

guide for qualitative extrapolation of  $|E_4(K)|^2/K^2$  when no quantitative theory of ionization is available. For this purpose measurements of  $f'/(2W)$  out to values of  $K^2=2$  or  $K^2=3$  are needed, so that values of  $|E_4(K)|^2/K^2$  can be determined out to or beyond its maximum. The accuracy of such an extrapolation can be increased in the following way. Assume, as seems reasonable, that as a function of  $C^2$  for large fixed  $K^2$ ,  $f'/(2W)$  has a maximum of fairly symmetrical shape near  $C^2=K^2$ . It then follows that for large  $K^2$  the ratio of  $|E_4(K)|^2$  to the inelastic scattering factor is close to unity or small compared to unity when  $C_{\max}^2$  is, respectively, much greater than or much less than  $K^2$  and that this ratio is close to  $\frac{1}{2}$  when  $C_{\max}^2$  is close to  $K^2$ . Numerical calculations for He and H show that when  $C_{\max}^2=K^2-1$ , or solving for  $K$ , when  $K=V_0$

$+(V_0^2+1-2\Delta E)^{1/2}$ , the ratio of  $|E_4(K)|^2$  to the inelastic scattering factor is equal to  $\frac{1}{2}$  to within 10%. Given  $V_0$ ,  $\Delta E$ , and measurements of  $f'/(2W)$  out to  $K^2=2$  or  $K^2=3$ , the experimental data would determine  $|E_4(K)|^2$  out to or past its maximum. Extrapolation would then be carried out by using the value of  $C_{\max}^2$  to determine approximately where the curve should be placed relative to the inelastic scattering curve. Except at low velocities, the relation  $C_{\max}^2=K^2-1$  determines a particular point through which the extrapolated curve should pass. Curves 1-4 of Fig. 2 illustrate the foregoing ideas for low, intermediate, and high impact velocities. The circled points labeled 2 and 3 were determined by setting  $|E_4(K)|^2$  equal to one-half the inelastic scattering factor at the value of  $K$  for which  $C_{\max}^2=K^2-1$ .

## Optical Third-Harmonic Coefficients for the Inert Gases

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Optical third-harmonic coefficients are calculated for the inert gases and are compared with recent experimental values. We find them to range from  $0.9 \times 10^{-39}$  esu/atom for He to  $222 \times 10^{-39}$  esu/atom for Xe. Our calculated values, expressed as ratios to the optical third-harmonic coefficient of He, compare favorably with one of two sets of recently reported experimental values.

RECENTLY New and Ward<sup>1</sup> measured the optical third-harmonic coefficient for the inert gases relative to glass. Since they did not measure the absolute values of the coefficient for any gas, they presented their values scaled to  $\alpha_{zzzz}(3\nu) = 4.5 \times 10^{-39}$  esu/atom for He. Also their data reduction scheme led to two sets of experimental values.

In this paper, we calculate the optical third-harmonic coefficients for the inert gases by a very simple procedure. We find that  $\alpha_{zzzz}(3\nu) = 0.9 \times 10^{-39}$  esu/atom for He. We also find that the calculated values for the other inert gases, relative to He, fall within the experimental error of one set of experimental values of New and Ward.

We base our calculations of  $\alpha_{zzzz}(3\nu)$  on a procedure commonly used to compute the linear polarizability. The linear polarizability is given by

$$\alpha_{zz}^L(\nu) = \frac{2e^2}{\hbar} \sum_{\text{electrons}} \sum_i \nu_{ig} Z_{gi} Z_{ig} \frac{1}{\nu_{ig}^2 - \nu^2}, \quad (1)$$

$\nu_{ig}$  being the frequency difference between some excited state  $i$  and the ground state  $g$ , with  $Z_{ig}$  the correspond-

ing dipole matrix element, summed over all excited states and over all electrons. Replacing the sum over all electrons by a constant  $N_0$  (which may be thought of as some effective number of electrons), replacing  $\nu_{ig}$  in  $(\nu_{ig}^2 - \nu^2)$  by some average energy  $\nu_0$ , and using the Thomas-Reiche-Kuhn sum rule, we obtain

$$\alpha_{zz}^L(\nu) \simeq \frac{N_0 e^2}{4\pi^2 m} \left[ \frac{1}{\nu_0^2 - \nu^2} \right]. \quad (2)$$

Using Eq. (2), Culbertson<sup>2</sup> obtained a good fit to the experimental index of refraction for the inert gases by regarding  $N_0$  and  $\nu_0$  as parameters for each gas. Culbertson's values for  $N_0$  and  $\nu_0$  are reproduced in Table I.

Using the expression for the nonresonant optical third-harmonic coefficient derived by Armstrong *et al.*<sup>3</sup>,

$$\alpha_{zzzz}(3\nu) = \frac{e^4}{\hbar^3} \sum_{\text{electrons}} \sum_{i,j,k} \nu_{ig} Z_{gi} Z_{ij} Z_{jk} Z_{kg} A_{ijk}, \quad (3)$$

<sup>2</sup> C. Culbertson and M. Culbertson, Proc. Roy. Soc. (London) **135A**, 40 (1932).

<sup>3</sup> J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Persham, Phys. Rev. **127**, 1918 (1962). Our Eq. (3) is their Eq. (2.22), except for a factor of 1/4 which has been removed as per Ref. 1.

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<sup>1</sup> G. H. C. New and J. F. Ward, Phys. Rev. Letters **19**, 556 (1967).

TABLE I. Comparison of calculated values for  $\alpha_{zzzz}(3\nu)$  for  $\lambda=6943 \text{ \AA}$  with experimental values. (A) Absolute calculated values for  $\alpha_{zzzz}(3\nu)$  (in  $10^{39}$  esu/atom). (B) Calculated value of  $\alpha_{zzzz}(3\nu)$  relative to He. (C) and (D) Two sets of experimental values from New and Ward for  $\alpha_{zzzz}(3\nu)$ .

	$N_0$	$\nu_0(10^{15} \text{ cps})$	(A) $\alpha(3\nu) _{\text{calc}}$	(B) $\frac{\alpha(3\nu)}{\alpha(3\nu)_{\text{He}}} _{\text{calc}}$	(C) $\frac{\alpha(3\nu)}{\alpha(3\nu)_{\text{He}}} _{\text{expt(i)}}$	(D) $\frac{\alpha(3\nu)}{\alpha(3\nu)_{\text{He}}} _{\text{expt(ii)}}$
He	1.224	6.19	0.9	1	1	1
Ne	2.411	6.26	1.7	1.89	1.75-2.85	1.64-1.98
Ar	4.352	4.12	28	31	25-40	13-16
Kr	4.932	3.57	71	79	72-128	23-34
Xe	5.548	3.00	222	246	183-327	58-86

where

$$A_{ijk} = \frac{1}{\nu_{ig}} \left[ \frac{1}{(\nu_{ig}+3\nu)(\nu_{jg}+2\nu)(\nu_{kg}+\nu)} + \frac{1}{(\nu_{ig}-3\nu)(\nu_{jg}-2\nu)(\nu_{kg}-\nu)} + \frac{1}{(\nu_{ig}-\nu)(\nu_{jg}+2\nu)(\nu_{kg}+\nu)} + \frac{1}{(\nu_{ig}+\nu)(\nu_{jg}-2\nu)(\nu_{kg}-\nu)} \right], \quad (4)$$

we proceed along the same lines as for the linear case. Replacing the sum over the electrons by  $N_0$  and replacing  $\nu_{ig}$ ,  $\nu_{jg}$ ,  $\nu_{kg}$  in (4) by an average energy  $\nu_0$  (after subtracting off the ground-state term), Eqs. (3) and (4) may be written as

$$\alpha_{zzzz}(3\nu) \cong \frac{N_0 e^4}{h^3} A_1 \sum_{i,j,k} \nu_{ig} Z_{gi} Z_{ij} Z_{jk} Z_{kg} + \frac{N_0 e^4}{h^3} A_0 \sum_{i,k} \nu_{ig} |Z_{gi}|^2 \nu_{kg} |Z_{gk}|^2, \quad (5)$$

where

$$A_1 = \frac{4(\nu_0^2 + \nu^2)}{(\nu_0^2 - 9\nu^2)(\nu_0^2 - 4\nu^2)(\nu_0^2 - \nu^2)}, \quad (6)$$

$$A_0 = -\frac{4}{\nu_0(\nu_0^2 - 9\nu^2)(\nu_0^2 - \nu^2)}. \quad (7)$$

Using the commutation relation, the Thomas-Reiche-Kuhn sum rule, and the equation of motion for the operator  $Z_{op}$ ,<sup>4</sup> it is easy to show

$$\sum_{i,j,k} \nu_{ig} Z_{gi} Z_{ij} Z_{jk} Z_{kg} = \frac{\hbar}{2\pi m} \sum_i |Z_{gi}|^2 \cong \frac{\hbar^2}{8\pi^2 m^2 \nu_0}. \quad (8)$$

Substituting Eq. (8) in Eq. (5), we find

$$\alpha_{zzzz}(3\nu) \cong \frac{N_0 e^4}{16\pi^4 m^2 \hbar} \frac{(\nu_0^2 + 6\nu^2)}{\nu_0(\nu_0^2 - 9\nu^2)(\nu_0^2 - 4\nu^2)(\nu_0^2 - \nu^2)}. \quad (9)$$

In Table I, we show our calculated values of  $\alpha_{zzzz}(3\nu)$  for  $\lambda=6943 \text{ \AA}$  where we have used Culbertson's values for  $N_0$  and  $\nu_0$ . Also shown are our calculated values for  $\alpha_{zzzz}(3\nu)$  relative to that of He (B), and these are compared with the two sets of experimental values (C) and (D) of New and Ward.

It appears that our relative calculated values agree within New and Ward's experimental error with their experimental set (C).

It is obvious that one may apply our simple procedure to calculate other third-order coefficients for the inert gases such as the dc hyperpolarizability  $\alpha(0;0,0,0)$ , the Kerr coefficient  $\alpha(-\nu;0,0,\nu)$ , etc.

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