Electric-field-induced optical rectification in nitrobenzene*

J. F. Ward and J. K. Guha[†]

The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109
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The first observation of dc-electric-field-induced optical rectification is reported. In this process a dc polarization is produced in a medium (in this case nitrobenzene) by the simultaneous presence of dc and optical electric fields. The relation between this process and the Kerr effect is found to be consistent with that predicted by permutation symmetry. A bolometerlike response also seen in these experiments is discussed.

Optical rectification[1] refers to the generation of a dc electric dipole moment in a medium by an optical beam propagating through it. Optical rectification and second-harmonic generation are both forbidden in centrosymmetric media but this symmetry restriction is lifted in the presence of a dc electric field. dc-electric-field-induced optical second-harmonic generation was first reported by Mayer[2]: we now wish to report a demonstration of dc-electric-field-induced optical rectification (DCIOR).

This process can be described by a coefficient $X(0;0, \omega, -\omega)$ which relates a dc polarization amplitude $\mathbf{P}^0$ to a product of optical and dc electric field amplitudes ($\mathbf{E}^\omega$ and $\mathbf{E}^0$ respectively):

$$\mathbf{P}^0 = \tfrac{3}{2}X(0;0, \omega, -\omega)\mathbf{E}^0\mathbf{E}^\omega\mathbf{E}^{\omega*} \qquad (1)$$

The factor $\tfrac{3}{2}$ and other details of conventions used here are discussed in Ref. 3. It may be noted that the analogous expression for the dc Kerr effect is

$$\mathbf{P}^\omega = 3X(-\omega;\omega, 0, 0)\mathbf{E}^\omega\mathbf{E}^0\mathbf{E}^0 \qquad (2)$$

and the elements of these two tensor coefficients are related by permutation symmetry[4]·

$$X_{ijkl}(-\omega;\omega, 0, 0) = X_{klji}(0;0, \omega, -\omega). \qquad (3)$$

Thus nitrobenzene, having the largest known Kerr coefficient, is the natural choice for a demonstration of electric-field-induced optical rectification. We have observed additional effects not related to DCIOR and these will also be described.

A schematic diagram of the apparatus is shown in Fig. 1. A 5-MW 20-nsec ruby laser pulse passes through a nitrobenzene-filled Kerr cell with electrodes typically maintained at a potential difference of 10 kV. Fast changes in this potential (with amplitudes in the mV range) generated by the passage of the laser beam are amplified and displayed on an oscilloscope. Provi-
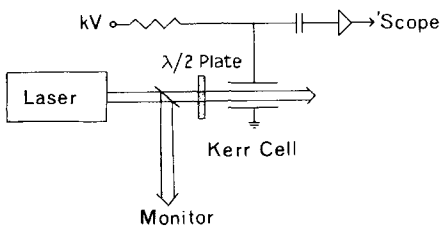
sion is made for monitoring and varying the laser power and rotating the plane of polarization of the linearly polarized incident beam. Oscilloscope traces for various values of the angle θ between the optical electric field and the applied dc field are shown in Fig. 2.

Two components of the signal shown in Fig. 2 may be distinguished: (i) A negative signal (tending to decrease $\mathbf{E}^0$) with time dependence similar to the laser power and with marked polarization dependence. (ii) A steplike positive signal with magnitude independent of laser beam polarization.

In addition, on a longer timescale than is shown in Fig. 2, a third component is seen: (iii) A negative signal with rise time ~1 μsec. We will return to a discussion of (ii) and (iii) after first considering (i) which we believe to be due to DCIOR.

It can be shown that the peak DCIOR signal voltage $V(\theta)$ is related to the nonlinear coefficient by

$$V(\theta) - V(\tfrac{1}{2}\pi) = -E^0 P \cos^2\theta[48\pi^2/n\epsilon wc]$$
$$\times [X_{yyyy}(0;0, \omega, -\omega) - X_{yyxx}(0;0, \omega, -\omega)]$$
$$(4)$$

and

$$V(0)/V(\tfrac{1}{2}\pi) = X_{yyyy}(0;0, \omega, -\omega)/X_{yyxx}(0;0, \omega, -\omega), \qquad (5)$$

where P is the peak laser power, ϵ is the dc dielectric constant of nitrobenzene, w is the width of the Kerr cell plates, and c is the speed of light. Forming the dif-

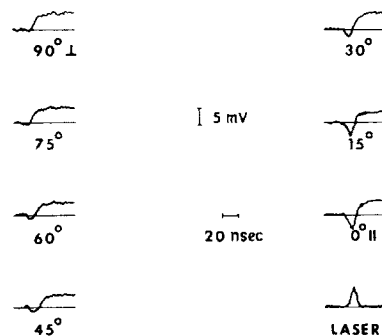FIG. 1. Schematic diagram of the apparatus.

FIG. 2. Tracings of oscilloscope photographs of the signal for various values of the angle θ between the optical and dc electric fields. The vertical scale refers to signal voltages at the oscilloscope where 5 mV corresponds to 4.2 mV at the cell unloaded by the preamplifier. The laser pulse is also shown.

ference $V(\theta) - V(\frac{1}{2}\pi)$ between observed signals serves to extract the polarization-dependent component (i). This difference is found to be linear in P, in E^0 [see Fig. 3(i)] and in $\cos^2\theta$ (see Fig. 4) as predicted by Eq. (4), and the measured magnitude of $V(\theta) - V\frac{1}{2}\pi$ together with Eq. (4) yields a value for the coefficient:

$$X_{yyyy}(0;0, \omega, -\omega) - X_{yyxx}(0;0, \omega, -\omega)$$

$$= +1.2\times10^{-10} \text{ esu} \pm 30\%, \tag{6}$$

where the uncertainty is mostly due to uncertainty in the laser power calibration. This value may be compared with

$$X_{yyyy}(-\omega;\omega, 0, 0) - X_{yyxx}(-\omega;\omega, 0, 0)$$

$$= nB\lambda/6\pi = +1.6\times10^{-10} \text{ esu}, \tag{7}$$

where B, the Kerr coefficient at 20 °C and 6943 Å, has been estimated as 2.78×10^{-5} esu from data given in Ref. 5. It should be noted that the optical pulse duration is much longer than orientational relaxation times for nitrobenzene so that the use of the dc Kerr coefficient here is appropriate. We conclude that the observed signal component (i) is due to DCIOR and that the numerical agreement between Eqs. (6) and (7) confirms the prediction [Eq. (4)] based on permutation symmetry.

The consequences of laser beam polarization modification by dc and optical Kerr effects should be considered. The DCIOR signal is not changed by either effect individually, and whereas the two effects in combination can produce a change, that change is negligibly small in these experiments. We see no evidence of self-focusing in the beam emerging from the cell.

The ratio $X_{yyyy}(-\omega;\omega, 0, 0)/X_{yyxx}(-\omega;\omega, 0, 0)$ has been measured[6] to be -2, and the corresponding ratio can, in principle, be extracted from the measured $V(\theta)/V(\frac{1}{2}\pi)$ using Eq. (5). In practice, however, lack of detailed knowledge of the step-function signal (ii) and
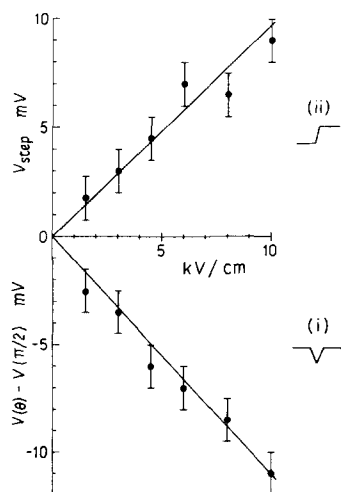

FIG. 3. Magnitude of signal components (i) and (ii) (see text) as functions of the applied dc electric field. Vertical scale refers to signal voltages at the oscilloscope input as in Fig. 2.
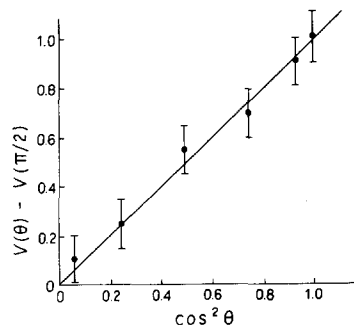

FIG. 4. Dependence of peak DCIOR signal on laser beam polarization. (Signal normalized to unity at $\theta = 0°$).

noise (see Fig. 1) preclude drawing a meaningful conclusion on this ratio from our data.

The step-function signal (ii), we believe, is due to optical absorption in the nitrobenzene leading to a decrease in the dielectric constant with increasing temperature at constant density (ρ). Such a signal would be positive going (tending to increase the applied dc field) and would evolve in time as the integral of the laser power and its magnitude (V_{step}) would have the same linear dependence on P and E^0 [Fig. 3(ii)] as the DCIOR signal but, in contrast to that signal, would be independent of polarization angle θ. The observed signal has all these characteristics and the measured ratios of step height to maximum DCIOR signal is about 0.8. An expression for this ratio may be written

$$\frac{V_{step}}{V(0) - V(\frac{1}{2}\pi)} = -\frac{\partial\epsilon}{\partial T}\bigg)_\rho \frac{kT\omega}{16\pi^2 C_v\rho B}, \tag{8}$$

where τ is the laser pulse duration and C_v is the specific heat of nitrobenzene. We use $\partial\epsilon/\partial T)_\rho = -0.2 °C^{-1}$ as an estimate for $\partial\epsilon/\partial T)_\rho$ and a measured value for the optical absorption coefficient[7] $k = 2.3\times10^{-3}$ cm^{-1} (corresponding to 0.5% absorption over the 2-cm length of our cell) to evaluate the expression on the right-hand side of Eq. (8). This yields the value 0.3 which, considering the uncertainties involved, we find to be in satisfactory agreement with the measured ratio, 0.8. It may be remarked that this response corresponds to a bolometer (of modest sensitivity) with fast (subnanosecond) response time. Such a bolometer could be realized for radiation of any frequency where a polar fluid of suitable absorption length and high resistivity is available.

The third signal (iii) is negative going with a time constant of about 1 μsec and varies erratically from shot to shot. We conjecture that this may arise from the generation of mobile charges from dust particles suspended in the nitrobenzene, within the laser beam.

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Diffraction-limited KrF and XeF lasers with a negative-branch unstable resonator*

T. J. McKee, B. P. Stoicheff, and Stephen C. Wallace

Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7
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Diffraction-limited performance has been achieved in discharge-excited KrF and XeF lasers by using an
unstable resonator configuration. A peak power of 5 MW (50 mJ) was produced from a Blumlein circuit
with stored energy of only 5 J.

Recent work on noble-gas halide exciplex lasers has led to their recognition as high-intensity sources of ultraviolet radiation.[1-4] Many of the efforts in this field have been aimed at scaling these lasers in standard configurations to larger active volumes and higher pulse energies. However, the large mode volume intrinsic to their operation also implies that an unstable resonator configuration[5] would lead to significant improvement in the output characteristics, particularly the spatial properties of the output beam. In this paper, we describe a high-brightness KrF/XeF laser employing a negative-branch unstable resonator. This novel design produces a 5-MW (50-mJ) pulse in a near-diffraction-limited beam from a modest Blumlein configuration having a stored energy of approximately 5 J.

A schematic diagram of the laser is shown in Fig. 1. The Blumlein circuit was fabricated from a copper-clad fiber-glass-epoxy-laminate circuit board[3] (92 cm ×122 cm×0.16 cm), etched where necessary to provide an insulating surface. The discharge channel (90 cm ×7 cm×3 cm) was made of glass, with quartz end windows slightly tilted, and with nickel-plated electrodes (87 cm long, separation 1.8 cm) cemented in place with epoxy. These electrodes were designed to provide an unsymmetrical excitation volume and uniform discharge: the cathode was a sharpened electrode of 0.1 cm radius at the point and the anode was flat faced, 1.2 cm wide. A triggered spark gap,[6] pressurized to 30 psi with nitrogen, initiated the discharge. At a maximum operating voltage of 30 kV, the energy stored in one half of the Blumlein circuit was estimated to be 5 J.

With the selection of helium : noble gas : fluorine as the laser medium, some care was required to ensure the safe handling of the fluorine. This problem was readily solved by using a dilute (2%) mixture of fluorine

in helium, and by keeping the total volume of fluorine at a minimum. A small Monel vacuum system was employed to prepare the gas mixture. After an initial degree of corrosion during passivation, the nickel-plated electrodes have successfully withstood the contact with fluorine, even after several months of operation and approximately 10^5 discharges.

The optics for the unstable resonator consisted of two concave mirrors (M_1 and M_2 with radii of curvature 100 and 200 cm, respectively, separated by 150 cm) and a diagonal coupling mirror as shown in Fig. 1. Mirror coatings of Al + MgF$_2$ optimized for the 2000—3000-Å region were used and gave reflectivities $R > 0.9$. The choice of a magnification of $m = 2$ was determined by the desired geometrical output coupling, $\gamma = 0.75$ where $\gamma = 1 - 1/m^2$. With this magnification, the maxi-
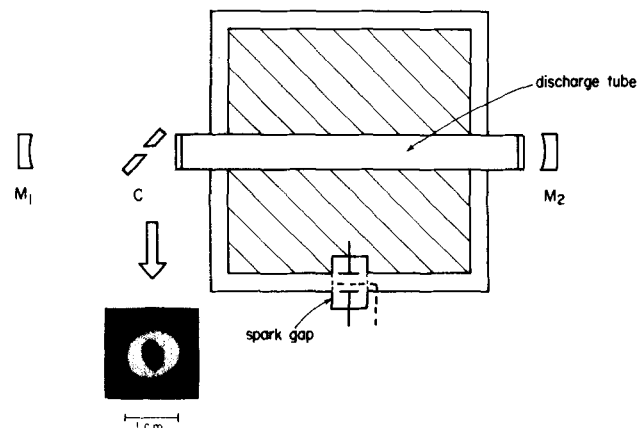

FIG. 1. Schematic diagram of the unstable resonator configuration. M_1 and M_2 are concave mirrors of 100 and 200 cm radius of curvature, respectively, and C is a planar coupling mirror. The shape of the output beam is shown in the inset.