no free parameters since $\Omega^3 \gamma_0^e$ is obtained directly from the *ab initio* calculation for H). The results for our sample of atoms and molecules agrees remarkably well with the scaling law, with the notable exception of points for the He and Ne atoms. The data points fall just 20% below the line, on average, if one excludes the points for He and Ne. Furthermore, recent unpublished measurements for Ne indicate that it is actually the relative magnitude of the successive dispersion coefficients that is exceptional in the case of Ne and that when this is accounted for the point for Ne in Fig. 2 will move much closer to the

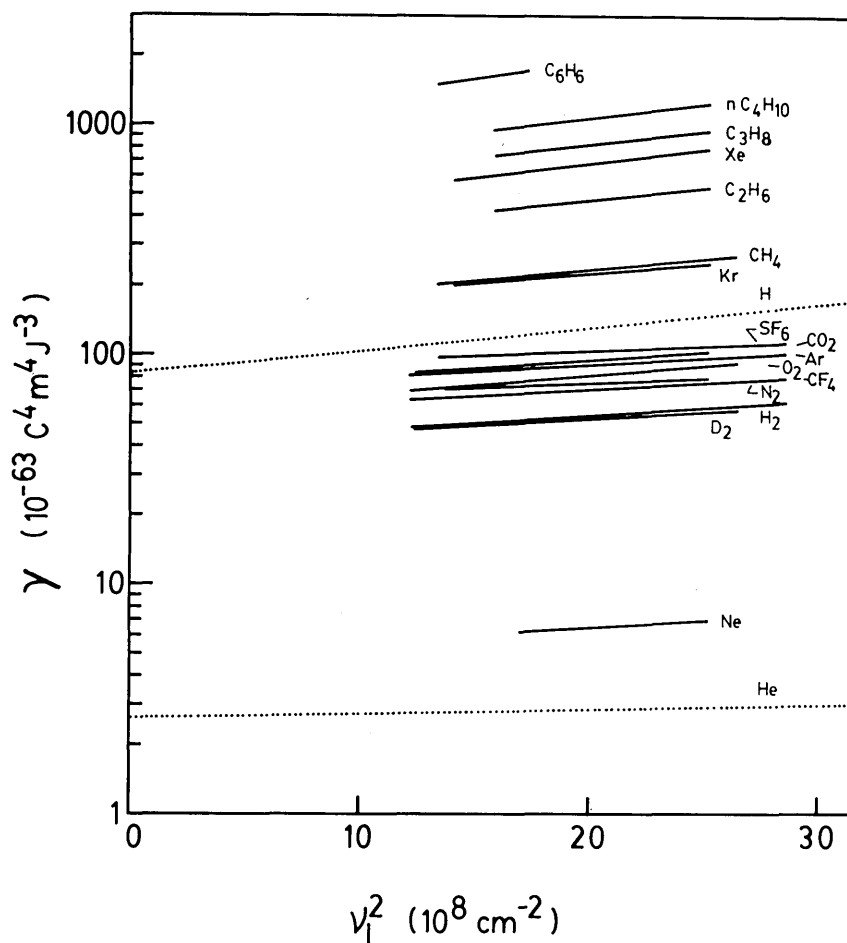


Fig. 1. Frequency dependence of the hyperpolarizability for several small molecules. The solid curves are from ESHG measurements at $\lambda = 458\text{--}700$ nm. The dotted curves are from *ab initio* calculations.

scaling-law curve. In contrast, a plot of γ (at $\lambda = 694.3$ nm) versus V would show that γ varies by more than an order of magnitude for molecules with the same V , even after He and Ne are excluded.

While the scaling law seems to agree with our data, all the molecules in our sample are relatively small. A better test of the scaling law requires more data, especially for much larger and more nonlinear molecules. Therefore, consider the measurements for the crystalline polydiacetylene-toluene sulfonate (PTS), for which the off-resonance value of $\chi^{(3)}$ has been measured as $\sim 3 \times 10^{-10}$ esu along the chains.¹⁷ To compare with our gas-phase measurements we first correct for the local field effect [Lorentz local field factors with $n = 1.88$ (Ref. 17) give a factor of 12] and take an isotropic average (another factor of 5). Then the microscopic susceptibility is calculated, using the measured volume per monomer unit.¹⁸ Finally, accounting for the numerical factor in the relation $6\chi^{(3)\text{mic}} = \gamma$ and making a reasonable estimate for the dispersion of γ , we find γ_0^e per monomer repeat unit for poly-PTS to be 1200 times as large as γ_0^e for benzene (the most nonlinear molecule in our sample of small molecules). The frequency parameter Ω is estimated to be 2.6 times smaller for PTS than for benzene (based on the ratio of the transition frequencies of the first absorption bands, at $\lambda = 640$ and $\lambda = 250$ nm in PTS and benzene, respectively¹⁹).

Thus $\Omega^3\gamma_0^e$ per monomer repeat for PTS is 70 times larger than the corresponding value for benzene. The volume per monomer repeat is $282 \text{ cm}^3/\text{mole}$ for PTS,¹⁸ 3.2 times larger than V for benzene. Assuming that the effective molecular size is one monomer unit, the scaling law underestimates $\Omega^3\gamma_0^e$ by a factor of 15. However, if the effective molecular size is 3600 monomer repeats, comparable with the polymer chain length, then the point for poly-PTS falls right on the scaling-law curve. Considering the large uncertainties in the above analysis, the result for poly-PTS disagrees insignificantly with the scaling-law curve for any reasonable estimate of the effective molecular size, and this may be taken as support for the validity of the scaling law, even for this conjugated polymer. It may be that the single-electron model on which relation (2) is based is particularly appropriate in this case since the optical response is dominated by an exciton.¹⁹ It seems that a wide range of validity for this scaling law has been obtained in exchange for a sacrifice of predictive power, in the sense that relation (2) does not allow one to calculate γ , Ω , or V from the detailed structural parameters of the system.

The main implication of the scaling law of relation (2) is that there are only two essential strategies for enhancing the macroscopic susceptibility $\chi^{(3)}$ of a material. Either one may increase the dispersion by moving the resonances of the

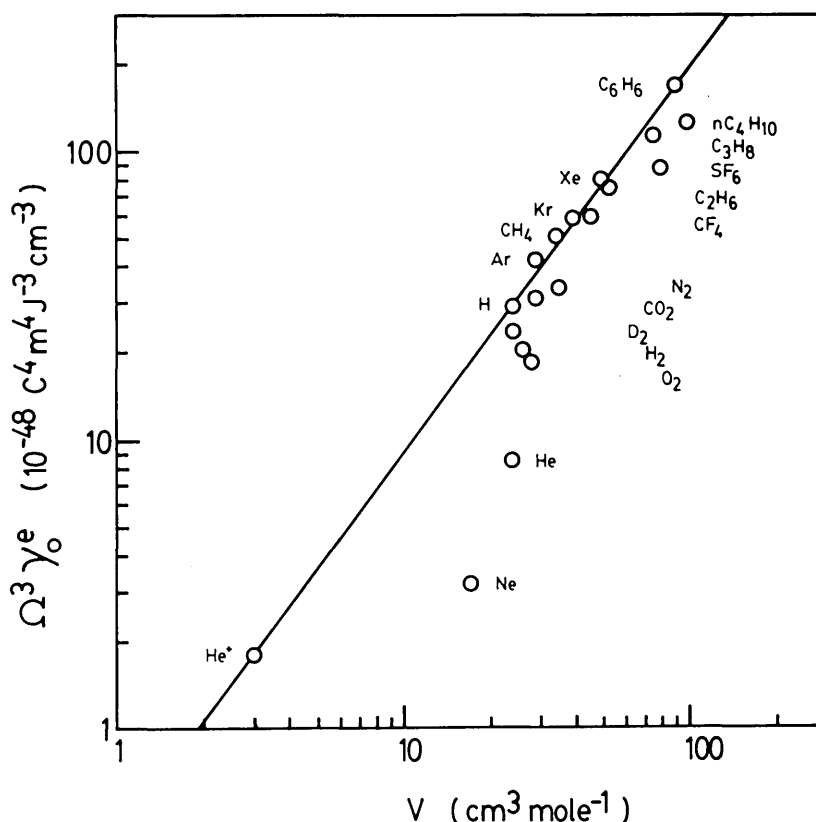


Fig. 2. Plot of $\Omega^3\gamma_0^e$ versus V for a range of small molecules. The dispersion data of Fig. 1 are used to calculate $\Omega^3\gamma_0^e$. The straight line is the prediction of the scaling law derived for hydrogenic atoms and ions [relation (2)].

system closer to the optical frequencies of interest or one may increase the effective size or delocalization length of the molecules. Dispersion makes a double contribution to the value of γ at optical frequencies since both γ_0^e and γ^e/γ_0^e increase with increasing dispersion. For a condensed phase $\chi^{(3)}$ has only a weak $V^{1/3}$ dependence on molecular volume, but this becomes significant when the delocalization length is increased to macroscopic dimensions.

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