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LASER-INDUCED FLUORESCENCE IN A MOLECULAR BEAM OF IODINE*

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Resonance fluorescence of the iodine molecule in a gas cell after excitation by 5145-Å light from an argon ion laser has been reported by Steinfeld.[1] We find that the laser induces a transition from a low-vibration, low-rotation level in the $X^1\Sigma_{0g}{}^+$ ground electronic state to a highly excited vibrational level in the $B^3\Pi_{0u}{}^+$ electronic state. The resonance fluorescence that is observed is in the spectral range 5000 Å-1.3 μ and corresponds to the decay of the excited level to a number of vibrational levels in the ground electronic state.

This Letter describes the observation of this fluorescence in a molecular beam of iodine, which, to our knowledge, is the first report of a laser-induced transition in a molecular or an atomic beam.

The apparatus is shown in Fig. 1. 5145-Å light from a single-longitudinal-mode[2] argon ion laser which can be tuned over a 4000-MHz range[3] is passed through a molecular beam of I_2 at right angles. The molecular beam is mechanically chopped at 29 Hz. The resonance fluorescence light is detected in a photomultiplier and the 29-Hz component of the signal is synchronously detected and recorded as the laser is scanned in frequency. A typical output signal [Fig. 2(a)] shows the resonance fluorescence signal in one channel, and the instantaneous power output of the laser as a function of laser frequency in the other. The resonance fluorescence first appears when the laser frequency is 510 MHz above that of the center of the gain curve of the laser and extends over approximately 1300 MHz. Figure 2(b) shows that under higher resolution, achieved by improved laser stability, the fluorescence signal consists of many lines. The width of sev-

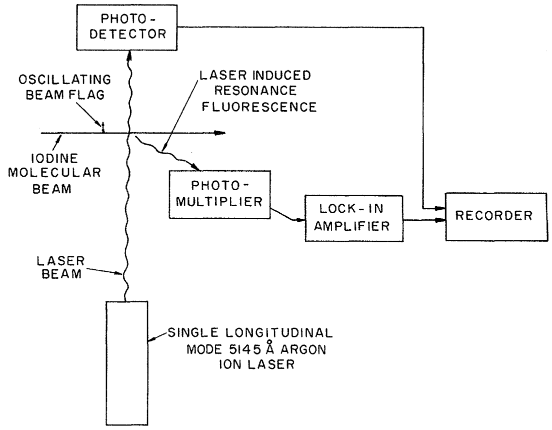

FIG. 1. Schematic diagram of apparatus.

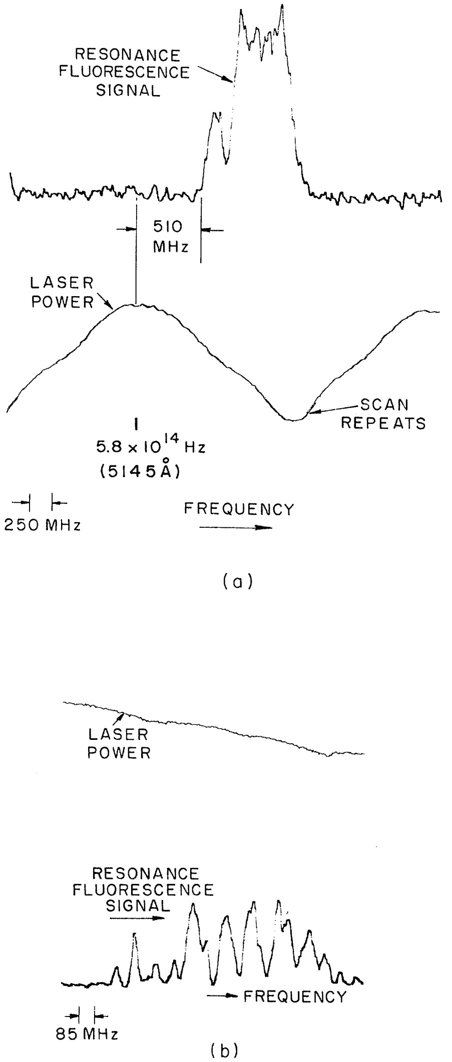

FIG. 2. Simultaneous recording of cw laser power and resonance fluorescence signal as the laser frequency is scanned over 3400 MHz (integration time 1/30 sec). (a) Low-resolution, laser instability (100 MHz). (b) High-resolution, laser instability (25 MHz).

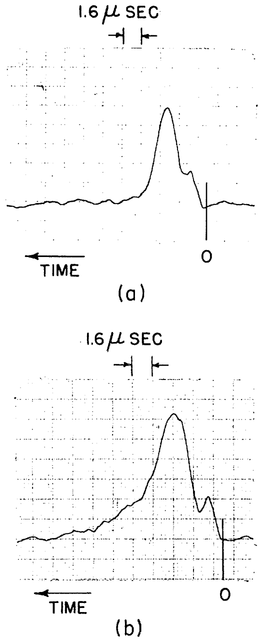

FIG. 3. Sampling data obtained with pulsed laser light. (a) Photomultiplier output attributable to laser light scattered in the apparatus versus time with molecular beam off. (b) Photomultiplier output with molecular beam on, showing the decay of the resonance fluorescence signal.

eral of the lines is approximately 25 MHz, which is no wider than the width of the laser as determined by a scanning, spherical, Fabry-Perot interferometer[4] having an inherent width of 12 MHz; this suggests that the natural width of any one of the lines may be narrower.

An estimate of the ultimate width of the lines may be made by measuring the lifetime of the excited state in the beam. Figure 3 shows results of an experiment in which the laser beam is pulsed and the output of the photomultiplier is recorded during and after the laser pulse by standard sampling techniques, with a boxcar integrator. Figure 3(a) shows the light pulse caused by scattering in the apparatus with the iodine beam off and Fig. 3(b) shows it with the beam on. The decay of the fluorescence signal gives a measure of the lifetime of the excited state, which is found to be 3.0 ± 0.5 μsec. The background pressure of I_2 in the beam chamber is less than 3×10^{-7} mm Hg, so that radiation entrapment plays no part in this measurement. The ultimate width of any of the resonance lines should be approximately 50 kHz.

We observed that the absorption saturates at a power spectral density of 1.4×10^{-4} W/cm^2-MHz, which indicates that the oscillator strength for the transition is 3.8×10^{-4}.

A direct measure of the fraction of molecules in the beam that are excited at saturation is approximately 2.6×10^{-4}. Since this absolute number is subject to some uncertainty, however, another estimate of the population fraction was obtained by absorption measurements in a gas cell of I_2 in the pressure range 5×10^{-3}-10^{-1} mm Hg. The gas cell gives the population fraction as 7.9×10^{-4}, with the oscillator strength obtained from the beam data.

The assignment for the rotational and vibrational levels is by no means clear. The upper vibrational level v' is high and, since the anharmonic vibration constants for such a high vibrational level in the $B^3\Pi_{0u}{}^+$ state are not known well,[5,6] we cannot use the calculated spectrum as a means of assigning v'', J'', and v', J'. Although it is certain that there is no λ doubling, since the transition is between states of $\Omega = 0$, the nuclear quadrupole splitting, $eqQ \sim -2900$ MHz,[7] no doubt complicates the spectrum. Based on (a) the fraction of molecules that partake in the transition, i.e., the partition function $f(v, J)$ in the ground state; (b) the calculated splitting arising from different J for low values of J based on the published values of the rotational constants[5,6] and the assumed value for eqQ; and (c) the absence of anti-Stokes resonance fluorescence above 5100 Å, our best guesses are the following: $v'' = 0, J'' = [3\text{-}5]$ to $v' = 43, J' = [4\text{-}6]$, or $v'' = 1, J'' = [8\text{-}10]$ to $v' = 49, J' = [7\text{-}11]$.

Furthermore, the gas-cell absorption measurements at a pressure of 10^{-1} mm Hg of I_2 revealed another absorption line, 23 times weaker, located approximately 1040 MHz below the center frequency of the laser gain curve.

The significance of our experiment lies in the possibility of using these resonance lines as a reference element in a feedback scheme for the long-term stabilization of the oscillation frequency of the argon laser. This preliminary experiment indicates that it should be possible to stabilize and reset the frequency to a few parts in 10^{13}, if the molecular beam is placed in the laser cavity. This program and a more thorough analysis of the spectrum will be the subject of future publications.

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[7] This value of eqQ of I in I_2 is an extrapolation from other halogen-halide diatomic molecules. A crude approximation to q based on the electronegativity difference of the atoms in the molecules would indicate that $q_{I_2} = q_I$.

TWO-PHOTON SPECTRUM OF A LIQUID

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We have observed the two-photon absorption spectrum of a liquid. This is to be distinguished from the two-photon absorption spectra of crystals where the collective nature of the excitations, i.e., the exciton and band structure, can have a strong influence on all absorption processes.[1-3] The optical absorption spectrum of a fluid, on the other hand, is primarily determined by the electronic states of the free molecules. Earlier attempts to observe this two-photon absorption in liquids have failed because of a frequency-independent, long-lived (1 μsec) absorption, which is due to suspended submicron particles.[4] This has been corrected in our work by repeated filtration with successively finer (~100 Å) Millipore filters to obtain an extremely clean sample of liquid α-chloronaphthalene. This liquid was chosen because it is easy to purify and resistant to oxidation, and possesses an absorption band in a region easily accessible to the ruby-laser plus xenon flash-lamp sources. A 14-cm path-length cell was used in the two-photon spectrometer[5] with typical laser powers of 10 MW.

Figure 1 shows a representative oscilloscope tracing of our measurements. The proof that this is a two-photon absorption folllows from the fact that the absorption temporally follows