

Persistent Antiholes in the Vibrational Spectra of Matrix-Isolated Molecules

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Persistent spectral antiholes, which correspond to increased absorption at the laser frequency, have been burned in an inhomogeneously broadened vibrational mode of ReO_4^- embedded in alkali halide host lattices. A new model is proposed to explain nonphotochemical hole and antihole burning.

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Persistent spectral hole-burning effects have been discovered in a wide diversity of systems ranging from organic molecules in organic glasses^{1,2} and crystals³ to color centers⁴ and ReO_4^- molecules⁵ in alkali halides. A common feature of these systems is the photostimulation of some process which destroys, or displaces in frequency, the optical absorption associated with those sites of an inhomogeneous spectral distribution which are in resonance with an irradiating laser. The resulting spectral holes which appear in the inhomogeneously broadened absorption band last many orders of magnitude longer than the lifetimes of the excited electronic or vibrational states involved. The lost centers sometimes reexpress themselves as antiholes at frequencies off resonance, but a universal feature of all persistent hole systems reported to date is the observation of decreasing absorption at the laser frequency with increasing irradiation time.

We report here on a related but unexpected behavior in which there is a persistent and narrow-band *increase* in absorption at certain burning laser frequencies. The system studied is the inhomogeneously broadened ω_3 vibrational mode of ReO_4^- molecules substitutionally doped into KI and RbI crystals. These systems show either persistent holes⁵ or persistent antiholes (pegs) depending upon the particular spectral position at which the irradiation occurs. One is intuitively comfortable with the idea that narrow-band laser radiation within an inhomogeneously broadened absorption line might lead to a burned hole through saturation, photodecomposition, photoinduced reorientation, or perhaps other processes which remove absorbers from the spectral region under irradiation. An increased absorption at the frequency of irradiation is not so easy to explain. A model is proposed which affords a simple explanation of both hole and peg formation by the same mechanism.

A number of CO_2 and N_2O laser transitions in

the vicinity of 925 cm^{-1} were used to test for persistent holes and pegs. The cw burning intensities used were in the range of 0.1 to 4 mW/cm²—many orders of magnitude smaller than the saturation intensity of 10 W/cm² reported earlier.⁶ In the latter stages of the experiments a tunable diode laser became available for spectroscopic measurements.

The samples were obtained from Czochralski-grown boules which were doped by adding KReO_4 to the melt. Three methods were used to obtain coincidences of the ω_3 absorption with the discrete laser frequencies available: The first relied simply on the natural coincidences which occur in heavily doped RbI (0.8 mole% KReO_4). The second method was to double-dope KI with 0.05 mole% KReO_4 and 2 mole% NaI. The alloyed host produces a number of perturbed ω_3 modes each of which is inhomogeneously broadened as shown in Fig. 1(a). These two sample preparation techniques have been described earlier.^{6,7} The last method also relied on forced inhomogeneous broadening, but was caused by the presence of a large number of dislocations introduced into a sample of KI+0.4% KReO_4 by hot pressing it at 100 °C and 2200 psi.

The basic experiments to test for a persistent hole or peg was to cool the sample to 1.4 K in the dark and then expose it to the laser by opening a shutter. The radiation transmitted by the sample showed the time development of the persistent hole or peg.

Four typical transmission growth curves are shown in Fig. 2, curves *a-d*. With the laser tuned to $\text{N}_2\text{O P19}$, curves *a* and *b* were obtained at laser intensities of 3.8 and 0.25 mW/cm², respectively, in a sample of KI+0.05% KReO_4 +2% NaI. The rising transmission indicates formation of conventional persistent holes.⁵ When the laser was tuned to $\text{N}_2\text{O P17}$, however, curves *c* and *d* (0.25 and 3.8 mW/cm²) were obtained. The increasing absorption with time in-

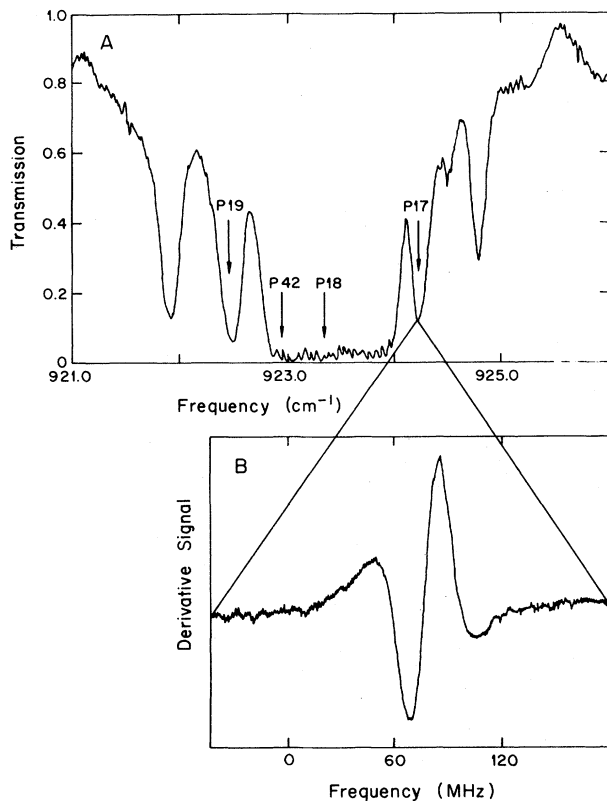


FIG. 1. (a) Infrared transmission spectrum of $\text{KI}:0.05\% \text{KReO}_4:2\% \text{NaI}$ in the region of the ω_3 vibrational mode. The multiple lines are the effects of the Na^+ ion located at different distances from the molecule. The unperturbed mode region is opaque for this sample thickness. Coincidences with N_2O and CO_2 laser lines (see Table I) are indicated. The sample temperature is 10°K and the spectrometer resolution is 0.04 cm^{-1} . (b) Diode-laser first-derivative spectrum of the peg at N_2O P17. The sample temperature is 1.4°K and the resolution is 7 MHz . The central feature (full width at half maximum = 28 MHz) corresponds to enhanced absorption.

indicates the growth of pegs. The essential observations drawn from these and other measurements is that for both holes and pegs, the growth rates increase with increasing intensity, while the final steady-state magnitudes of both effects are intensity independent. Most apparent from curves *b* and *c* of Fig. 2 is that the hole is much larger than the peg and takes somewhat longer to develop. Further analysis shows, however, that neither curve depends exponentially on time, although both curves do show qualitatively the same nonexponential time dependence. (See Fig. 2, curves *e* and *f*, which represent the same data as in curves *a* and *c* plotted on a logarithmic scale.)

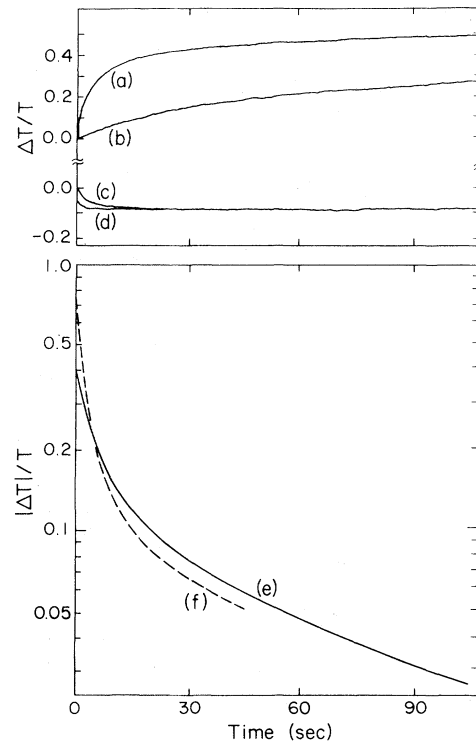


FIG. 2. Transmission growth curves for persistent holes and pegs. The sample is $\text{KI} + 0.05 \text{ mole}\% \text{KReO}_4 + 2 \text{ mole}\% \text{NaI}$. The rising hole traces occur at P19 and the falling peg traces at P17 of the N_2O pump laser. Curves *a* and *d*, laser intensity = 3.8 mW/cm^2 . Curves *b* and *c*, laser intensity = 0.25 mW/cm^2 . Note that $\Delta T/T \equiv (T(t) - T_{\text{initial}})/T_{\text{initial}}$ in each of these four traces. Curves *e* and *f*, semilogarithmic plots of the same hole and peg data as in curves *a* and *c*, respectively, above. The peg data in curve *f* is scaled by $\times 10$ for convenience. In each of these traces $|\Delta T|/T \equiv |T_{\text{final}} - T(t)|/T_{\text{final}}$.

The quantum efficiency⁵ η_e (the number of centers that stop absorbing at the laser frequency divided by the total number of photons absorbed) for a hole or peg in $\text{KI}:\text{KReO}_4:\text{NaI}$ can be estimated from Fig. 2. For the P19 hole $\eta_e = 1 \times 10^{-6}$ and for the P17 peg $\eta_e = 1 \times 10^{-4}$.

One systematic effect which emerged from these experiments is that for a fixed laser frequency and a given sample preparation technique, strictly holes or strictly pegs were burned as the beam waist location was varied over the face of the sample. Although the magnitude of the effect did vary from spot to spot, no evidence appeared for a substantial competition or admixture of the two effects. This uniqueness of the sign of the hole-burning effect allows assignments to be made for each sample at each laser coincidence. These

TABLE I. Persistent holes and pegs observed at 1.4 K for three different systems.

System	Laser coincidences	ω_p (cm ⁻¹)	Experimental feature
KI + 0.4% KReO ₄ (pressed)	N ₂ O P17	924.15	Peg
	N ₂ O P18	923.25	Peg
	CO ₂ 10P42	922.91	Hole
	N ₂ O P19	922.36	Hole
	N ₂ O P17	924.15	Peg
KI + 0.05% KReO ₄ + 2% NaI	N ₂ O P18	923.25	Hole
	CO ₂ 10P42	922.91	Hole
	N ₂ O P19	922.36	Hole
	CO ₂ 10P42	922.91	Hole
	N ₂ O P19	922.36	Hole
RbI + 0.8% KReO ₄	N ₂ O P22	919.65	Hole
	N ₂ O P23	918.65	Peg
	N ₂ O P26	916.00	Hole

results are listed in Table I. Further, with the diode laser, the peg effect in KI:KReO₄:NaI was found to be the same independent of the spectral position within the resolved component coincident with P17 in Fig. 1(a)

Finally, spectroscopic measurements of pegs and holes were made with a low-power diode laser. A first-derivative spectrum of the peg at N₂O P17 in KI:KReO₄:NaI is shown in Fig. 1(b). The line shape corresponds to a central line of enhanced absorption with a full width at half maximum of 28 ± 5 MHz, but surrounded by broad wings of decreased absorption. The small asymmetry is due to laser-induced perturbations of the spectrum. The overall shape is a negative replica of the persistent hole which had been observed earlier for another ω_3 transition at CO₂ 10P42, and whose shape had been accounted for by reorientational tunneling between librational levels occurring during nonradiative vibrational decay.⁵

A model which qualitatively accounts for the persistent hole and peg phenomena is illustrated in Fig. 3. The tetrahedral symmetry of the ReO₄⁻ molecule demands that a double configurational degeneracy occur within a cubic site. However, if the cubic symmetry is lowered by local lattice strain gradients, then the two configurations labeled A and B in Fig. 3 become inequivalent. A similar argument can be used to describe the two configurations in the excited vibrational state, labeled A' and B'. Although the random nature of the strain field produces distributions

of all these energy levels, the important features with respect to hole and peg production can be demonstrated with the four levels shown in Fig.

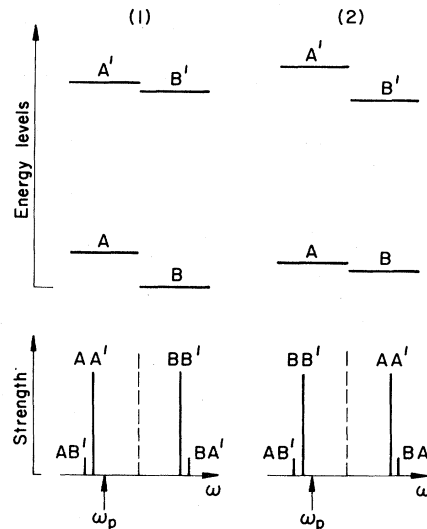


FIG. 3. Photoinduced reorientation model for ReO₄⁻ in alkali halides. The top figure shows the lowest-energy levels for the spherical top molecule in the ground and the first excited vibrational states. Two possible configurations denoted by A (A') and B (B') occur for each zero libration state. Arrangement (1) has the double-well asymmetry of the two ground-state configurations larger than for the two excited states and arrangement (2) has the opposite. The bottom of the figure shows the line strengths vs frequency for each of the transitions in the two arrangements. The laser pump is at frequency ω_p .

3. In arrangement (1) the potential-well asymmetry in the ground state is larger than the asymmetry in the excited state, while in arrangement (2) the opposite holds. For both arrangements the well asymmetry is assumed to be large compared to the tunnel splitting of two degenerate configurations so that the infrared selection rule strongly favors transitions within a given configuration. These transition strengths are labeled AA' and BB' in the lower part of Fig. 3. We propose that the nearly forbidden transitions between configurations, labeled AB' and BA' , are the pathways that lead to the persistent elastic polarization of the resonant molecules.

Energy-level arrangement (1) shown in Fig. 3 will give rise to persistent spectral holes when the laser frequency ω_p is not symmetrically located with respect to the AA' and BB' translational frequencies. For the example shown, the laser pump drives centers from A to B via the overlap of the laser with the homogeneous width of the AB' transition. Since the number in A decreases, the strength of AA' decreases and a hole appears at the pump frequency ω_p .

Persistent spectral pegs will occur for energy-level arrangement (2) shown in Fig. 3. As pictured at the bottom of the figure, the laser pump ω_p again drives centers from A to B via the AB' transition. Increased absorption now occurs near ω_p since the dominant absorption results from the overlap of the homogeneous width of the BB' transition with the laser line and not the AA' transition.

Application of the analysis of Ref. 5 to the model of Fig. 3 shows that in the presence of an inhomogeneous distribution of the mean level splittings, $(E_{AA'} + E_{BB'})/2$, and of the inequivalence energies $E_{A'B'}$ and E_{AB} , the laser-induced redistribution of orientations will give rise to a feature near the pump frequency of the form illustrated in Fig. 1(b). The spectral width of this feature is essentially the homogeneous linewidth if, as assumed in the analysis, the typical inequivalence energies $E_{A'B'}$ and E_{AB} are less than the homogeneous linewidth of the transitions. The important new feature of the reorientation mechanism proposed here is that the redistribution of orientations leads to a burned hole only if $\langle E_{AB}^2 \rangle > \langle E_{A'B'}^2 \rangle$, i.e., only if inequivalence is dominated by the ground-state splitting. In contrast, the feature becomes a peg if the excited-state

splittings dominate, $\langle E_{A'B'}^2 \rangle > \langle E_{AB}^2 \rangle$. The various distinct resolved components illustrated in Fig. 1(a) are thought to be associated with ReO_4^- - Na^+ near pairs with well defined relative positions which in turn define the relative magnitudes of the ground- and excited-state inequivalence, hence whether a specific component will yield pegs or holes.

Earlier models for persistent nonphotochemical hole burning^{1,5} have relied on a configurational change during deexcitation to shuffle centers from one configuration to another. The observation of persistent pegs for ReO_4^- in alkali halides is not compatible with such relaxation processes. If, however, the configurational change actually occurs during the optical excitation by means of the "forbidden" interconfiguration transitions then, in general, both persistent pegs and holes are possible.

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