

the field dependence of $1/\tau_n$ in pure Kr (0.97 Torr) and in a mixture of Kr (0.9 Torr) and He (53 Torr). At the same Kr pressure the relaxation rate in low fields is decreased in the presence of He. This comes indeed from the shortening of τ_{c1} as is also revealed by the broadening of the curve giving the field dependence of $1/\tau_n$. As expected, in high fields relaxation rates are the same: Direct measurements in pure He had previously shown that Rb-He collisions have a negligible effect at 53 Torr.

A detailed analysis, to be published elsewhere, shows that the above picture leads to a satisfactory quantitative description of the main features of interaction I. The metastable states of the alkali-metal-rare-gas pair have not been observed directly in scattering experiments; such an observation seems unlikely because the unrelated resonances are so narrow ($\hbar\tau_{jN}^{-1}/kT \approx 10^{-6}$). On the other hand, the relaxation of alkali metals is obviously very sensitive to their existence; their probability of being formed is indeed small, but the time during which the disorienting interaction lasts and its correlation time are approximately 10^4 times longer

than in ordinary collisions. The same remark holds for actual bound states.

We have observed a very similar behavior of the relaxation of Rb in Xe and Ar.

We are grateful to Dr. C. Bouchiat, Dr. D. Kleppner, and Dr. P. Sabatier for stimulating discussions about the theoretical interpretation of the results, and to Dr. P. L. Bender for most helpful comments on the manuscript.

¹M. Aymar, M. A. Bouchiat, and J. Brossel, Phys. Letters **24A**, 753 (1967), hereafter referred to as PR1.

²M. A. Bouchiat, J. Phys. Radium **24**, 379, 611 (1963); M. A. Bouchiat and J. Brossel, Phys. Rev. **147**, 41 (1966).

³Any observable Q_i relaxing exponentially with time τ_i is associated with a disorientation cross section σ_i given by $1/\tau_i = N_0 \sigma_i \bar{v}_{rel} \rho / p_0$; N_0 is the number of atoms per cc at pressure p_0 ; \bar{v}_{rel} is the relative velocity.

⁴R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).

⁵A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **73**, 455 (1959); Fr. von Busch, H. J. Strunck, and Ch. Schlier, Z. Physik **199**, 518 (1967).

⁶We are indebted to Dr. Bender for stressing the importance of three-body collisions.

GENERATION OF A PHASE-MATCHED OPTICAL THIRD HARMONIC BY INTRODUCTION OF ANOMALOUS DISPERSION INTO A LIQUID MEDIUM

Paul P. Bey, John F. Giuliani, and Herbert Rabin

Naval Research Laboratory, Washington, D. C.

(Received 31 July 1967)

The use of anomalous dispersion in producing phase matching in nonlinear optical processes has been recognized in several references in the nonlinear-optics literature,¹⁻⁴ and the anomalous dispersion associated with the strong infrared resonance inherent in quartz has been employed in producing a far-infrared difference frequency.⁵ The present Letter provides the first experimental evidence that phase matching may be achieved in a nonlinear optical process by introduction of anomalous dispersion into a normally unmatched medium.

The principle is indicated schematically in Fig. 1. Curve *a* shows the normal dispersion of a medium and the typical index mismatch, $\Delta n = n_h - n_f$, between two frequencies ω_h and ω_f . In the harmonic generation process here under consideration, these are the harmonic

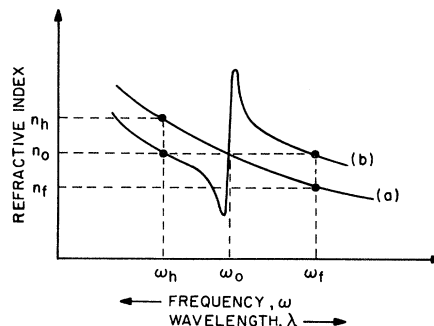


FIG. 1. Principle of phase matching by anomalous dispersion. Curve *a* shows a normally dispersive medium with $n_h > n_f$ at the frequencies ω_h and ω_f . Curve *b*, the same medium after the introduction of anomalous dispersion centered at ω_0 , resulting in identical indices n_0 at the two frequencies.

and fundamental frequencies, respectively. Upon introduction of an appropriate resonant absorption at an intermediate frequency ω_0 , where $\omega_f < \omega_0 < \omega_h$, the associated anomalous dispersion produces a modified refractive index shown in Curve *b*. Under suitable conditions, corresponding to sufficiently large oscillator strength and concentration of resonant absorbers, the modified indices at ω_f and ω_h may be made equal to a common value n_0 , and phase matching in harmonic generation results.

Attention in the present work has been directed to the production of phase-matched third harmonic of the neodymium laser line at 1.06μ by introduction of dye molecules into a liquid medium. The system consists of the dye fuchsin red, $C_{22}H_{24}N_3Cl$, dissolved in hexafluoroacetone sesquihydrate, $(CF_3)_2CO \cdot 1.5H_2O$.⁶ (For brevity the solvent will be referred to simply as "HS.") The choice of HS as the liquid medium is based on its high solvency for fuchsin, an unusually low index mismatch in the pure state between 1.06μ and the third-harmonic wavelength at $353 m\mu$ ($\Delta n = 0.014$), and as shown in Curve *b* of Fig. 2, high optical transparency from the infrared into the ultraviolet. The interest in fuchsin arises from a large dispersive effect in solution, and accordingly its possible use for index matching over an extended wavelength range as first noted by Maker, Terhune, and Savage.² Furthermore, the principal absorption of fuchsin in HS at $570 m\mu$ occurs at a satisfactory intermediate wavelength between 1.06μ and $353 m\mu$ as shown in Curve *c*, and fuchsin in HS also shows good optical transparency at the fundamental wavelength. The principal disadvantage is the relatively high absorption at $353 m\mu$, and it is the occurrence of a partial window seen in Curve *d* which allows the buildup of third-harmonic signal.

The experimental data were obtained with a giant pulsed Korad K1QP neodymium glass laser with a mode-selecting-output resonant reflector, Q switched with Kodak No. 9740 dye. Laser pulses of 20- to 30-nsec widths at half-maximum were monitored with an ITT photodiode and recorded on a Tektronix 519 oscilloscope. The peak laser power was $1.0 MW/cm^2$ on the average; however, spatial intensity variations observed across the beam undoubtedly contributed to larger local power densities. The third-harmonic signal was isolated from the laser beam with band-pass Corning-

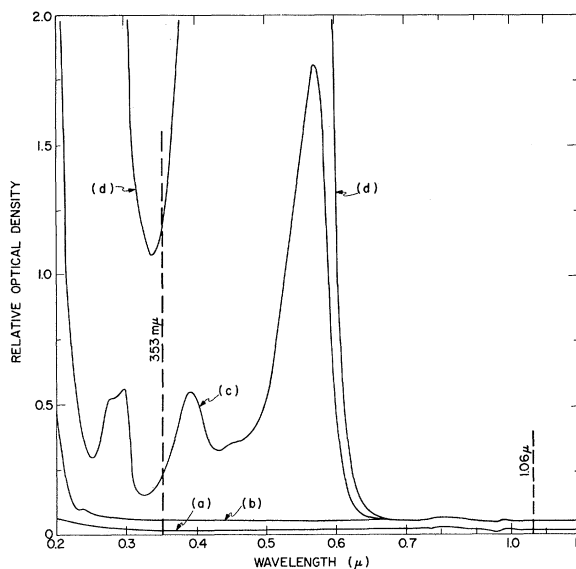


FIG. 2. Optical absorption spectra obtained with a Cary model No. 14 spectrophotometer: (a) base line of the instrument, (b) hexafluoroacetone sesquihydrate (HS), (c) fuchsin in HS, 1 g/liter, and (d) fuchsin in HS, 20 g/liter. Curves *b* through *d* are data as measured in a fused-quartz liquid cell of sample path length 0.0105 cm. The positions of the neodymium laser line at 1.06μ and its third harmonic at $353 m\mu$ are indicated.

glass filters before detection with an Amperex 56TUV photomultiplier and subsequent recording with a Tektronix 585A oscilloscope. The presence of third harmonic at $353 m\mu$ was confirmed with a Bausch and Lomb grating monochromator to within $\pm 4.2 m\mu$. Third-harmonic pulses showed typical narrowing compared with the fundamental pulse as is characteristic of this third-order process.

The generation of third-harmonic radiation as a function of concentration of fuchsin in HS is shown in Fig. 3 for a normalized fundamental power of $1.0 MW/cm^2$. This normalization assumes a third-power law between the intensities of the third-harmonic radiation and the fundamental, i.e., $I^3\omega \propto (I\omega)^3$. The data show a clearly defined resonance peaking near a critical dye concentration of approximately 44 g/liter. The wings of this resonance are associated with harmonic signal generated in the windows of the fused-quartz liquid cell, the unmatched dye solution, and other elements in the optical path.

The sharp resonance in Fig. 3 is attributed to the production of phase-matched third-harmonic radiation. This interpretation is supported by refractive index measurements at

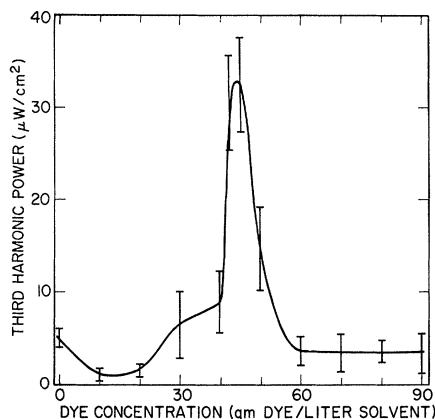


FIG. 3. Peak intensity of third-harmonic radiation at $353\text{ m}\mu$ as a function of concentration of fuchsin in HS as measured in a fused-quartz liquid cell of sample path length 0.0503 cm . All data are normalized for a fundamental laser power of 1.0 MW/cm^2 according to a variation of intensity of the third harmonic as the cube of the fundamental. The indicated values extend over the extremes in data obtained in three to eight separate laser shots at each concentration.

$1.06\text{ }\mu$ and $353\text{ }\mu$ which will be reported later in a more complete account of this work. The difficulty in precisely measuring refractive index in the presence of strong absorption at $353\text{ m}\mu$ does not allow an exact determination of the index-matched dye concentration. The data, nevertheless, indicate a crossing over of the fundamental and harmonic indices in passing through the region of resonance shown in Fig. 3.

Also left for subsequent discussion in the explanation of the theoretical shape of the resonance of Fig. 3 which can be described in the small-signal approximation by an expression

of the form

$$I^3 \omega \propto \chi^2 \frac{\{e^{-3\alpha_1 l} + e^{-\alpha_3 l} - 2e^{-[\frac{1}{2}(3\alpha_1 + \alpha_3)]l} \cos(l\Delta k)\}}{(\Delta k)^2 + [\frac{1}{2}(\alpha_3 - 3\alpha_1)]^2},$$

where χ is the appropriate third-order susceptibility, α_1 and α_3 the linear absorption coefficients at the fundamental and third-harmonic frequencies, l the path length through the liquid sample, and $\Delta k = k_3 - 3k_1$, where k_1 and k_3 are the wave vectors at the laser and harmonic frequencies, respectively. The maximum of the resonance in Fig. 3 occurs for $\Delta k \approx 0$ and is attained in the presence of strong third-harmonic absorption amounting to 670 cm^{-1} for α_3 . Clearly, harmonic conversion efficiency is enhanced by minimizing α_3 , and work in this direction is currently underway.

The authors are pleased to acknowledge valuable discussions with Professor David L. Dexter during the course of this investigation.

¹P. A. Franken and J. F. Ward, *Rev. Mod. Phys.* **35**, 23 (1963), p. 29.

²P. D. Maker, R. W. Terhune, and C. M. Savage, in *Proceedings of the Third Conference on Quantum Electronics*, Paris 1963, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 1563.

³N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965), p. 85.

⁴J. A. Giordmaine, *Phys. Rev.* **138**, A1599 (1965); see p. A1606.

⁵F. Zernike, Jr., and P. R. Berman, *Phys. Rev. Letters* **15**, 999 (1965).

⁶The dye was obtained from Fisher Scientific Co., catalog No. A803, and the solvent from E. I. du Pont de Nemours and Co. Both were used as received, without additional treatment.