Efficient selective optical excitation for isotope separation, using short laser pulses

J.-C. Diels
Center for Laser Studies, University of Southern California, Los Angeles, California 90007
(Received 8 September 1975)

Propagation of short ($\lesssim T_2$, where T_2 is the phase relaxation time) light pulses through absorbing media consisting of two ensembles of two-level systems of slightly different transition frequency is considered here. It is shown that one group of absorbers can be totally excited (inverted) while the other is returned to ground state. The effect of inhomogeneous broadening is illustrated by examples of propagation (numerical simulation) of properly shaped pulses through media having a linewidth equal to 1/5 of the frequency separation between the two transitions. The initial proportion of the two-level mixture is: 5% of the element to be excited, 95% of the element to be kept in ground state. The selective excitation capabilities of a Gaussian pulse and a zero-area pulse are compared.

I. INTRODUCTION

Isotope separation with lasers is based on selective optical excitation of a transition of the element to be extracted. The present study deals exclusively with the selective optical-excitation process, disregarding further processing of the optically excited molecules. Pulsed flashlamp-pumped dye lasers are the most promising for this application because of their tunability and relatively high efficiency. Little consideration, however, has been given to the optical-pumping process itself. There seem to be two fundamental limitations to the efficiency of conventional optical excitation:

(i) The ratio of upward transitions (excitation) to the number of incident photons is maximum for the lowest light intensities. The quantum efficiency is then maximum when the rate of production of excited states approaches zero. At saturation intensities, the rate of excitation is high but the quantum efficiency decreases to zero with increasing irradiating power.

(ii) The absorbing lines have to be well separated. This is seldom the case for electronic transitions of medium-heavy to heavy elements. Even in the case of a light element such as lithium, off-resonance pumping of the unwanted isotope can occur with a powerful light source tuned to resonance with the selected species. The selectivity of the optical excitation may therefore become very poor at high power levels.

It is shown here that by using short pulses in the coherent interaction regime a total excitation (population inversion) of a selected isotope is possible with quantum efficiency close to one, while the other is left in the ground state. This selection occurs even though the pulse spectrum overlaps both lines. In one of the schemes proposed here, the exciting radiation is even chosen resonant with the "unwanted-isotope" absorption line. The selective excitation process is illustrated first with a simple example, assuming that the line broadening (Doppler and collision broadening) can be neglected.

For comparison, a discussion of the saturation regime and its limitation follows. Computer-simulation results are presented to determine the effect of inhomogeneous broadening and the useful propagation distance, for various excitation schemes: a square pulse, a Gaussian pulse, a square zero-area pulse, and a "Gaussian" zero-area pulse.

In all of the numerical examples, the initial mixture contains 5% of the isotope to be selected and 95% of the unwanted isotope. The frequency separation between both absorption peaks is taken to be five linewidths. The parameters of the initial pulse are optimized for the separation process. Next, the propagation of this pulse is simulated, and the selective excitation is found to be enhanced with propagation distance. The price for the optimized efficiency and separation factor is that the pulse shape, energy, and duration are no longer arbitrary. However, a wide variety of pulse shapes are found which conserve their selective excitation properties after propagation over long distances. As will be shown in a subsequent paper, many of the results presented here can be transposed to two-photon transitions. However, the enhancement of the separation factor with propagation distance through pulse reshaping is unique to the dipole transition considered here.

II. SIMPLIFIED MODEL

A. Square pulse (π-2π) selection

A plane wave of average frequency $\omega + \langle\dot{\varphi}\rangle$, where

$$\langle\dot{\varphi}\rangle = \int_{-\infty}^{\infty} \mathcal{E}^2\dot{\varphi}\,dt \Big/ \int_{-\infty}^{\infty} \mathcal{E}^2\,dt$$

and of wave vector k propagating along a direction

z is described by

$$E(z,t)=\mathcal{E}(z,t)\exp\{i[\omega t+\varphi(z,t)-kz]\}+\text{c.c.} \tag{1}$$

In the slowly-varying-envelope approximation, the semiclassical Bloch-Maxwell equations relating field and polarization can be written[1]

$$\dot{u}=(\Delta\omega-\dot{\varphi})v-u/T_2\ , \tag{2}$$

$$\dot{v}=-(\Delta\omega-\dot{\varphi})u-v/T_2-\kappa\mathcal{E}w\ , \tag{3}$$

$$\dot{w}=\kappa\mathcal{E}v-(w-w_0)/T_1\ , \tag{4}$$

$$\frac{\partial\mathcal{E}}{\partial z}+\frac{n}{c}\dot{\mathcal{E}}=-\frac{2\pi\omega}{nc}\int_{-\infty}^{\infty}vg(\delta)\,d\delta\ , \tag{5}$$

$$\mathcal{E}\left(\frac{\partial\varphi}{\partial z}+\frac{n}{c}\dot{\varphi}\right)=-\frac{2\pi\omega}{nc}\int_{-\infty}^{\infty}ug(\delta)\,d\delta\ . \tag{6}$$

Here, u and v are, respectively, the in-phase and 90°-out-of-phase components of the polarization and $w=p(N_2-N_1)$ describes the population difference between the upper and lower levels of the nondegenerate transition. A phenomenological phase relaxation time T_2 for the polarization and an energy relaxation time T_1 for w are included. The inhomogeneous broadening is described by the function $g(\delta)$. In $\kappa=2p/\hbar$, p is the dipole moment of the transition. $\Delta\omega=\omega_0-\omega+\delta$ is the difference between the light frequency and a particular transition frequency. Pulses of light will often be characterized by their area, which is the value of the Fourier amplitude

$$\kappa\left|\tilde{\mathcal{E}}(\Omega)\right|=\kappa\int_{-\infty}^{\infty}\mathcal{E}e^{i(\omega t-\Omega t+\varphi)}dt$$

at the average pulse frequency $\langle\Omega\rangle=\omega+\langle\dot{\varphi}\rangle$.

Let us assume first that the pulse duration is shorter than all relaxation times, and that the inhomogeneous broadening can also be neglected. Assuming two lines corresponding to two distinct isotopes,

$$g(\delta)=\begin{cases}1, & \text{for } \delta=0 \text{ and } \delta=\Delta\omega_0\\ 0, & \text{otherwise}\ .\end{cases}$$

Let us consider a square pulse, without phase modulation, of amplitude $\mathcal{E}_1$ and duration τ, driving the polarization described by Eqs. (2)–(4). If

$$\Delta\omega_0\tau=\sqrt{3}\ \pi \tag{7}$$

and

$$\theta=\kappa\mathcal{E}_1\tau=\pi\ , \tag{8}$$

a complete population inversion will be achieved for the line at resonance, while the line off-resonance will be left in the ground state after the pulse has been switched off. The resonant excitation corresponds to a "π pulse" or a rotation of the pseudopolarization vector by an angle of 180°, while the off-resonance excitation corresponds to a $\tau(\Delta\omega^2+\kappa^2\mathcal{E}^2)^{1/2}=2\pi$ pulse, or a complete cycle of the pseudopolarization vector.

The decrease of pulse energy

$$\mathcal{T}=\frac{nc}{4\pi}\int_{-\infty}^{\infty}\mathcal{E}^2\,dt$$

with distance is given by[1]

$$\frac{d\mathcal{T}}{dz}=-\frac{\omega}{\kappa}\Delta w\ , \tag{9}$$

where $\Delta w/2p=(w_\infty-w_0)/2p$ is the number of upwards transitions induced by the light pulse. We see from (9) that the quantum efficiency of this selective excitation is equal to unity.

Before a more detailed analysis of the use of coherent interaction properties for efficient isotope separation is made, a short discussion of the limitations of a classical pumping scheme is presented.

B. Rate-equations approach

The inhomogeneous broadening will at first be neglected in this section. For pulses long compared with the phase relaxation time T_2, the following rate equations can be derived from the system of equations (2)–(4):

$$\dot{w}=-\frac{T_2}{1+\Delta\omega^2T_2^2}\kappa^2\mathcal{E}^2w-\frac{w-w_0}{T_1}\ . \tag{10}$$

For a square pulse of amplitude $\mathcal{E}$ and duration τ applied at resonance with the line I and off-resonance by an amount $\Delta\omega_0$ from the line M, a "separation factor" s can be defined as

$$s=\frac{\Delta w_I/2w_{0I}}{\Delta w_M/2w_{0M}}=\frac{1+\Delta\omega_0^2T_2^2+\kappa^2\mathcal{E}^2T_1T_2}{1+\kappa^2\mathcal{E}^2T_1T_2}\ . \tag{11}$$

At low power levels, where the separation factor is maximum, a fraction $1/(1+\Delta\omega_0^2T_2^2)$ of the "unwanted" transition M is excited. If the lines are five linewidths (T_2^{-1}) apart, the maximum separation factor s that can be achieved here is only 26. If the pulses are not short compared with the energy relaxation time T_1, the quantum efficiency of the absorption is reduced:

$$\eta=\left(\frac{\omega}{\kappa}\right)\Delta w\Big/\left(-\frac{d\mathcal{T}}{dz}\right)$$

$$=1\Big/\left(1+\frac{\tau}{T_1}+\frac{1+\Delta\omega^2T_2^2}{\kappa^2\mathcal{E}^2T_1T_2}e^{-\tau/T_1}\right). \tag{12}$$

The essential feature of the conventional excitation in Eq. (11) is that the separation factor *de-*

creases with increasing power. Therefore in an actual separation process the enrichment factor would decrease with the production rate. The decrease of separation factor with increasing power is inevitable in the steady-state approach, where the homogeneous broadening cannot be neglected. In Sec. III we will consider pulses short compared with T_2, and only an inhomogeneous broadening need be taken into account.

In the rate-equation approach, the separation factor is more difficult to evaluate if the line broadening is both homogeneous and inhomogeneous. However, the line integrations can be performed analytically in the case of an inhomogeneous Lorentzian broadening (inhomogeneous relaxation time T^*), and for the condition

$$1+\kappa^2\mathcal{E}^2T_1T_2=T_2^2/T^{*2}$$

yielding a separation factor

$$s=1+\tfrac{1}{4}\Delta\omega^2T^{*2}\ .$$

If the lines are five (total) linewidths apart for $T^*=T_2$, the maximum (zero-field limit) separation factor is again only 26. The same maximum separation factor applies also in the limit of pure Lorentzian inhomogeneous broadening ($\Delta\omega_0=5T^*$).

C. Figure of merit

For the same separation factor, preference would be given to the scheme that requires the smallest power for the maximum number of excited molecules. This can be expressed by requiring that the dimensionless quantity

$$r=\frac{(\omega/\kappa)\Delta w_I}{2\alpha_I\mathcal{T}}\,\frac{w_{0M}\Delta w_I}{w_{0I}\Delta w_M}$$

or (13)

$$r=\left|\frac{\Delta w_I}{2w_{0I}}\right|\frac{w_{0M}\Delta w_I}{w_{0I}\Delta w_M}\,\frac{(\text{linewidth})}{\int_{-\infty}^{\infty}\kappa^2\mathcal{E}^2\,dt}$$

be the largest possible, where α_I is the linear absorption coefficient at the selected isotope frequency,

$$\alpha_I=4\pi\omega\kappa w_{0I}g_1(0)/nc\ .$$

This number will prove useful in the selection of the parameters of the initial pulse. From (12) and (13), $r\le\frac{1}{2}\eta s$, with the equality holding for linear absorption.

III. SQUARE PULSE (π-2π) SELECTIVE EXCITATION

The propagation of a square pulse satisfying conditions (7) and (8) is highly nonlinear. Phase modulation of the pulse will occur because the main absorption line is off-resonance. In addition, some light will be reemitted at the pulse tail, and the steep flanks of the square pulse will be differentiated. Deeper insight into the problem therefore requires numerical computation. Some results are presented in Fig. 1. The absorption lines are assumed to be inhomogeneously broadened. In all numerical examples, the line profile is choosen to be the Gaussian

$$g(\delta)=(1/\delta_{av}\sqrt{\pi})\exp[-(\delta/\delta_{av})^2] \qquad (14)$$

The mixture is composed initially of 5% of the isotope to be separated (with its transition frequency resonant with the radiation frequency) and 95% of another isotope having the corresponding absorption line off-resonance by an amount $\Delta\omega_0=5\delta_{av}$. The fractional excitation of both species as the square pulse propagates through the medium is plotted in Fig. 1. Distances are expressed in units of linear absorption lengths α_M^{-1} at the resonance frequency of the main—off-resonance—line ($\alpha_I=\frac{1}{19}\alpha_M$). The effect of finite inhomogeneous broadening of the lines is to reduce the inversion of the resonant transition and partially excite the main isotope. It is, however, remarkable that the latter excitation drops by a factor of 10 during propagation, while the highly distorted pulse still achieves nearly complete inversion. A somewhat naive interpretation of this effect is that a hole is burned in the pulse spectrum by the main line. Observation of the pulse Fourier transforms versus propagation distance qualitatively supports this argument.

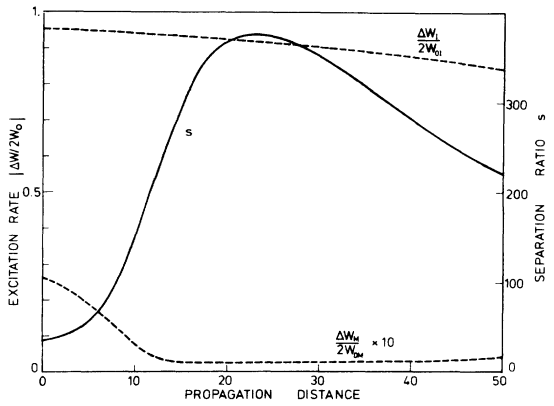

FIG. 1. π-2π separation with a square pulse. The initial pulse has a width of $\tau=\frac{1}{5}\sqrt{3\pi}\delta_{av}^{-1}$ and an amplitude of $\kappa\mathcal{E}_0=5\delta_{av}/\sqrt{3}$. The medium consists of two groups of two-level systems, both having an inhomogeneously broadened line profile $g(\delta)=(A/\delta_{av}\sqrt{\pi})\exp[-(\delta/\delta_{av})^2]$, with $A_I=0.05$ for the group I and $A_M=0.95$ for the second group (M). The spacing between the transition frequencies of I and M is $5\delta_{av}$. The radiation is applied on-resonance with the group I. The excitation rates and separation factor s are shown as a function of propagation distance (in units of the linear absorption length α_{0M}^{-1} at the resonant frequency of the line M).

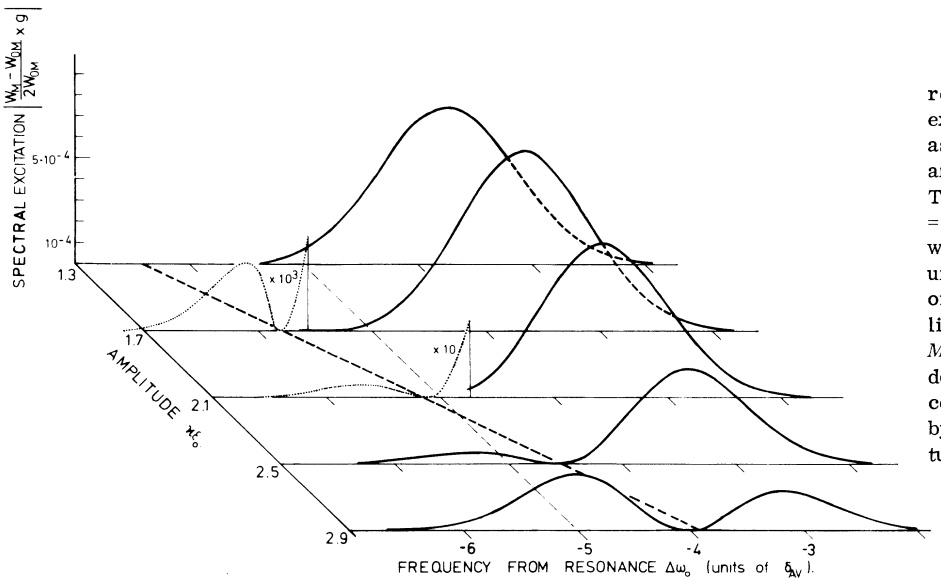

FIG. 2. Three-dimensional representation of the spectral excitation of the transition ***M*** as a function of amplitude of an applied Gaussian pulse. The exciting pulse is $\kappa\mathcal{E} = \kappa\mathcal{E}_0 \exp[-(t\delta_{av}/0.788)^2]$, where $\kappa\mathcal{E}$ is expressed in units of δ_{av}. The frequency origin is the center of the line I. The center of the line M is indicated by the dash-dot line. The dashed line connects points left unexcited by the pulse (transition returned to the ground state).

The efficient excitation of the isotope over very large propagation distances is due to the conservation property of the area $\theta = \pi$,[2] as can be observed from the numerical computation (not shown in Fig. 1). The efficiency of the pumping of the selected isotope decreases with propagation distance, partly because the effect of the dispersion of the main line is to repel the average pulse frequency,[1] which therefore does not remain resonant with the transition I. Complicated reshaping and phase modulation resulting from the nonlinear propagation is observed in the numerical simulation (not shown here).

The conditions (7) and (8) are not the only ones that would yield selective excitation with a square pulse. One could consider also a square pulse corresponding to an uneven number of π rotations of the pseudodipole vector for the molecule I and an even number for the molecule M. The conditions for the pulse width and amplitude are

$$\Delta\omega_0\tau = \pi(4n+3)^{1/2}\,, \tag{15}$$

$$\kappa\mathcal{E}\tau = (2n+1)\pi\,, \tag{16}$$

where n is a positive integer. Only the lowest value of n (zero) need be considered, which corresponds to lower intensities and shorter pulses. The requirement that the pulse length be shorter than T_2 puts a lower limit on the smallest isotope shift to be resolved,

$$\Delta\omega_0 \gg \pi(4n+3)^{1/2}/T_2\,. \tag{17}$$

Therefore $n=0$ is clearly the best choice.

The laser associated with an efficient scheme of isotope separation should be efficient too. Square pulses can be approximated either by chopping away the front and tail of a Q-switched pulse with a Kerr cell,[3] or by using nonlinear intracavity elements.[4] All of these techniques involve some energy losses from the laser pulse. Therefore a reduced efficiency of the source is the price that is paid in the present scheme for the improved efficiency of the optical selection.

The square pulse is obviously the best choice for an infinitely sharp line but is not necessarily the optimal shape for π-2π separation in the presence of inhomogeneous broadening. When excited off-resonance with the Gaussian "π pulse" $\kappa\mathcal{E} = (\sqrt{\pi}/\tau)\exp[-(t/\tau)^2]$, the population of the main line is left with a "dip" which moves across the line (from $-\delta_{av}$ to $+\delta_{av}$) as the pulse width is varied from $0.65\delta_{av}^{-1}$ to $0.97\delta_{av}^{-1}$. An optimal pulse width of $\tau = 0.79\delta_{av}^{-1}$, which corresponds to the dip centered with the line, is chosen. For that pulse width it is shown in Fig. 2 how the spectral excitation varies with the amplitude of the applied pulse. The π pulse corresponds to an amplitude of $\kappa\mathcal{E}_0 = 2.25\delta_{av}$. The dashed line shows the center of the dip moving across the absorption line (of which the center is indicated by a dash-dot line) when the amplitude of the pulse is varied. The advantage of working in the coherent interaction regime to incoherent excitation is dramatically demonstrated by Fig. 3, which shows the variation of the excitation rates and separation factor with pulse amplitude (or area). In the incoherent case, or with pulses longer that T_2, the separation factor is maximum for zero-amplitude radiation and decreases to zero with increasing light power [Eq. (11)]. For Gaussian pulses shorter than T_2, however, the excitation rate of the "rare element" *and* the separation factor reach a maximum for a

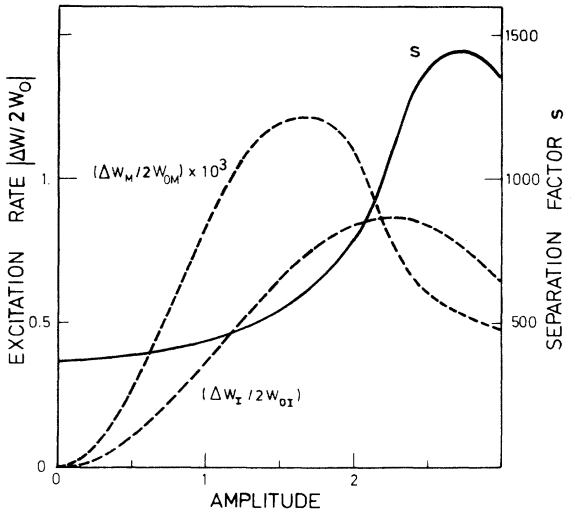

FIG. 3. Total excitation of the transitions M and I (dashed lines) and separation factor s (solid line) as a function of the amplitude $\kappa\mathcal{E}_0$ (in units of δ_{av}) of the Gaussian pulse $\kappa\mathcal{E} = \kappa\mathcal{E}_0 \exp[-(t\delta_{av}/0.788)^2]$.

pulse area close to $\theta \simeq \pi$ (Fig. 3). In this plot the pulse width is constant ($\tau = 0.788$). Since the separation factor remains large for all pulse amplitudes $0 < \kappa\mathcal{E}_0 < 3$, the full cross section of a laser beam would be usable in a separation device based on this scheme.

The results of Fig. 3 can be used to compute the excitation and separation factors over the total cross section of a beam of finite size. For a Gaussian beam profile, numerical integration yields an average excitation of the rare element $\langle \Delta w_I / 2w_{0I} \rangle = 0.269$; for the main line the average excitation is $\langle \Delta w_M / 2w_{0M} \rangle = 0.000\,424$. In contrast to conventional excitation, where the average separation factor is smaller than in the weak intensity limit, the computed average separation factor here is $\langle s \rangle = 636$, nearly twice the value for a weak pulse of the same temporal dependence (Fig. 3). For comparison, numerical computation has been made in the case of conventional excitation [Eq. (10)] of the excitation averaged over the entire cross section of the same Gaussian profile. This calculation shows that in order to achieve the same average excitation of 0.269 over the entire beam cross section (as obtained with coherent excitation) the field strength in the center of the beam has to be such that $\kappa^2\mathcal{E}^2 T_1 T_2 = 11.5$. The two-level systems are then driven far into saturation, which implies a reduced separation factor. For instance, under this saturation condition, a separation factor of 400 in the center of the beam could be obtained only if $\Delta\omega \simeq 70 T_2^{-1}$ and no inhomogeneous broadening is present.

The evolution with distance of its separation properties, as reshaping of an initially Gaussian pulse takes place through propagation in the medium, is illustrated in Fig. 4. The initial pulse has an amplitude of $\kappa\mathcal{E}_0 = 2.89\delta_{av}$ and a width $\tau = 0.788\delta_{av}^{-1}$, corresponding to an area of $\theta = 4.035$, and is applied on-resonance with the isotope I (5% abundance) and five linewidths off resonance from the main line M. The excitation rate and separation factor are plotted as a function of propagation distance, expressed in units of resonant absorption lengths at the frequency of the main isotope. As in the case of the square-pulse excitation illustrated in Fig. 1, the separation ratio is enhanced in the first 50 absorption lengths. Since the initial pulse area is larger than π, reshaping towards a 2π hyperbolic-secant-shaped pulse occurs,[1,2] with a corresponding decrease of the excitation rate of the resonant line.

Comparison of Fig. 1 with Figs. 2–4 clearly demonstrate that the Gaussian pulse shape is much more efficient in deactivating (returning to the ground state) an off-resonant inhomogeneously broadened transition than a square pulse.

The present analysis is carried out in the plane-wave approximation. Off-resonant coherent interaction results in wave-front distortion leading to self-focusing and defocusing effects.[2] However, in the observation of self-induced transparency off-resonance over propagation distances not exceeding five linear absorption lengths[5,6] these wave-front distortion effects appeared to be negligible. For the particular medium considered here, the contribution to the wave-front distortion would come from the main line, since the rare element is on-resonance. It should be noted that the computer calculations presented here do

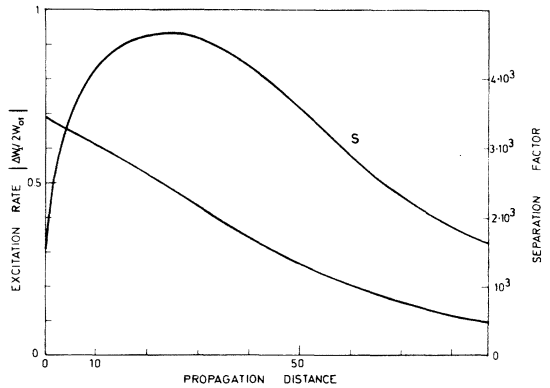

FIG. 4. Propagation of the Gaussian pulse $\kappa\mathcal{E} = 2.89\exp[-(t\delta_{av}/0.788)^2]$ through the same medium as described in Fig. 1. The excitation rate of the rare element I (resonant with the radiation) and the separation rate s are shown as a function of propagation distance (in units of α_{0M}^{-1}).

not extend beyond five linear absorption lengths off-resonance from the main line or at resonance with the selected transition. Therefore self-focusing–defocusing effects can be neglected.

IV. ZERO-AREA PULSE EXCITATION

A zero-area pulse has a special phase modulation such that the area of the pulse is zero. A simple example is that of a symmetric shape for the electric field amplitude and a phase jump of π in the middle of the pulse. Another equivalent description is that of a signal with constant phase whose amplitude has a sign opposite in the first half of the pulse to the sign in the second half. Anomalous transmission effects of such a pulse have been studied theoretically and experimentally.[5,7] Nonlinear transmission occurs because part of the energy lost by the first half of the pulse is restituted to the second half by stimulated emission. As a result of this stimulated emission, the medium is returned to the ground state by the tail of the pulse. It is therefore proposed here to use the zero-area pulse *at resonance* with the unwanted isotope M, exciting the rare component I off-resonance. One predictable advantage of this configuration is that frequency-pulling effects will be less important than in the cases where the main line M is off-resonance. Indeed, in the later cases with the mean pulse frequency being shifted away from the main line, the resonance condition with the selected transition is destroyed.

The case of a square zero-area pulse will be considered first, for comparison with the excitation scheme previously considered. The conditions for selective excitation are now

$$\kappa\mathcal{E} = \Delta\omega_0 \,, \tag{18}$$

$$\Delta\omega_0\tau = \pi\sqrt{2} \,. \tag{19}$$

The pulse amplitude is $\Delta\omega_0/\kappa$ for $0 < t < \frac{1}{2}\tau$ and $-\Delta\omega_0/\kappa$ for $\frac{1}{2}\tau < t < \tau$. Here, in contrast to the cases discussed previously, the transition on-resonance with the radiation is returned to the ground state, while the transition off-resonance by the amount $\Delta\omega_0$ is completely inverted. Comparison with the conditions (7) and (8) shows that a factor of $\sqrt{6}$ more energy is required for the zero-area pulse separation process. The pulse duration is, however, slightly shorter for the same amount off-resonance.

The influence of inhomogeneous broadening on square-pulse selective excitation is seen from Fig. 5 to be much more important for the zero-area case than in the case of the π-2π separation. The selection properties of the square zero-area pulse are shown as a function of the pulse duration for the 5% mixture taken as example in this paper. For the pulse corresponding to the conditions (18) and (19) ($\frac{1}{2}\theta$ = area of the first lobe $= \pi/\sqrt{2}$ in Fig. 5) nearly total excitation of the transition I is achieved, but an appreciable fraction of the transition M is seen to be also excited.

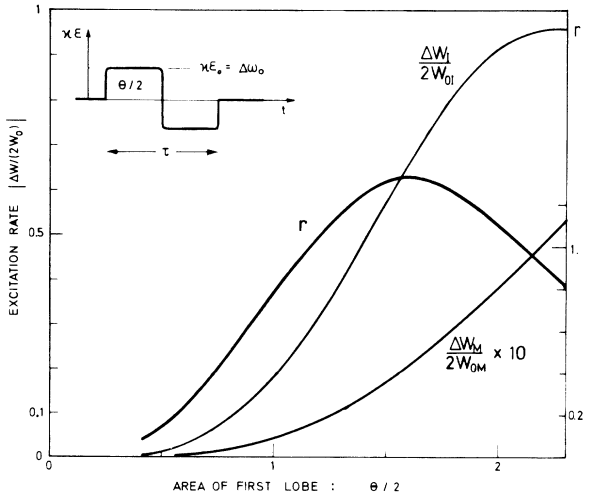

FIG. 5. Excitation rates and "figure of merit" r of a square zero-area pulse as a function of the area of its first lobe or its pulse width, for a constant pulse amplitude ($\kappa\mathcal{E} = \Delta\omega_0 = 5\delta_{av}$).

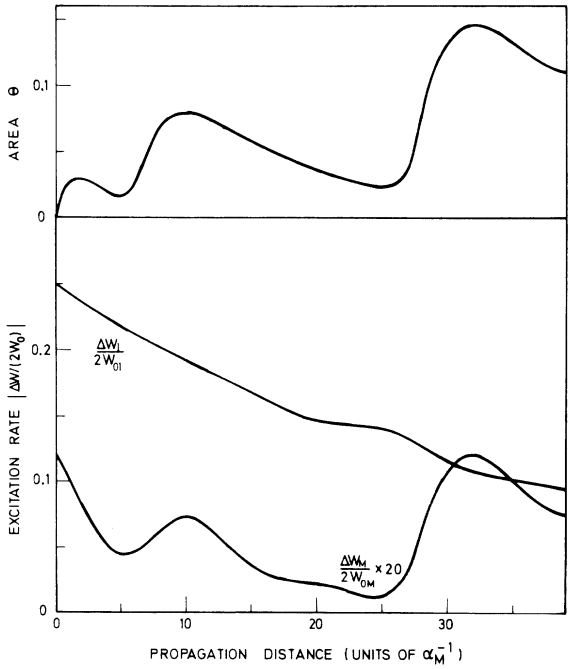

FIG. 6. Propagation of a square zero-area pulse. The excitation rates and pulse area (defined as the Fourier amplitude of the pulse at the resonance frequency of the main line) as a function of propagation distance (expressed in units of linear absorption lengths at the resonance frequency of the main line M).

The "figure-of-merit" number r is therefore seen to have a maximum for smaller values of $\frac{1}{2}\theta$ (or τ).

Results of a computer simulation of the propagation of a pulse with initial value corresponding to $\frac{1}{2}\theta = 1.111$ ($\kappa\mathcal{E} = 5\delta_{av}$) are illustrated in Fig. 6. As in the case of the unmodulated square pulse (Fig. 1), the "residual" excitation of the main transition $|\Delta w_M/2w_{0M}|$ drops with propagation distance. The naive interpretation that the improved selectivity is due to "hole burning" from the main line in the pulse spectrum is seen to have some qualitative value. Indeed, the variations of $|\Delta w_M/2w_{0M}|$ with distance are clearly correlated to the variations of θ (Fourier amplitude of the pulse at the resonance frequency of the transition M) in Fig. 6. A gradual increase of θ—and therefore an increase of $|\Delta w_M/2w_{0M}|$—is to be expected because the weak off-resonance line I repells the mean carrier frequency of the pulse. Interferences between the various nodes of the zero-area pulse at different frequencies propagating with different velocities[5] probably cause the observed oscillations of the value of θ with distance. The highest separation factor is about two-thirds of the highest value reached in the example of Fig. 1.

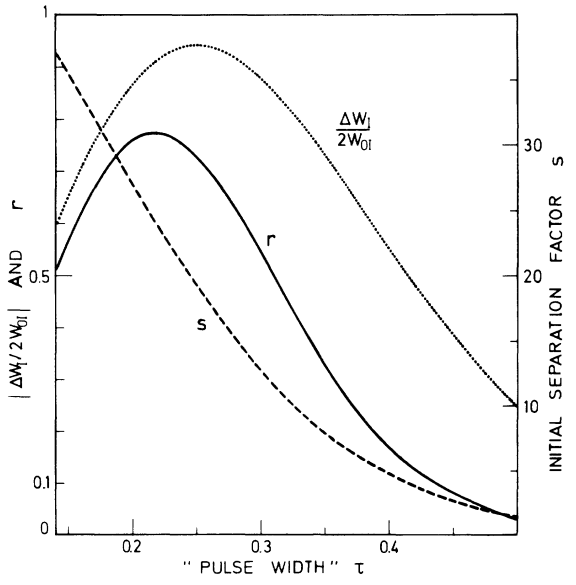

FIG. 7. Excitation rate of the rare element (dotted line), separation factor (dashed line), and "figure of merit" r (solid line) of a Gaussian-generated zero-area pulse, as a function of pulse width τ. The area of the Gaussian generatrix is maintained constant and equal to $\pi\sqrt{2}$.

$$\kappa\mathcal{E} = \frac{\sqrt{2\pi}}{\tau}\left\{\exp\left[-\left(\frac{t-\tau/2}{\tau}\right)^2\right] - \exp\left[-\left(\frac{t+\tau/2}{\tau}\right)^2\right]\right\}.$$

In the presence of inhomogeneous broadening, the zero-area pulse satisfying the conditions (18) and (19) may not be the best choice for optimal separation. The dependence of separation properties on pulse width for a zero-area pulse composed of two Gaussian lobes is illustrated in Fig. 7. Such a signal can be constructed by delaying 50% of a Gaussian pulse by an uneven number of half wavelengths in a Michelson-type interferometer.[5] It should be noted that neither this type of zero-area pulse shaping nor the one used by Grieneisen *et al.*[7] involves any loss of electromagnetic radiation, as the generation of a square pulse would. It can be seen from Fig. 7 that the excitation of the main line M decreases with decreasing pulse width. It can indeed be argued that with decreasing pulse width, the frequency difference between the two peaks of the "Camel-shaped" Fourier spectrum of the zero-area pulse increases, which makes the increase of separation factor plausible (because of the reduced interaction with the main line M at resonance). Here also, the high values of the excitation rate of the group I clearly demonstrate that classical arguments based solely on Fourier or field amplitudes are inappropriate. The major difference between this excitation scheme and the π-2π selection is that the separation factor has its higher values for much shorter pulses. This is an advantage, since it implies that the optical selection can be made at a higher pressure with zero-area pulses than with normal Gaussian pulses

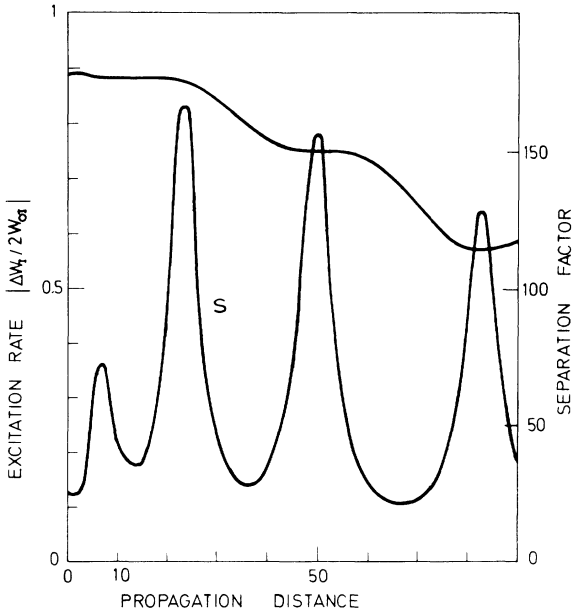

FIG. 8. Propagation of the Gaussian zero-area pulse of Fig. 7 corresponding to $\tau = 0.2089$.

(the pressure determines the collision time T_2, which has to be longer than the pulse duration). The evolution of the separation properties with propagation distance of a "Gaussian" zero-area pulse is illustrated in Fig. 8. The input pulse was choosen to be

$$\kappa\mathcal{E} = \frac{\sqrt{2\pi}}{0.21}\left\{\exp\left[-\left(\frac{t-0.105}{0.21}\right)^2\right] - \exp\left[-\left(\frac{t+0.105}{0.21}\right)^2\right]\right\} \tag{20}$$

($\kappa\mathcal{E}$ given in units of δ_{av} and t in units of δ_{av}^{-1}) which, from Fig. 7, combines a high excitation rate with a moderate pulse energy. The variation of separation factor with distance does not peak at as high values as for the pure Gaussian pulse (Fig. 4). However, in the present example, the input pulse is *not* optimized for higher separation ratio.

It is difficult to compare directly the zero-area excitation with the conventional steady-state approach because the physical conditions are different. The merit of the method proposed here, as compared to long-pulse excitation, depends upon the relative values of the energy relaxation time T_1, the phase relaxation time T_2, the Doppler width δ_{av}, and the isotope shift, and thus on the choice of a particular system. As an example, let us consider a model where $T_1 = 2T_2 = 8\delta_{av}^{-1}$, with an isotope shift of $5\delta_{av}$. The separation properties shown in Fig. 8 for the zero-area pulse of Eq. (20) apply to this medium, since the pulse width is shorter than T_2 ($\tau \simeq \frac{1}{20} T_2$). Figure 8 shows roughly 80% excitation for the rare element for a long propagation distance, with an average separation factor of approximately 80. Let us now consider selective excitation of the same medium with a square pulse of duration $\tau \gg T_2$, of the same energy as the zero-area pulse ($\int \kappa^2\mathcal{E}^2 T_2\, dt = 46.5$), applied now at resonance with the rare element. It is of course impossible to achieve 80% excitation with pulses longer than T_2. Neglecting the inhomogeneous broadening, Eq. (11) shows a separation factor of only $s = 2.6$ and an excitation of $|\Delta w_I / 2w_{0I}| = 0.497$ for a pulse width of $\tau = 32T_2$. For a much longer pulse of the same energy, $\tau = 400T_2$, Eq. (11) gives a separation factor of approximately 80, while the excitation drops to $|\Delta w_I / 2w_{0I}| = 0.39$. Still lower figures would result if the inhomogeneous broadening was taken into account.

In conclusion, there is a wide range of possibilities for quantitative excitation of a particular isotope using coherent interaction properties. Selective excitation using either Gaussian or zero-area pulses has been compared for a particular mixture. Propagation of a Gaussian pulse through the medium is seen to lead to higher separation factors. On the other hand, the possibility of using shorter pulses and denser matter may be a definite advantage of the zero-area pulse scheme. The choice of one or the other scheme, which depends upon a number of practical considerations in a specific application, is beyond the scope of this paper.

ACKNOWLEDGMENTS

Stimulating discussions with Professor E. L. Hahn, Professor M. Bass, and Professor J. H. Marburger are gratefully acknowledged. Early development of the computer programs was made at the Gesellschaft für Wissenschaftliche Daten Verarbeitung while the author was with the Max Planck Institute, Göttingen. I am indebted to Professor F. P. Schäfer of the Max Planck Institute for unlimited computer time.

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