

Hyperpolarizability dispersion measured for neon

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(Received 28 September 1987)

The hyperpolarizability of neon (γ_{Ne}) is determined by an electric-field-induced second-harmonic-generation (ESHG) experiment at several wavelengths in the visible region. The deviation from Kleinman symmetry is also measured. The dispersion curve obtained from this experiment allows one to critically assess the previous nonlinear-optical measurements for Ne and allows a reliable estimate of the static value of γ_{Ne} . The bounds obtained for the static γ_{Ne} are 75 a.u. $< \gamma_{\text{Ne}} < 93$ a.u. The results of recent *ab initio* calculations are considered in the light of this revised estimate for γ_{Ne} .

INTRODUCTION

The hyperpolarizabilities of atoms and molecules are related to a wide range of phenomena, from nonlinear optics to intermolecular forces.^{1,2} Theoretical calculations and experimental investigations have been motivated as much by the desire to design better molecular nonlinear-optical materials as by the wish to obtain a full quantitative understanding of the origin and dynamics of the nonlinear response of atoms and molecules.^{3,4} Calculations for the one- and two-electron systems H, He, H_2^+ , and H_2 are able to yield accurate results for the second hyperpolarizability γ , but only by employing methods which cannot be extended to larger systems.⁵⁻⁸ In the case of many-electron atoms or molecules the calculations required in order to obtain γ are difficult and often of questionable reliability. Since even a single internuclear coordinate greatly complicates an accurate *ab initio* calculation of γ for a molecule, atoms are by far the simplest many-electron systems in which one may study issues such as the importance of electron correlation in the calculation of γ . Neon has the special merit of being the smallest many-electron atom that may also be easily studied experimentally. However, the few previous experimental measurements⁹⁻¹³ of γ_{Ne} are not much more accurate than the *ab initio* calculations¹⁴⁻²⁰ that they are called upon to test. To rectify this situation we have made the electric-field-induced second-harmonic-generation (ESHG) measurements reported below.

EXPERIMENT

The experimental apparatus is similar to that previously described in detail elsewhere.²¹⁻²⁸ A cw laser beam from an argon-ion laser or a dye laser is weakly focused through a sample cell containing the gas in which second-harmonic generation takes place. A static field breaks the symmetry of the system, permitting coherent generation of the second-harmonic signal. The signal is strongly enhanced by periodic phase matching, accomplished by arranging the electrodes so that the field alternates in direction every coherence length.^{21,25} The coher-

ence length of the gas is adjusted to match the fixed spacing of the electrodes by varying the gas density. The electrode spacing is 2.69 mm, resulting in optimal pressures in the range 25–87 atm (at 18–24°C) for Ne and He in the experiments reported here. The applied field is about 1.2 kV/mm, limited to avoid breakdown in the Ne gas. The fundamental beam has a power of 0.4–1.0 W at the sample. A combination of double-prism spectrometer and glass filters separates the second-harmonic beam, which is then detected by a photon-counting photomultiplier tube. The background is about 0.3 counts/sec, while the peak signal is typically 150 counts/sec. To measure deviations from Kleinman symmetry, a Soleil-Babinet compensator is inserted into the optical path before the cell and used to manipulate the polarization state of the fundamental beam. The dye-laser wavelength was calibrated using a spectrometer and a Ne spectral lamp. Gas pressures were measured by a Bourdon-tube test gauge with an accuracy of ± 0.16 atm. High-purity (99.999%) gases were used in the experiment.

The experiment involves the measurement of various ratios. With the optical-field and static-field polarizations set parallel, the ratio of hyperpolarizabilities γ_{zzzz} for the sample gas Ne and the reference gas He is obtained from the relation^{21,24}

$$\gamma_{\text{Ne}}/\gamma_{\text{He}} = (S_{\text{Ne}}^{(2\omega)}/S_{\text{He}}^{(2\omega)})^{1/2} (\rho_{\text{Ne}} n'_{\text{Ne}}/\rho_{\text{He}} n'_{\text{He}})^{-1}, \quad (1)$$

where $n' = (n_0^4 n_{\omega}^3 n_{2\omega})^{1/6}$, $S^{(2\omega)}$ is the peak signal, ρ is the number density, and n_{ω} is the refractive index at frequency ω of the gas at phase match. Peak signal and optimum density are determined by a least-squares fit to the measurements of second-harmonic signal versus sample density. Sample densities were computed from the measured pressures and temperatures using the virial equation of state.²⁹ Refractive indices were calculated from tables using the measured densities.^{30,31} The local-field corrections given by n' are very small, about 0.2%, and nearly cancel to give a negligible net correction of about 0.02%. By setting the optical-field and static-field polarizations first parallel and then perpendicular, with all other conditions held constant, the ratio of the independent tensor

TABLE I. Results of the present ESHG measurements for Ne. Results are for the component γ_{zzz} unless otherwise indicated.

λ (nm)	ν (cm^{-1})	$\rho_{\text{He}}/\rho_{\text{Ne}}$	$\gamma_{\text{Ne}}/\gamma_{\text{He}}$	$(\gamma_{zzz}/\gamma_{zzz})_{\text{Ne}}$	$\gamma_{\text{Ne}}(10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3})$
594.4	16817	1.864 ± 0.008	2.20 ± 0.03		6.22 ± 0.08
514.5	19430	1.881 ± 0.012	2.28 ± 0.02	2.971 ± 0.006	6.63 ± 0.06
488.0	20487	1.872 ± 0.014	2.36 ± 0.03	2.96 ± 0.02	6.95 ± 0.09

components of γ is measured as the ratio²²

$$\gamma_{zzzz}/\gamma_{zzxz} = (S_{\parallel}^{(2\omega)}/S_{\perp}^{(2\omega)})^{1/2}. \quad (2)$$

This ratio was measured for Ar as well as Ne, as a check for systematic errors. In all cases, measurements were made in coupled triplets (*ABABA...*) in order to cancel drifts. Only a pair of triplets were feasible at each wavelength for the $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ measurements because of the limited amount of Ne gas available.

The error bars of about $\pm 1\%$ for the hyperpolarizability-ratio determinations have about equal contributions from the statistical uncertainties and from the density uncertainties due to the limited accuracy of the pressure gauge. The measured phase-match density ratio $\rho_{\text{He}}/\rho_{\text{Ne}}$ has a reproducibility of $\pm 0.1\%$ even though the accuracy of the ratio is only about $\pm 0.6\%$. The accuracy of the Kleinman symmetry measurements is determined mainly by photon-counting statistics since the signal with perpendicular fields is weak, about 20 counts/sec for Ne at $\lambda = 514.5$ nm. Since previous measurements have demonstrated that deviations from Kleinman symmetry are insignificant for Ar over the visible,²² the measured ratio $\gamma_{zzzz}/\gamma_{zzxz}$ for Ar (3.001 ± 0.004 at $\lambda = 514.5$ nm) was used to normalize the raw Ne measurement (2.972 ± 0.005 at $\lambda = 514.5$ nm), thereby removing possible residual systematic errors at the expense of slightly increasing the statistical uncertainty of the final result 2.971 ± 0.006 at $\lambda = 514.5$ nm). The uncertainty of the analogous measurement at $\lambda = 488.0$ nm is much larger, essentially because the signal was several times weaker at $\lambda = 488.0$ nm than at $\lambda = 514.5$ nm. Our experimental results are summarized in Table I.

ANALYSIS AND DISCUSSION

To extract the static value of γ_{Ne} from the experimental results presented in Table I we must take account of the frequency dependence of γ_{Ne} . When the applied field frequencies $\omega_1, \omega_2, \omega_3$ are much smaller than the lowest transition frequency of the system, the quantum-mechanical expression for γ_{zzzz} may be expanded as an even power series in the effective frequency ω_L .²⁶

$$\gamma_{zzzz}(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) = A(1 + B\omega_L^2 + C\omega_L^4 + \dots), \quad (3)$$

where

$$\omega_L^2 = \omega_{\sigma}^2 + \omega_1^2 + \omega_2^2 + \omega_3^2, \quad (4)$$

$\omega_{\sigma} = \omega_1 + \omega_2 + \omega_3$, and $A = \gamma_{zzzz}(0; 0, 0, 0)$ is the static hyperpolarizability. For the dc Kerr effect [$\gamma(-\omega; 0, 0, \omega)$],

ESHG [$\gamma(-2\omega; \omega; \omega, 0)$], and third-harmonic generation [THG, $\gamma(-3\omega; \omega, \omega, \omega)$], one has $\omega_L^2 = 2\omega^2$, $6\omega^2$, and $12\omega^2$, respectively. In the single-effective-resonance-frequency approximation the coefficient B of Eq. (3) is exactly the same for all nonlinear-optical processes in a given atom,²⁶ a result which is also supported by the results of accurate *ab initio* calculations for the H and He atoms.^{5,6} These calculations for the H and He atoms^{5,6} also show that Eq. (3) is accurate to better than 1% even when γ has increased to more than 1.5 times the static value, so an expression with the form of Eq. (3) should accurately represent our measurements as well as allowing a comparison with previous measurements from other nonlinear-optics experiments. The least-squares fit of $A(1 + B\omega_L^2)$ to our ESHG measurements of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ gives

$$\gamma_{\text{Ne}}/\gamma_{\text{He}} = (1.88 \pm 0.11)[1 + (0.96 \pm 0.27) \times 10^{-10} \text{ cm}^2 \nu_L^2], \quad (5)$$

where ν is in cm^{-1} . Our measurements of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ and the curve fitted to them are plotted versus ν_L^2 in Fig. 1.

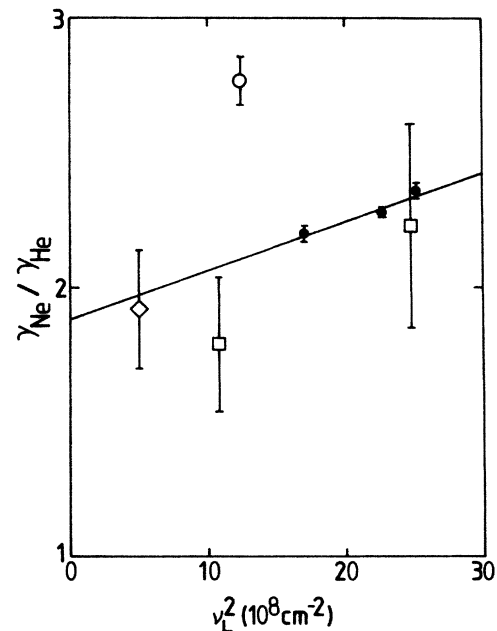


FIG. 1. Experimental measurements of the hyperpolarizability ratio $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ (see Tables I and II) made by the dc Kerr effect (diamond), ESHG (circles), and THG (squares) are plotted vs ν_L^2 [see Eq. (4)]. The straight line is a least-squares fit [see Eq. (5)] to the present ESHG measurements (filled circles).

TABLE II. Results of the previous nonlinear-optical measurements for Ne.

Process	λ (nm)	ν_L^2 (10^8 cm^{-2})	$\gamma_{\text{Ne}}/\gamma_{\text{He}}$	$(\gamma_{\text{zzzz}}/\gamma_{\text{zxxz}})_{\text{Ne}}$
dc Kerr	632.8	4.99	$1.92 \pm 0.22^{\text{a}}$	
ESHG	694.3	12.44	$2.77 \pm 0.09^{\text{b}}$	$3.01 \pm 0.05^{\text{c}}$
THG	1055	10.78	$1.79 \pm 0.25^{\text{d}}$	
THG	694.3	24.85	$2.23 \pm 0.38^{\text{e}}$	

^aReference 9.

^bReference 10.

^cReference 11.

^dReference 12.

^eReference 13.

The results of hyperpolarizability measurements for Ne from previous dc Kerr, ESHG, and THG experiments^{9–13} are collected in Table II and are also plotted versus ν_L^2 in Fig. 1. One sees that only one point in Fig. 1 deviates significantly from the straight-line fit to our ESHG measurements [Eq. (5)].

Figure 1 bears further examination. Two of the previous experiments^{9,12} actually obtained absolute measurements of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ from which we have calculated $\gamma_{\text{Ne}}/\gamma_{\text{He}}$. There are several reasons for making comparisons in terms of the ratio. Systematic errors in the measurements for He and Ne can reasonably be expected to cancel in the ratio because the experimental parameters for He and Ne are so similar. Thus, the dc Kerr effect results for γ_{Ne} and γ_{He} are both 25% high but their ratio agrees very well with Eq. (5).⁹ However, despite the fact that it is a ratio, the result of the previous ESHG experiment deviates from Eq. (5) by many times its stated uncertainty.¹¹ This is the only point that shows such a large discrepancy; it should probably be discarded. The other reason for working with the ratio $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ is that the dispersion of γ_{He} has in effect been factored out, making the curve for the ratio flatter. This makes an extrapolation to $\nu_L^2=0$ more reliable.

To obtain γ_{Ne} from $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ we employ the result for ESHG from a recent, accurate ($\pm 0.1\%$) *ab initio* calculation of γ_{zzzz} for the He atom,⁶

$$\gamma_{\text{He}} = 41.90 \text{ a.u.} [1 + (0.4515 \times 10^{-10} \text{ cm}^2) \nu_L^2 + (0.2048 \times 10^{-20} \text{ cm}^4) \nu_L^4], \quad (6)$$

where 1 a.u. = $6.2360 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ for γ . Applying Eq. (6) to our measurements of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ gives the values of γ_{Ne} listed in Table I. From Eqs. (5) and (6) we obtain the estimate $\gamma_{\text{zzzz}} = 79 \pm 5 \text{ a.u.}$ for the static hyperpolarizability of Ne. Fitting $A(1 + B\nu_L^2)$ to the γ_{Ne} values in Table I gives

$$\gamma_{\text{Ne}} = (4.65 \pm 0.33) \times 10^{-63} \text{ C}^4 \text{ m}^4 \text{ J}^{-3} \times \{1 + [(1.78 \pm 0.34) \times 10^{-10} \text{ cm}^2] \nu_L^2\}, \quad (7)$$

from which one deduces that the measured value of γ_{Ne} at $\nu_L^2 = 25 \times 10^8 \text{ cm}^{-2}$ is nearly a factor of 1.5 times larger than the static value of γ_{Ne} . The dispersion is large enough that it is probably inadequate to ignore the higher order terms of Eq. (3) when analyzing the experimental

results if an accurate extrapolation to $\nu_L^2=0$ is desired, but the data now available is insufficient by itself to determine the higher coefficients of Eq. (3). To proceed we look to the *ab initio* results for H and He for guidance.^{5,6} If all the coefficients of Eq. (3) are positive for γ_{Ne} just as for γ_{H} and γ_{He} , then the upper and lower bounds on the static value of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ will be the lowest measured value of $\gamma_{\text{Ne}}/\gamma_{\text{He}}$ and the lowest probable zero intercept for a straight line fitted to the data, respectively. The bounds on the static hyperpolarizability are thus $1.8 < \gamma_{\text{Ne}}/\gamma_{\text{He}} < 2.2$, or alternatively, $75 \text{ a.u.} < \gamma_{\text{Ne}} < 93 \text{ a.u.}$ If we assume $\gamma_{\text{Ne}}/\gamma_{\text{He}} = 2.0$ ($\gamma_{\text{Ne}} = 84 \text{ a.u.}$) at $\nu_L^2=0$, then fitting Eq. (3) to the data will give a coefficient B only half as large as that in Eq. (7). At $\nu_L^2 = 25 \times 10^8 \text{ cm}^{-2}$, γ_{Ne} will be just a factor of 1.3 times larger than the static value, and the $C\nu_L^4$ dispersion term will be half as large as the $B\nu_L^2$ term. For comparison, at the point where γ_{He} has increased 1.3 times the $C\nu_L^4$ dispersion term is just $\frac{1}{4}$ the size of the $B\nu_L^2$ term.⁶

To more accurately determine the static value of γ_{Ne} , measurements at smaller ν_L^2 are needed. Either ESHG measurements at near-infrared wavelengths or dc Kerr measurements in the visible would be suitable. The phase-match density for ESHG in the near-infrared region becomes inconveniently high ($\rho \propto \lambda^3$),²¹ and such an experiment would require a large amount of expensive Ne gas since the cell must be refilled for every measurement. Since absolute measurements can be made in a dc Kerr experiment, it has the potential advantage that one need not alternate fills of Ne and He for every measurement. But a dc Kerr experiment actually measures $\frac{3}{2}(\gamma_{\text{zzzz}} - \gamma_{\text{zxxz}})$,⁹ which is equal to γ_{zzzz} only when $\gamma_{\text{zzzz}}/\gamma_{\text{zxxz}} = 3$ (Kleinman symmetry),²² so one is forced to consider the effect of deviations from Kleinman symmetry. At low frequencies the calculated deviations from Kleinman symmetry for the H and He atoms obey the simple relation^{5,6}

$$\gamma_{\text{zzzz}}/\gamma_{\text{zxxz}} = 3(1 \pm B'\nu_L^2), \quad (8)$$

where the + sign applies for the dc Kerr effect and the – sign applies for ESHG (the same coefficient B' applies in either case). The ratios $\gamma_{\text{zzzz}}/\gamma_{\text{zxxz}}$ measured by ESHG for the inert gas atoms increase in the sequence He < Ne < Ar < Kr < Xe, passing through the value 3 at Ar.²² Since the Kleinman symmetry deviations measured for He and Ne are only slightly different, our conjecture

is that Eq. (8) is valid for Ne as well as for He. Fitting Eq. (8) to the ESHG measurements of $\gamma_{zzzz}/\gamma_{zzxz}$ in Table I gives $B' = (0.043 \pm 0.008) \times 10^{-10} \text{ cm}^2$ for Ne (the previous measurement,¹¹ listed in Table II, is consistent with our measurements but has no significant effect on the fit). Using Eq. (8) with the fitted coefficient for Ne allows one to calculate the correction required to extract γ_{zzzz} from a dc Kerr effect measurement. At $v_L^2 = 5 \times 10^8 \text{ cm}^{-2}$ the correction is only 0.1%. Furthermore, if one is only interested in extrapolating to $v_L^2 = 0$, the correction is not even necessary unless one combines dc Kerr effect measurements with other nonlinear-optical measurements. Thus, there seems to be no essential problem to prevent one from obtaining a greatly improved estimate of the static γ_{Ne} by means of ESHG or dc Kerr measurements at low v_L^2 .

Finally, we will consider the results of the *ab initio* calculations of γ_{Ne} in the light of our experimental findings. One may distinguish two levels of approximation for the atomic wave functions employed in these calculations. Calculations within the self-consistent-field Hartree-Fock (SCF-HF) approximation employ a wave function constructed as a single configuration of one-electron orbitals. Electron correlations are neglected at this level of approximation. To include the electron-correlation contributions a calculation must in effect employ a wave function composed of several electron configurations. The relevant calculations for Ne are listed in Table III.¹⁴⁻²⁰ Only the many-body perturbation-theory (MBPT) calculation²⁰ goes beyond the HF approximation. All the calculations except the variation perturbation-theory (VPT) calculations^{16,17} use the finite field method, and all the calculations except the numerical HF (NHF) calculation¹⁸ employ a finite basis set. The accuracy of a calculated higher-order property such as γ is strongly dependent on the size and flexibility of the chosen basis set,^{19,20} so the coupled HF (CHF) (Refs. 14 and 15) and VPT (Refs. 16 and 17) calculations done without optimized basis sets are probably unreliable. Even with basis-set optimization, the basis sets for the two most recent SCF-HF calculations^{19,20} may still be inadequate to allow the HF limit for γ_{He} to be approached. The NHF calculation¹⁸ is immune to the basis-set selection problem and may well give the best estimate of the HF limit for γ_{Ne} . The NHF

TABLE III. Static hyperpolarizability of Ne from various *ab initio* calculations.

Method	γ_{Ne} (a.u.)	Reference
CHF	50	14
CHF	42	15
VPT	65	16
VPT	54	17
NHF	70	18
SCF	78	19
SCF	63.9	20
MBPT(2)	95.8	20
MBPT(3)	80.5	20
MBPT(4)	104.6	20

result $\gamma_{\text{Ne}} = 70$ a.u. lies just below our experimental lower bound. The various SCF results and the experimental bounds on the static γ_{Ne} are shown in Fig. 2. The SCF results for γ_{Ne} tend to increase with improving basis set, but they are all at or below the experimental lower bound.

The results of the MBPT calculations for γ_{Ne} , complete to second, third, and fourth order, with respect to the electron-correlation perturbation, are given in Table III and are also plotted versus order in Fig. 2.²⁰ The convergence of the MBPT series is clearly very poor for γ_{Ne} , so the fourth-order correlation correction is likely to be an unreliable estimate of the total correlation correction. It is probably better to estimate the correlation contribution as the difference between the NHF result $\gamma_{\text{Ne}} = 70$ a.u. and the experimental result $\gamma_{\text{Ne}} = 84 \pm 9$ a.u. In this way one determines that the electron-correlation contribution is about 20% of the static γ_{Ne} , and that fourth-order MBPT overestimates the correlation contribution by a factor of 3. By way of comparison, in the case of He where one has an essentially exact result for the static γ_{He} (41.9 a.u.) (Ref. 6) as well as knowing the HF limit for γ_{He} (36.0 a.u.),¹⁵ the electron-correlation contribution is just 16% of the total static γ_{He} .

Results for the dispersion of γ_{Ne} are also obtained from the VPT calculations.^{16,17} However, fitting Eq. (3) to the data for γ_{Ne} in Ref. 17 gives a v_L^2 dispersion coefficient nearly four times smaller than the experimentally determined coefficient in Eq. (7). Even allowing that the dispersion coefficient in Eq. (7) probably overestimates B of Eq. (3) by a factor of 2 due to neglect of higher terms, the VPT result for the dispersion is still nearly a factor of 2 times too small.

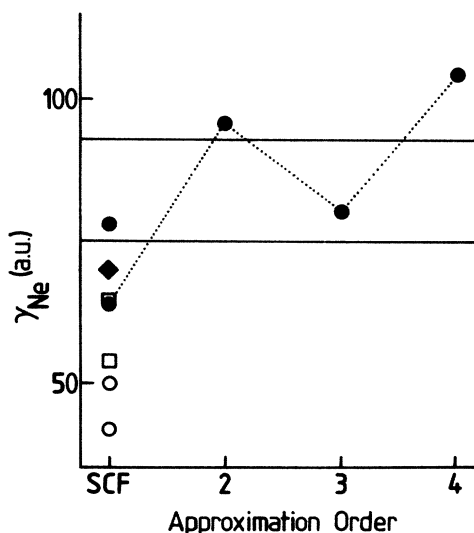


FIG. 2. Values of the static γ_{Ne} from the *ab initio* calculations listed in Table III are plotted vs order with respect to the electron-correlation perturbation. At the SCF level the calculation methods are CHF (open circles), VPT (open squares), SCF with an optimized basis set (filled circles), and NHF (filled diamond). The calculation of electron-correlation corrections is by MBPT (filled circles). The horizontal lines are the experimental bounds.

In summary, we have performed nonlinear-optical measurements for Ne with sufficient accuracy to allow a critical assessment of the previous experimental results and a meaningful consideration of the extrapolation to $\omega=0$ in order to extract the static value of γ_{Ne} . The extrapolation of the present data is somewhat equivocal so that our experimental estimate of the static value of γ_{Ne} is only reliable to $\pm 10\%$. The accuracy of this experimental estimate could be improved by an order of magnitude by further ESHG measurements in the near infrared or by a series of accurate dc Kerr effect measurements in the red. Comparison of our present experimental esti-

mate of the static value of γ_{Ne} with the results of SCF-HF calculations indicates that the electron-correlation contribution to γ_{Ne} is only about 20%, and that the fourth-order MBPT calculation overestimates the correlation contribution by a factor of 3.

ACKNOWLEDGMENTS

We thank David Bishop for making available the results of his work prior to publication. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

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