Table II. Relative transition probabilities for $H_2(^1\Sigma_g^+, v'=0) \rightarrow H_2^+(^2\Sigma_g^+, v=0\text{-}5)$.

Transition	Experimental This work	 Electron impact[a]	Theoretical Franck-Condon factor[b]
0-1	0.47	0.53	0.47
0-2	0.83	0.91	0.89
0-3	1.00	1.00	1.00
0-4	0.78	0.35	0.87
0-5	0.71	0.35	0.65

[a] See reference 7.
[b] See reference 11.

it is not known to what extent preionization is contributing to the ion-efficiency curve. As the electron-impact 0-4 and 0-5 probabilities seem to be low, it appears that preionization is relatively more important at the lower levels.

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SATURATION OF A RESONANT OPTICAL DOUBLE-QUANTUM TRANSITION

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We have observed production of violet and infrared radiation from potassium vapor which can be attributed unambiguously to a resonant double-quantum absorption transition. The output of a giant-pulse ruby laser is used to generate stimulated Stokes emission in the near infrared. The two simultaneous pulses are employed then to excite potassium atoms in the ground state $(4s_{1/2})$ to an excited state $(6s_{1/2})$. The excited atoms subsequently cascade down, and intense infrared $(6s\text{-}5p)$ and violet $(5p\text{-}4s)$ radiation is observed. The fact that both the red ruby and the Raman-Stokes pulses are required for the excitation is a clear indication of the double-quantum process. We present theoretical arguments for the saturation of the excitation, and then describe the experimental arrangement.

Multiple quantum transitions were discussed first by Goeppert-Mayer[1] in 1929, and were observed first in the laboratory in the microwave region by Hughes and Grabner.[2] The theory of these transitions occuring under the influence of highly coherent applied fields has been discussed in the experimental papers[2,3] and in detail by Salwen,[4] Hack,[5] Javan,[6] and others.[7] The observation of double-quantum transitions in the optical region of the spectrum has been made possible by the development of lasers, and the simple energy-level scheme of cesium vapor was employed in the experiment of Abella,[8] which followed the first observation of double-quantum absorption into a broad band in an inorganic crystal.[9] Subsequently, such absorption has been found in a wide variety of materials: other doped inorganic crystals,[10] organic crystals,[11] and organic liquids.[12] Saturation of the absorption transition has not been possible. Only in part is the absence of saturation a consequence of the breadth of the upper levels. Another crucial factor in determining the saturation is the position of the intermediate state with respect to the quantum energies in the radiation fields. Yatsiv[13] has suggested the enhancement of multiple-quantum transitions by intermediate-state resonances, which was demonstrated by Cohen and Whiffen,[14] and Javan and Szöke[15] have discussed the enhancement of optical-frequency mixing using resonant phenomena. These treatments have to be modified in the present case because the applied fields are not sufficiently monochromatic. The following calculation shows that with presently obtainable giant-pulse powers it is possible to saturate the double-quantum transition if the applied frequencies are close enough to intermediate single-quantum intervals. This idea led to an examination of atomic systems whose energy levels are separated by frequencies corresponding to high-power lasers. The availability of laser generators using stimulated Raman scattering[16] permits much flexibility in the energy-level scheme, and it was found that the energy-level scheme of potassium vapor is very suitable for resonant double-quantum saturation. The simplicity of the structure of this alkali atom permits reliable theoretical calculations.

The giant-pulse ruby laser creates a pulse of the order of 1-MW/cm^2 peak power lasting roughly 20 nsec, at a frequency which can be varied by thermal tuning of the ruby crystal. The wave number of the beam is 14 401.6 cm^{-1} at 0°C, and has a variation with temperature[17] -0.135 cm^{-1}/°C. The low-lying energy levels[18] of potassium are shown in Fig. 1. It should be noted that the separation of the $6s_{1/2}$ and $4p_{3/2}$ levels is 14 407.76 cm^{-1}, and that the separation of the $4p_{3/2}$ and $4s_{1/2}$ levels is 13 042.89 cm^{-1}. Radiation at the former frequency can be obtained by cooling the ruby to around -40°C, and at the latter by stimulated Raman scattering in an appropriate material. Stokes emission[16] from 1-bromonaphtalene is downshifted by 1363 cm^{-1}, so that a beam of Stokes light at 13 044 cm^{-1} is readily obtainable.

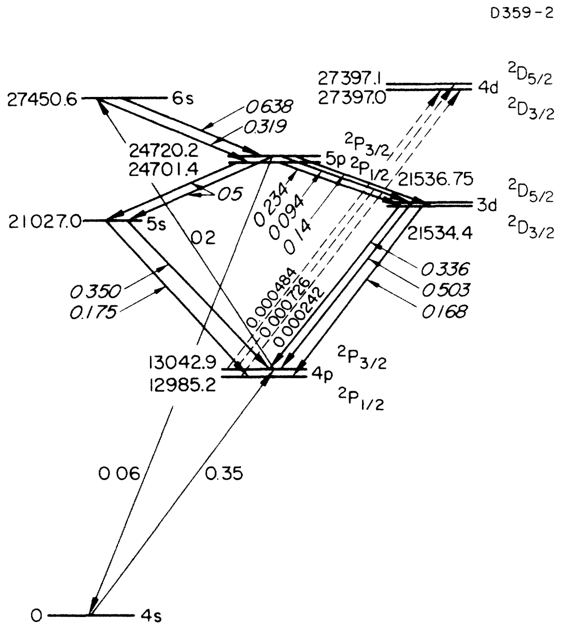

FIG. 1. Energy levels and emission f numbers in potassium.

Theoretical considerations.–We consider the case for which $\omega_{-1}-\omega_{21} \gg 1/T_2$, so that the probability for double-quantum absorption exceeds that for the off-resonant single transitions $1 \rightarrow 2 \rightarrow 3$. The effective matrix element for the calculation of the population of the $6s_{1/2}$ state under the application of the ruby and the Stokes fields is

$$R_{31} = \frac{\langle 3|\mu_z|2\rangle\langle 2|\mu_z|1\rangle E_0 E_{-1}}{\omega_{-1}-\omega_{21}+i/T_2}, \tag{1}$$

where the power flux in the two beams is given by $2cE_0^2$ and $2cE_{-1}^2$. For convenience, we have labeled the $4p_{3/2}$ level as level 2, the $6s_{1/2}$ as level 3, and the ground level as level 1. T_2 is the coherence time of the excitation, and is dominated by the coherence time of the Stokes pulse. The Stokes power spectrum has a half-intensity width of 2 cm^{-1}, corresponding to a coherence time of 5.3 psec. The coherence time for Doppler broadening at 300°C in potassium is 200 psec. At a vapor pressure of 0.1 Torr the expected collision broadening for the resonance lines ($4p$-$4s$), based on Gregory's measurements on cesium,[19] yields a coherence time of 500 psec.[20] Therefore, the coherence time for the excitation is $T_2 = 5.2$ psec. The matrix elements of the dipole moment can be obtained from known values of the oscillator strengths. Those needed in Eq. (1) have been measured,[21] and the measurements have been combined with the calculations of Anderson and Zilitis[22] to obtain the oscillator strengths shown in Fig. 1. The resulting value for the matrix element is such that $d = 2R_{31}/\hbar^2 = 0.0098/(\delta+i)$ psec^{-1}, where the departure from the resonance with the $4p_{3/2}$ state is given by $\delta = (\omega_{-1}-\omega_{21})T_2$. In obtaining the matrix element we have chosen for illustration a ruby-laser field of 1.37×10^4 V/cm corresponding to a flux of 1 MW/cm^2, and $E_{-1} = 432$ V/cm corresponding to a Stokes power flux of 1 $\mathrm{kW/cm^2}$.

If a steady state can be obtained, the probability of occupying the third level is given by

$$\rho_{33}=\tfrac{1}{2}S/(1+\Delta^2+S), \qquad (2)$$

where S is the saturation parameter, and Δ measures the departure from the double-quantum resonance, $\Delta=(\omega_{-1}+\omega_0-\omega_{31})T_2$. The saturation parameter is $S=(dT_2)^2n$, where n is the number of random Stokes pulses during the lifetime, T_1, of the upper state: $n=T_1/T_2$. The natural lifetime of the $6s_{1/2}$ level is 70 nsec, which is longer than the duration of the Stokes pulse, so that a steady state will not be obtained in the absence of more rapid damping of the excitation. In that case, we should solve the rate equations for the transient populations. The solution appears to be obvious; the only change will be to use for T_1 the duration of the pump process, which is about 20 nsec. In that case, $n=3850$, and

$$S=10.0/(1+\delta^2). \qquad (3)$$

Note that in our estimate of the saturation parameter we have employed very conservative values for the fluxes at the ruby and Stokes frequencies, and have used a very short time for the coherence time of the double-quantum absorption. Nevertheless, S is so large that saturation is obtained even with frequency mismatches of the order of several wave numbers. With saturation and a vapor pressure of 0.1 Torr the computed gain at sereral infrared transitions is of the order of several hundred per cm.

One may notice from Fig. 1 that the separation of the $4d_{3/2}$ and $4p_{1/2}$ levels is 14 412.94 $\mathrm{cm^{-1}}$. The ruby crystal will produce a laser beam at this wave number if cooled to -100°C, and one could look for a material with a Stokes shift of 1428 $\mathrm{cm^{-1}}$ in order to excite the $4d_{3/2}$ state by resonant double-quantum pumping. However, the dipole matrix element between the $4p_{1/2}$ and $4d_{3/2}$ states is very much smaller than that between $4p_{3/2}$ and $6s_{1/2}$. For equally advantageous choices of the frequency detuning factors, the saturation factor is only 1.1×10^{-4} times the value quoted in Eq. (3).

The intense laser fields may be expected to ionize the potassium atoms by a multiphoton process. Many calculations of multiphoton ionization rates have been made recently,[23] since the development of the laser. In our case the matrix element will be greatly enhanced by the resonances. An estimate of the rate may be arrived at simply by noting that the $6s_{1/2}$ level will be saturated and calculating the rate of ionization from the $6s_{1/2}$ level. This state in K is sufficiently like the corresponding state in H that we may use Kramers's formula for the photoionization cross section[24] to compute an ionization rate from the $6s_{1/2}$ state; in the presence of a radiation flux of 1 $\mathrm{MW/cm^2}$ this rate is $1.6\times10^6\ \mathrm{sec^{-1}}$. The rate is high enough to be seen, but not high enough to cause an appreciable loss of excited atoms.

Experimental considerations.—A rotating-mirror giant-pulse ruby laser is used as the exciting source with the stimulated Raman scattering from any one of a choice of several Raman materials. Of the Raman materials that were tried, nitrobenzene gave the best excitation, presumably because of the higher amount of Stokes radiation obtainable with this liquid. The exact double-quantum resonance for nitrobenzene is obtained when the laser is operated at 25°C. Because of the saturation, and of the width of the Stokes radiation, the width of the thermal resonance is of the order of tens of degrees. We therefore chose to operate the ruby laser at a point dictated by experimental convenience, which was 0°C.

Preliminary experiments were conducted using a potassium-vapor spectral lamp to verify our excitation mechanism and to enable us to adjust the monochromators and photodetectors. The rather low vapor pressure in the potassium lamp prevented any serious measurement of the saturation phenomena but clearly showed the very strong excitation. Further work was done using a potassium cell 10 cm long with sapphire windows. One window was mounted with a bellows in order to allow rough alignment of the windows for parallelism. The stainless-steel body of the cell was heated with a separate heater wire, and the windows were placed in tube furnaces in order to keep the windows at a higher temperature than the rest of the cell. This insures that potassium does not condense on the windows. The cell was heated to 330°C. The laser and Stokes powers are monitored by using beam splitters to sample a small portion of the energy incident upon the potassium cell. The output from the potassium cell is arranged to go either to a two-meter Bausch and Lomb dual-grating spectrograph with a photomultiplier detector for the visible, or a Perkin-Elmer 98G monochromator, and a lead-selenide infrared detector.

Strong radiation has been observed in the violet at 4048 Å and in the infrared at 3.66, 2.722, and 1.243 μ. The other lines in the visible could not be monitored directly because of the proximity of the laser and the Stokes frequencies to the most interesting transitions.

The strong radiations are not observed if (a) the Raman cell is removed, or (b) the potassium cell is not heated above room temperature.

In order to assure that the recorded signals were not spurious or due to noise, the monochromators were detuned slightly from the emission lines and all the signals were drastically reduced. Figure 2 shows some typical oscilloscope traces. In Fig. 2(a) the lower trace shows the relative laser power, while the upper trace, which is offset horizontally for convenience, shows both the Stokes power (positive) and the electronically delayed violet signal (negative). The time scales for all photographs is 0.2 μsec/division. Figure 2(b) is the same as 2(a) with the Stokes monitor disconnected; Fig. 2(c), however, is taken with the spectrometer slightly detuned from the 4048Å line.

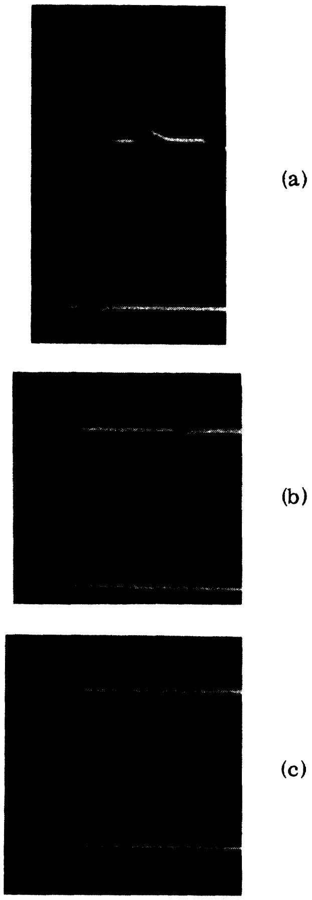

FIG. 2. Oscilloscope traces. Bottom trace in each section monitors the giant-pulse laser. Upper traces represent (a) Stokes energy (up) and violet 4048Å potassium line (down); (b) violet line; and (c) violet line with monochromator off-set.

We are exceedingly grateful to Dr. John M. Richardson, Dr. Charles H. Wilcox, and Dr. George F. Smith for their enthusiastic encouragement and support of our research. Robert Hallden and Dr. Donald H. Close rendered invaluable assistance in the execution of the experiments. We wish to thank also Dr. Ronald C. Knechtli and Dr. Hans Heil for sharing with us information on the design of the potassium cell, which was expertly constructed by Alex Robertson.

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CALCULATIONS OF SOUND VELOCITIES IN CRYSTALLINE HELIUM AT ZERO TEMPERATURE*

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(Received 16 August 1965)

Solid helium is a crystal which cannot be treated by the traditional theory of lattice dynamics,[1] since its zero-point kinetic energy is approximately equal to its potential energy. In fact, de Wette and Nijboer have recently shown[2] that a calculation of the vibrational frequencies of crystalline helium using the harmonic approximation yields *imaginary* frequencies for each point of the Brillouin zone. In this Letter, we treat this problem by using the time-dependent Hartree approximation,[3,4] together with the results of variational calculations of the ground-state energy using correlated trial wave functions.[5,6] We report calculations of sound velocities for various densities of crystalline helium at zero temperature, and we estimate the Debye θ as a function of density. Satisfactory agreement with existing experimental information is achieved.

The starting point of our approach is the Hartree approximation, which assumes that the ground-state wave function factors into a product of single-particle functions:

$$\Psi(\vec{\mathrm{r}}_1,\cdots,\vec{\mathrm{r}}_N)=\prod_{i=1}^{N}\varphi_0(\vec{\mathrm{r}}_i-\vec{r}_i),$$

where $\vec{r}_i$ is the ith lattice vector. The main success of this approximation[7] is that it has a solution of crystalline character, i.e., $\varphi_0(\vec{\mathrm{r}})$ is localized about $r=0$. However, the Hartree approximation fails to take account of short- and long-range correlations. If the interatomic potential is of short range, then short-range two-body correlations are important in lowering the total energy. In addition, long-range correlations are necessary in order to obtain the correct low-lying spectrum of collective excitations, and thus the correct low-temperature specific heat.

The short-range correlations can be approximately treated within the context of a variational calculation.[5,6] The trial wave function is assumed to be of the form

$$\Psi(\vec{\mathrm{r}}_1,\cdots,\vec{\mathrm{r}}_N)=\prod_i\varphi_0(\vec{\mathrm{r}}_i-\vec{r}_i)\prod_{j<k}f(|\vec{\mathrm{r}}_j-\vec{\mathrm{r}}_k|),\qquad(1)$$

where $f(r)=\exp[-Kv(r)]$, and K is a variational parameter. For helium, we take $v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$, with $\epsilon=10.22^\circ\mathrm{K}$ and $\sigma=2.556$ Å. The variational calculation can be carried out by truncating the cluster expansion of the ground-state energy; this method yields an upper bound to the ground-state energy that is accurate to a few percent.[8] It turns out that $\varphi_0(\vec{\mathrm{r}})$ calculated in this way is well approximated by a Gaussian, $\varphi_0(\vec{\mathrm{r}})\cong(A/\pi)^{3/4}\exp(-Ar^2/2)$, so that the ground-state wave function can be characterized by just two parameters, A and K, which vary with density, mass, and crystal structure. Further, the effect of the correlations can be viewed as replacing the interatomic potential $v(r)$ in the Hartree equation by[9] an *effective* potential $W(r)$,

$$W(r)=[v(r)+(\hbar^2K/M)\nabla^2v(r)]\exp[-2Kv(r)],\qquad(2)$$

where M is the atomic mass. Thus the correlation function not only softens the hard core, but also enhances the attractive part of the well.

The collective modes are a natural consequence of the time-dependent Hartree approximation.[3,4] In this approach, the factorization

$$\Psi(\vec{\mathrm{r}}_1,\cdots,\vec{\mathrm{r}}_N;t)=\prod_i\varphi(\vec{\mathrm{r}}_i-\vec{r}_i,t)$$

is assumed for all times in the presence of a weak, space- and time-dependent perturbation. The collective-mode frequencies are the poles of the linear response function. These phonons

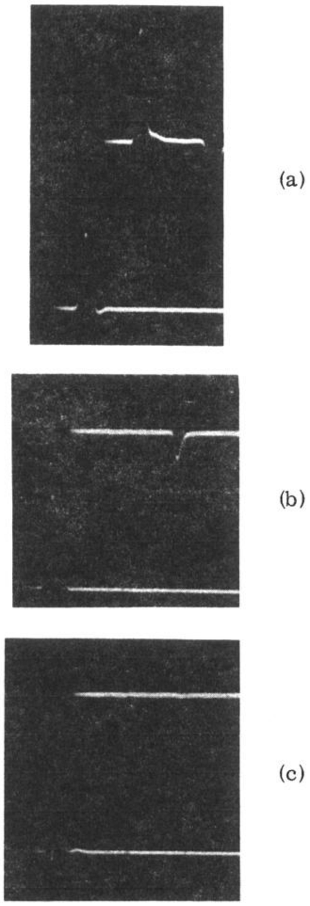

FIG. 2. Oscilloscope traces. Bottom trace in each section monitors the giant-pulse laser. Upper traces represent (a) Stokes energy (up) and violet 4048Å potassium line (down); (b) violet line; and (c) violet line with monochromator off-set.