K. K. Rebane. *Phononless lines in laser spectroscopy of molecules and crystals.* 1. *The phononless line—an optical analog of the Mössbauer line.* Phononless lines (PLL) in the optical spectra of impurities, in particular impurities of large molecules in solid matrices, are an interesting and striking phenomenon. Spectra which contain phononless lines have a set of extremely characteristic properties which have served as a basis for distinguishing them as a special class of spectra. PLL, especially PLL of a purely electronic transition, at low temperatures are extremely narrow, have high peak intensity, and provide record high sensitivity and selectivity of spectral investigations.

These properties can be summarized most compactly in the following statement: PLL are an optical analog of a Mössbauer line.[1–3] The fundamental reason for this analogy lies in the symmetry of the harmonic-oscillator Hamiltonian with respect to coordinates and momenta.

However, there are two substantial differences between purely electronic transitions and Mössbauer lines: 1) the broadening of a phononless line, in particular of a purely electronic transition, due to the inhomogeneous construction of the matrix, is much greater than for a Mössbauer line; 2) a purely electronic transition acts directly on the electron system of the material (molecule), which opens up possibilities at a new level for highly selective photochemistry.

The last ten years have seen the development of methods based on use of narrow laser lines which permit one to avoid inhomogeneity braodening. It has become possible to

perform high-resolution spectroscopy of large molecules and also other impurity systems. For example, it is possible now to study at optical frequencies the splitting of energy levels of impurities in solid matrices due to interaction of the nuclear spins, i.e., transitions which traditionally are studied by means of nuclear magnetic resonance.[7]

2. *Photochemical hole-burning in spectra.* Photochemical hole burning[4-6] has become a popular method of avoiding inhomogeneity broadening. Under excitation by a narrow laser line of frequency ω, those molecules whose purely electronic transitions are in resonance with ω are strongly affected and undergo photochemical transformations, as a result of which their purely electronic transitions disappear. In the spectrum (for example, of absorption or excitation) at a frequency ω there is formed a hole—an extremely narrow region of reduced intensity. Photochemical hole burning is not only a method of high-resolution spectroscopy, but also an effective method of highly selective photochemical action on matter, which opens up new possibilities which are interesting for science and which have promise for practical use.

3. *Spectrally selective memory.*[8] A very promising idea is to use photochemical hole burning to create a spectrally selective memory for computers. Exploratory studies in this direction are being carried out at a number of leading companies involved in computer technology (IBM and others). It is quite realistic to burn out and to detect selectively from neighboring regions holes of width 10^{-3} cm^{-1}. In an inhomogeneous band of width 10^3 cm^{-1} it is possible to place 10^4–10^5 such holes, i.e., at one point of space (in an area whose dimensions are determined by the diffraction limit $\lambda \times \lambda$, where $\lambda \approx 10^{-4}$ cm is the wavelength of the laser light) it is possible to write up to ten bits of information. One square centimeter of such spectrally selective optical memory contains up to 10^{13} bits of information. Serious and interesting problems arise in filling a memory with a content of 10^{12}–10^{13} bits/cm^2 in realistic time intervals. A more general problem lies in the complete utilization of the fundamentally new possibilities opened up by photosensitive media in which, in addition to the space coordinates for recording information, there is a coordinate in the frequency of the light, including the possibility of achieving space-time holography.

4. *Photochemically accumulated stimulated light echo.*[9] If a light pulse with an intensity distribution as a function of time $\rho(t)$ passes through a medium which has a photochemically selective sensitivity, then a hole of complicated shape is burned. At low intensity and for a small attenuation of the pulse in passing through the sample, the formation of the holes is reasonably well described in the linear approximation. Then the distribution of the depth of the hole as a function of frequency is given by the expression $|\sigma(\omega)|^2$—the square of the modulus of the Fourier transform of $\rho(t)$. The phases of $\sigma(\omega)$ will be lost. However, if we trace the hole by two successive pulses $\rho_0(t)$ and $\rho_1(t-\tau)$ which are shifted by an interval τ, where $\tau < T_2$ (T_2 is the phase relaxation time), then the Fourier transform of the sum of the two pulses will be modulated by a factor $\cos \omega\tau$. (If there is a train of pulses $\Sigma_{k=100}\, \rho_k(t-k\tau)$, then $\cos \omega\tau$ is replaced by a function

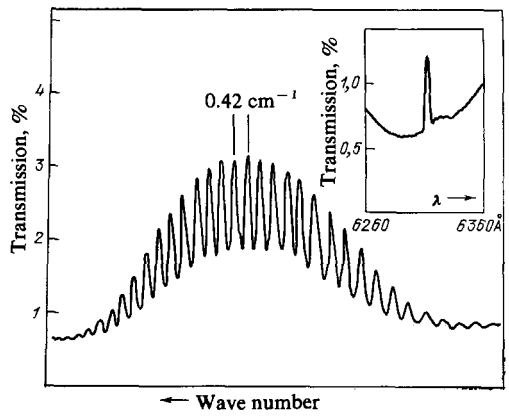

FIG. 1.

with a period $2\pi\tau^{-1}$ which is the sum of a Fourier series whose coefficients are determined by the form of ρ_k.) In Fig. 1 we have shown the transmission spectrum of a photosensitive sample (10^{-3} mole % porphyrazine in polystyrene at 1.8 K) after irradiation by identical pulse trains obtained by replication of single pulses of duration 2–3 psec and spectral width 5.5 cm^{-1} in a Fabry-Perot interferometer with a 12-mm base line, which corresponds to a delay $\tau = 80$ psec between the pulses in the train and an interval 0.42 cm^{-1} between the maxima in the spectrum; the repetition frequency of the pulse train is 82 MHz.[9] In the insert of Fig. 1 we have shown the same transmission spectrum over a wider range with crude spectral resolution. It is evident that, considering $\rho_0(t)$ as a standard and $\rho_1(t-\tau)$ as a signal pulse, we can record the information existing in $\rho_1(t)$. The pattern of holes shown in Fig. 1 is preserved for many days at helium temperatures.

Now if at a time convenient for the experimenters we send to a sample with a spectral hologram of this type, by the same route traveled by the burning pulses, a probing pulse, then to a good approximation the sample will act as a linear filter. This means that the periodic modulation in frequency should be manifested in the appearance of an echo—in re-

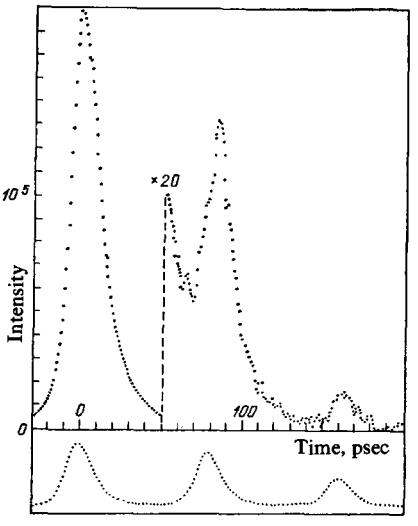

FIG. 2.

production of the train of pulses delayed by $k\tau$ ($k = 0, 1, 2$) (in the case of modulation exactly in accordance with $\cos \omega\tau$ it will result in the appearance of a single echo pulse).

In Fig 2 we have shown the time response of the sample for which the transmission spectrum is given in Fig. 1.[9] To the right of the probing pulse which has passed through the sample we can see echo pulses delayed in time by 80 and 160 psec. Below for comparison we have given a portion of the train of pulses which burned the holes. We note that from the damping of the pulses it is possible also to estimate the phase relaxation time T_2, which turns out to be in the range 200–300 psec.

It should be emphasized that the photochemically accumulated stimulated spin echo does not require high intensities of laser pulses. The burning of the holes, and even more so the probing, is carried out in great detail. The basis of the phenomenon is provided by the high photochemical quality of the material, which is due to the well expressed purely electronic lines in the spectra of the material. Here the echo is extremely strong. In Fig. 2 the first amounts to 2–3% of the main part of the probing pulse. By choice of the composition of the photosensitive material and optimum regimes of burnout, Rebane *et al.*[9] have been able to increase the intensity of the first-order echo to 30% of the zero order and to observe echos of five orders.

The average intensity in the burning was 0.1 mW/cm^2 and the peak intensity was 0.1 W/cm^2, while the irradiation dose was about 20 mJ/cm^2, i.e., the time of bombardment was 200 sec or the action of $1.6 \cdot 10^9$ pulse trains was stored. The probing pulses were 10^3 times weaker than the burning pulses, i.e., in one reading pulse there were 10^2 photons/cm^2.

Photochemically accumulated stimulated light echo can be used also to obtain light pulses which are inverted in time. For this it is necessary in the burnout to send first the signal pulse and then, with a delay τ, the reference pulse. Probing of the resulting spectral hologram by a reference pulse attenuated by 1000 times reproduces in the form of an echo the shape of the signal pulse but inverted on the time scale.

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