T dependent in the range 1-4 K because of the smallness of the width Δ_c defined below Eq. (3). However, the observed increase in $1/\tau$ by about a factor 2 in going from 1 to 4 K can be understood by taking into account the T dependence of the reaction cross section which was assumed to be constant in deriving (9). The nearest neighbor (nn) position can be reached along six times as many channels via a next nn position (nnn) as via a collinear path. Therefore consider only the formation of a nn pair via a nnn position. When the split rotational levels of a nnn ortho pair are compared with those of a nn pair, one finds that all the levels of the nnn pair match within a range of order Δ_c some level of the nn pair, except for the lowest level from which, therefore, no resonant transitions are possible. Assuming a Boltzmann distribution over the levels of the nnn pairs, we obtain the result that the probability of the last jump, and hence $1/\tau$, is about a factor 2 smaller at 1 K than at 4 K, in qualitative agreement with experiment.

We have also done the calculations for para-deuterium impurities in solid orthodeuterium and find that the jump probability is about 7×10^{-3} times that in hydrogen, the main difference being the smaller nuclear magnetic dipole moment. Hence at $c = 1\%$ we expect a reaction time constant of about 300 h, corresponding to a reduction in the single para signal of about 15% in 50 h. Preliminary measurements[1] have not revealed any diffusion but the duration of the observation is not reported and more extensive measurements are clearly of interest. Finally, we mention that for HD impurities in H_2 no conversion is possible. On the other hand, the interchange of an HD molecule (which has $J=0$) with a para H_2 molecule is not inhibited by the quadrupolar coupling and, in spite of the heavier mass of the HD, may lead to a finite quantum diffusion. The observation of this effect is, of course, much more difficult, since the HD impurities do not have any pronounced tendency to form pairs.

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[1]L. I. Amstutz, J. R. Thompson, and H. Meyer, Phys. Rev. Lett. 21, 1175 (1968).
[2]T. Nakamura, Progr. Theor. Phys. 14, 135 (1955).
[3]V. F. Sears and J. Van Kranendonk, Can. J. Phys. 42, 980 (1964).
[4]*Progress in Reaction Kinetics*, edited by G. Porter (Pergamon, New York, 1961), Vol. 1.
[5]S. A. Boggs, private communication.
[6]W. R. C. Prior, private communication.
[7]J. F. Jarvis, H. Meyer, and D. Ramm, Phys. Rev. 178, 1461 (1969).
[8]R. A. Guyer and L. I. Zane, Phys. Rev. 188, 445 (1969).
[9]M. Bloom, private communication.
[10]J. A. Krumhansl and S. Y. Wu, Phys. Lett. 28A, 263 (1968).
[11]J. Noolandi, Can. J. Phys. 48, 2032 (1970).
[12]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. Press, Oxford, England, 1961), Chap. VIII.
[13]A. B. Harris, L. I. Amstutz, H. Meyer, and S. M. Myers, Phys. Rev. 175, 603 (1968).

High-Intensity Resonance on the Simple Vibrator $CaF_2:H^-$ †

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The vibrational spectrum for an H^- ion on an F^- site in CaF_2 is that of a perturbed spherical harmonic oscillator. The $\Delta n = 1$ frequencies lie between 928 and 977 cm^{-1}. Tunable CO_2 lasers have enabled us to study saturation of the single fundamental $(0\rightarrow1)$ and stepwise excitation to each of the three $n=2$ levels. A decay-time value T_1, based on a crude measurement of the saturation parameter W, accounts for the residual linewidth at low temperatures. We discuss "additivity" of stepwise frequencies and polarization "scrambling."

Elliott *et al.*[1] were able to observe in infrared absorption the first four allowed (Γ_5) levels of the local-mode system $CaF_2:H^-$. These included a first-, a second-, and two third-harmonic components. From the four frequencies, they inferred the coefficients of the four leading terms in an expansion of the potential $V(x,y,z)$ describing displacements of the H^- ion from the cell cen-

ter,

$$V = Ar^2 + Bxyz + C_1(x^4 + y^4 + z^4) + C_2(y^2x^2 + z^2x^2 + x^2y^2) + \cdots .$$

The levels of other than Γ_5 symmetry were then located by calculation from this potential. The transitions studied in various investigations[1,2,3] are detailed in Fig. 1; there is uniformly good agreement on frequencies. Fortunately for our pruposes, the various $\Delta n = 1$ resonance are well separated.

In the present work we use two CO_2 lasers tunable over many lines in the 900- to 1100-cm^{-1} region. Each uses a diffraction grating for one of the reflectors. Generally similar, they both employ pulsed discharges of ~350-μsec duration. One (hereafter referred to as QS) is Q switched by spinning the grating like a flywheel; it generates pulses of up to 20 kW power and of ~400-nsec duration, on 80 lines.[4] The other (NQS) generates 10- to 30-W pulses of a duration correlated with the discharge, and on 130 lines.[5] The insert to Fig. 1 shows the coverage which our discrete laser lines afford upon the fundamental, ω_{01} (other resonances are wider). Because ω_{01} is near the CO_2 *band center* $00^01\text{-}10^00$, these lines are

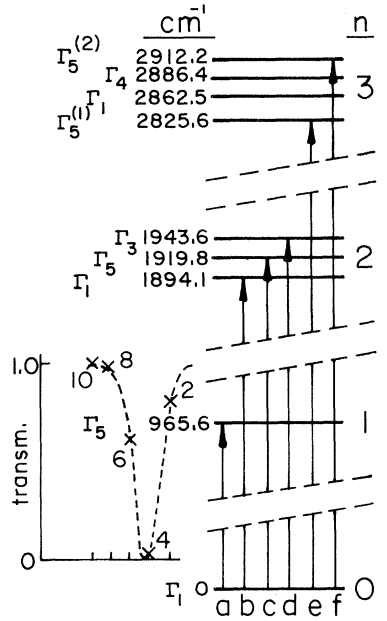

FIG. 1. Spectrum at ~20°K, adapted from Ref. 1. Transitions studied in succeeding investigations are as follows: (i) Ref. 1, infrared absorption, lines *a*, *c*, *e*, *f*; (ii) Ref. 2, IR, uniaxial stress, lines *a*, *b*, *c*, *d*; (iii) Ref. 3, Raman scattering, lines *a*, *b*, *c*; (iv) present work, lines *a*, *b*, *c*, *d*. Inset: observed relative transmission on 10^00 lines $R(2)$, $R(4)$, $R(6)$, $R(8)$, and $R(10)$, at ~90°K.

relatively weak; QS gives ~5 kW. Two BaF_2 lenses placed as Dewar windows focus the beam(s) on the sample and recollimate beyond it. When the two beams are used together, they are adjusted to illuminate a common spot, but from distinct cones of solid angle.

The discharge is most readily pulsed at a high rate, such as 360 sec^{-1}. But we employ synchronous intracavity choppers to reduce the time-average thermal load on the gratings and at the CaF_2 crystal. Some degree of short-term local heating of the material exposed to the QS pulse is unavoidable, however. No appreciable changes of the spectrum occur unless the temperature T rises above ~100°K (Ref. 1, Figs. 6, 4, 3). Little conduction occurs during the pulse. Taking a CaF_2 volume corresponding to a *stationary*,[6] single-mode, diffraction-limited spot and one absorption length, we find that T should approach room temperature. Our data do not support any such large rise of T. But there are indications (see below) of a thermally induced increase of absorption in the wings of ω_{01}, asymmetrically, corresponding to at most $T = 120$°K, for a short depth.

Despite any such ambiguity, there was a clear expectation that flux densities available with the focused QS beam should suffice to saturate the centers for some depth into the crystal, even at 290°K; and this has proved to be the case. This in turn permits a search for stepwise excitation, $n = 1$ to $n = 2$. Transient effects such as nutation could *not* be expected. Even in the limit of low temperature, there is a "residual linewidth"[1,7] of ~0.7 cm^{-1}, which suggests a maximal coherence time of ~7 psec (at ~80°K we have ~1.0 cm^{-1}, ~5 psec). The rise and fall times of our QS pulses are much longer, so that our observations must belong to the steady-state limit. Actually, any contributions of inhomogeneity and of instrumental breadth to the measured width should be subtracted. But lines of this defect are believed to be homogeneous for any T. A temperature-independent spontaneous decay process fixes the residual width and a maximal coherence time (see Ref. 7 and below).

Figure 2(a) shows, as a simple demonstration of saturation, temporal narrowing of the transmitted pulse relative to the incident pulse (QS beam only). Figure 2(b) displays graphs constructed from points on Fig. 2(a), to investigate whether the transmitted intensity is (i) solely a function of the instantaneous incident intensity, corresponding to saturation (such effects will be

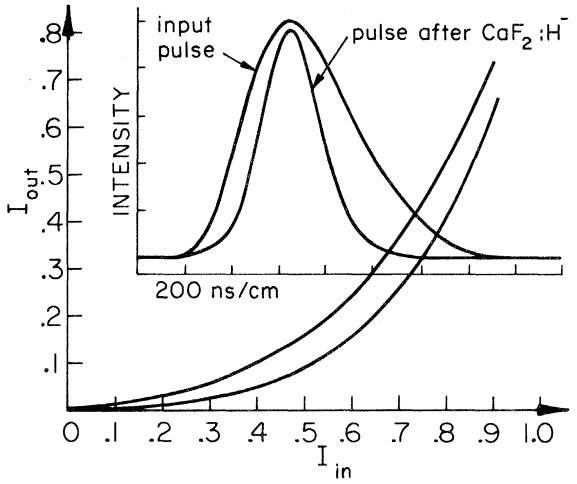

FIG. 2. (a) Above: oscilloscope traces showing narrowing of transmitted $R(6)$ pulse relative to incident pulse, at ~80°K. (b) Below: plots of I_{out} vs I_{in} constructed from the rising and from the falling portions of the pulses above.

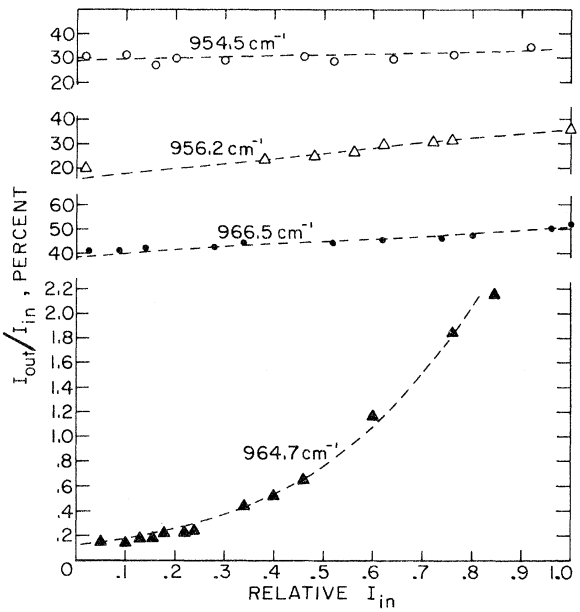

FIG. 3. I_{out}/I_{in} vs I_{in}. Filled symbols are data for ~90°K, where $\omega_{01}=965.1$ cm^{-1}, width $=1.2$ cm^{-1}. Open symbols are data at ~290°K, where $\omega_{01}=957.8$ cm^{-1}, width $=8.7$ cm^{-1}. Given laser frequencies for triangles are near the respective peaks; those for circles are in the wings.

referred to as "fast"), or (ii) dependent upon the history—presumably upon the integral over previous intensities; this might be taken as a thermal effect ("slow"). Both sorts of effects are clearly present; but saturation is the dominant one except for late portions of the pulse, where the slow effect obviously dominates.

Figure 3 also demonstrates saturation; but here we plot the *fractional* transmitted intensity, using only peaks from pulses of varied heights (by attenuation). Undoped CaF_2 samples of the same thickness show constant transmission, ~90 %. The curves plotted are fits by a simple theory including, in addition to saturable absorption by H^- ions, a small unsaturable component due to the lattice,

$$(1/I)(dI/dx) = -\alpha_L - \alpha_H/(1+WI), \tag{1a}$$

where the quantities are defined by context. The integral in closed form is

$$WI_{in} = [(\alpha_L+\alpha_H)/\alpha_L]\{(I/I_{in})^{-\alpha_L/\alpha_H}\exp[-(\alpha_L/\alpha_H)(\alpha_L+\alpha_H)x]-1\}$$
$$\times\{(I/I_{in})-(I/I_{in})^{-\alpha_L/\alpha_H}\exp[-(\alpha_L/\alpha_H)(\alpha_L+\alpha_H)x]\}^{-1}. \tag{1b}$$

We cite parameter values for the curve in Fig. 3 pertaining to the peak of the line at ~90°K (larger heating effects are expected at ~290°K): $\alpha_L = 2.8$ cm^{-1}, $\alpha_H = 175$ cm^{-1}, and $WI_{in}(\max) = 0.36$. Our estimate of $I_{in}(\max)$ is very rough because the spot diameter d is poorly known. Taking $d = 80$ μm and 3 kW available at the sample, we find $I_{in}(\max) = 6\times10^7$ W cm^{-2}, $W = 6\times10^{-16}$ cm^2 erg^{-1} sec.

In the limit of high intensity, $WI \gg 1$, we can write two expressions for the power per unit volume absorbed by defects:

$$(\tfrac{1}{2}n)\hbar\omega_{01}/T_1 = -dI/dx = \alpha_H/W. \tag{2a}$$

Here n is the volume density of defects, and T_1 is the vibrational lifetime. Using $\sigma \equiv \alpha_H/n$, we find

$$T_1 = \tfrac{1}{2}\hbar\omega_{01}W/\sigma, \tag{2b}$$

which is independent of n. Fain[8] has given the first equation of (2a) on the basis of a rather general model of a homogeneous resonance with T_1 and T_2 treated explicitly; T_2 drops out.

For σ we use a value $\sigma_{peak} = 8.2\times10^{-18}$ cm^2 inferred from $\int\sigma(2\pi c)^{-1}d\omega = 1.56\times10^{-17}$ cm; the latter result is based on data of Shamu, Hartmann, and Yasaitis.[9] Here there enter a determination of n by neutron scattering, a spectrographic study of α_H, and use of the relation $\sigma \equiv \alpha_H/n$. Then Eq. (2b) gives $T_1 = 7$ psec.[10]

The quantitative uncertainties are *large*, but

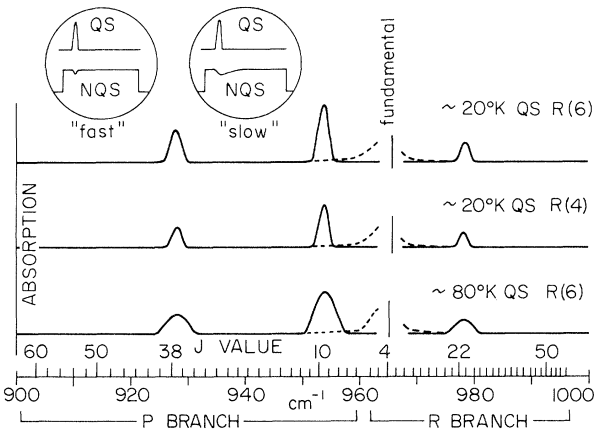

FIG. 4. Inset above: oscilloscope traces showing "fast" and "slow" effects. Below: plots vs NQS frequency. Full curves show the fast effect; dashed curves show the slow effect.

the implied *decay* width (homogeneous, obviously) checks well with the residual width and with the assertion by Hayes *et al.*[7] that the residual width is due to decay. They also state that the "temperature-dependent ···width" is due to "phonons scattered ···without change in the vibrational state" (but with randomization of phase; evidently also of polarization—see below).

In Fig. 4 we depict, for NQS beams of various frequencies, the changes of transmitted intensity caused by a pulse from QS. The most prominent effect is stepwise absorption, $n=1$ to $n=2$; this is a fast effect, faithful to the temporal shape of the QS pulse. There is a slow component of absorption (persisting for a few microseconds) for frequencies in the wing of the fundamental, asymmetric to the low-frequency side. We *tentatively* attribute this to simple changes of line shape with rising temperature, so that a NQS frequency in the wing encounters additional absorption.

Each of the three $n=2$ levels of Elliott *et al.*[1] was indeed observed in stepwise absorption, *at* the energy determined in the prior work. That is, the frequencies add, $\omega_{01}+\omega_{12}=\omega_{02}$, in each case. This is perhaps less trivial than it seems. There might occur relaxation of the vicinal lattice ions after excitation of the H^- to $n=1$, with a consequent change of ω_{12} for the newly defined "vertical" transitions. The point is that we have a very good case of a local excitation *weakly* coupled to lattice phonons. From Ref. 1 we have quite distinct "no-phonon" lines (dominant), "one-phonon" lines (weak), and "multiphonon" lines (not observed). Our $n=1$ to $n=2$ lines, *as well as* the fundamental, are no-phonon lines, characteristic of a system *incapable* of relaxation.

Our naive expectation was that, with our Brewster-window lasers, we could confirm polarization selection rules in stepwise excitation. Suppose that we drive ω_{01} with E_x radiation from QS, and then with NQS study the $n=2$, Γ_5 frequency for stepwise excitation. This $n=2$ mode is largely like xy; one should find a null effect if E_x is used again for NQS. Briefly, $E_xE_x \rightarrow \Gamma_1, \Gamma_3$ only; $E_xE_y \rightarrow \Gamma_5$ only. Experimentally one finds *each* line in *each* polarization. There seems to be "scrambling" of the three $n=1$, Γ_5 components before the second absorption. Attributing this to phonons, we attempted "freeze-out" with liquid helium, but the scrambling remains. The test is probably spoiled by the QS-pulse heating effect.

We have made rather sensitive tests for effects of the choice of QS frequency used to drive the fundamental upon the apparent positions of the second-step resonances. Any inhomogeneous component of the line shape could produce such an effect. Two NQS frequencies, one on each wing of a second-step resonance, are compared for the intensity of absorption—first QS on one wing of the fundamental, and then on the other. No such shift is discernable. With the frequency of QS well removed from ω_{01}, we sought NQS absorption as the *sum* of the two laser frequencies passed through an ω_{02}; this also gives a null result.

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[1]R. J. Elliott, W. Hayes, G. D. Jones, H. F. MacDonald, and C. F. Sennett, Proc. Roy. Soc., Ser. A 289, 1 (1965).

[2]W. Hayes and H. F. MacDonald, Proc. Roy. Soc., Ser. A 297, 503 (1967).

[3]R. F. Harley, J. A. Harrington, and C. T. Walker, Bull. Am. Phys. Soc. 15, 297 (1970).

[4]L. C. Lee, M. Gundersen, and W. L. Faust, Opt. Commun. 1, 291 (1970).

[5]L. C. Lee and W. L. Faust, Opt. Commun. 2, 111 (1970).

[6]Rotation of the grating during the QS pulse may cause the spot to sweep ~40 μm.

[7]W. Hayes, G. D. Jones, R. J. Elliott, and C. F. Sennett, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965), p. 475.

[8]V. M. Fain and Ya. I. Khanin, *Quantum Electronics*, translated by H. S. W. Massey (Massachusetts Institute of Technology Press, Cambridge, Mass., 1969), Eq. 23.23.

[9]R. E. Shamu, W. M. Hartmann, and E. L. Yasaitis, Phys. Rev. 170, 822 (1968). Actually the *second harmonic* was studied, because the fundamental was excessively dense. The relative strength integrals are known from Ref. 1.

[10]A Lorentz-broadened vibrator characterized by a known frequency and width, by mass m_H, and by charge $|q|=e$ would have σ_{peak} much larger and T_1 so small as to be quite inconsistent with the observed width. The strength-integral value cited corresponds to $|q| = 0.18e$. Note that $|q|$ enters as the square.

Magnetization Induced by Optical Pumping in Antiferromagnetic MnF_2†

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We have generated magnetization in antiferromagnetic MnF_2 by selectively pumping the lowest $^6A_1 \rightarrow {}^4T_1$ sublattice excitons (or exciton-magnon band) with a pulsed, tunable dye laser. Intersublattice relaxation processes were studied by observing the creation and decay of specific excitations, as induction signals. The exciton relaxation time decreases with increasing temperature and pumping power. We interpret this as intersublattice relaxation assisted by thermally excited magnons.

We have generated magnetization in antiferromagnetic MnF_2 by selectively creating sublattice excitons and magnons with a pulsed, tunable dye laser. The magnetization changes, and those due to subsequent relaxation processes, were observed as induction signals. This enables us to measure, in the time domain, very small intersublattice couplings ($\sim 10^{-5}$ cm^{-1}), of the type leading to Davydov splitting. The technique promises to be useful for studying the dynamics of specific excitations which are resonantly created by pumping with tunable lasers.

The magnetic moment of a two-sublattice antiferromagnet which is excited to one of its exciton (or magnon) levels $\Gamma_{A,B}$ is

$$M(t) = [n_A(t) - n_B(t)]\langle \Gamma_A | \vec{\mu} | \Gamma_A \rangle, \quad (1)$$

where $n_A(t)$ and $n_B(t)$ are the numbers of excitons on sublattices A and B, respectively, at time t, and $\vec{\mu}$ is the magnetic dipole operator. The possibility of having $n_A(t) \neq n_B(t)$ depends on two main factors: (i) A scheme (in this case optical pumping) can be devised to populate one sublattice preferentially. This requires that any magnetic domains have substantially the same orientation. (ii) The transfer of excitation (TOE) between sublattices must be slower than, or comparable to, the observation time. Experiments on magnetization induced by optical pumping have been reported for paramagnetic systems.[1,2] The physical mechanisms operating in these cases are quite different from those responsible for what we observe in antiferromagnetic MnF_2.

In the present work we resonantly excite the lowest magnetic dipole (Γ_1^+, Γ_2^+) exciton ($E1$) in MnF_2 at 18 418 cm^{-1} or the associated electric dipole exciton-magnon band at 18 476 cm^{-1}. These arise from the $^6A_1 \rightarrow {}^4T_1$ transition of the Mn^{2+} ions.[3] Selective pumping of the excitons is made possible by applying [110] stress which lifts the sublattice degeneracy. The laser is then tuned to excite a particular sublattice exciton[4] Γ_A or Γ_B, where

$$\sqrt{2}|\Gamma_A\rangle = |\Gamma_1^+\rangle - |\Gamma_2^+\rangle \quad \text{and} \quad \sqrt{2}|\Gamma_B\rangle = |\Gamma_1^+\rangle + |\Gamma_2^+\rangle. \quad (2)$$

Stress measurements by Dietz[5] showed that any Davydov splitting of (Γ_1^+, Γ_2^+) is much less than the linewidth (0.5 cm^{-1}). Measurements of the thermalization of the intrinsic emission from $E1$ show that when the sublattices are out of resonance by 5 cm^{-1} the TOE rate between sublattices is less than 10^4 sec^{-1} below 2°K.[6] Thus for a single-domain crystal the conditions (i) and (ii) can be satisfied.

The situation is somewhat more complicated in the case of exciton-magnon pumping. Under [110] stress the exciton-magnon band splits into components excited by $\vec{E} \| [110]$ and $\vec{E} \| [1\bar{1}0]$, corresponding to an exciton on sublattice A and a magnon on sublattice B and *vice versa*. This selection rule is a consequence of the short range of the interion exchange coupling[3,7] so that the inter-