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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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

FIG. 1. Tracing of oscilloscope photograph showing two-photon absorption in α-chloronaphthalene. Upper trace is of the Q-switched laser pulse. Lower trace shows the absorption of the xenon pulse.

accurately the laser pulse. In addition, it has been verified that this absorption is linearly proportional to the intensity of the laser pulse. Figure 2 shows the two-photon absorption spectrum of α-chloronaphthalene as well as the one-photon spectrum. The two-photon spectrum contains two bands: a fairly weak transition appearing as a shoulder at 35 000 cm^{-1} and a strong peak at 42 000 cm^{-1}. Comparison with energy levels as derived from the one-photon spectrum shows that there is a one-photon electronic state at 35 000 cm^{-1} but there is no state that corresponds to the two-photon peak at 42 000 cm^{-1}.

To analyze the two-photon spectrum we make the assumption that parity is still a good quantum number for the electronic transitions even though α-chloronaphthalene is not a centrosymmetric molecule. This is supported by the very close similarity between the band intensities and positions in the one-photon spectra of α-chloronaphthalene and naphthalene.[6-8] In the latter case, parity is a good quantum number. In one-photon spectra, allowed electric dipole transitions are g ← u ← g or u ← g ← u. The peaks in the one-photon spectrum are "u" final states. If the final state is not pure g, but rather achieves g character through vibrational perturbations, then the two-photon cross section should be about 2 orders of magnitude weaker than for the case of a pure final g state.

The position of the shoulder at 35 000 cm^{-1} in the two-photon spectrum is coincident with the "u" state seen in the one-photon spectrum. The closeness of these one- and two-photon peaks and the weakness of the two-photon transition strongly indicate that this final state is a vibronically mixed state. Also, the cross section for this absorption is consistent with vibronically induced two-photon absorptions in other organic molecules.[9,10]

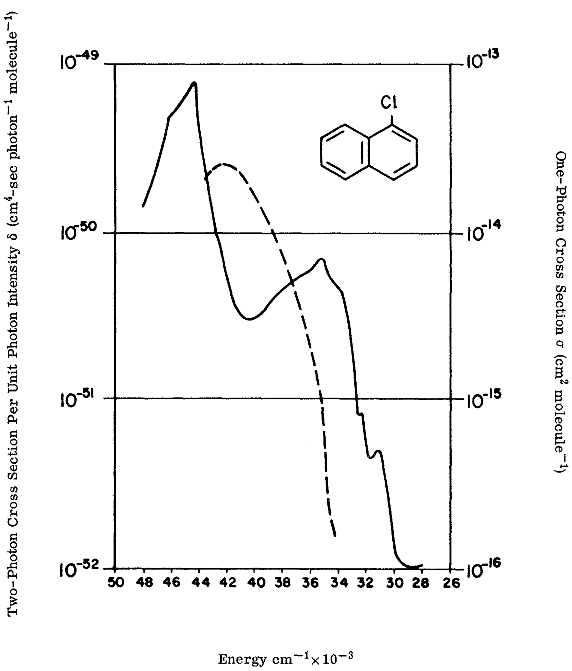

FIG. 2. Spectra of α-chloronaphthalene. The solid curve is the one-photon spectrum and the dashed curve is the two-photon spectrum.

The absence of any "u" state at 42 000 cm^{-1} together with the strength of this two-photon transition strongly suggests that this final state is a pure "g" state. In addition, there is indirect evidence that a "g" state exists at this energy (42 000 cm^{-1}). This is based on the observation of a g triplet state in napthalene at 49 000 cm^{-1} which implies a g singlet state somewhat higher in energy (Hund's rule).[11] Recalling the known similarity of naphthalene to α-chloronaphthalene, we therefore expect a "g" triplet in the vicinity of 40 000 cm^{-1}, strongly suggesting that the two-photon peak at 42 000 cm^{-1} involves a transition to the corresponding "g" singlet state. In the Platt classification this state is called a ^1K_b.[12] In naphthalene this ^1K_b state is classified in group-theoretical notation as the $^1A_{1g}$.

The important result of this work is the observation and assignment of a molecular "g" excited singlet state which is not detectable by one-photon spectroscopy or by two-photon spectroscopy of crystals.

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PLASMA WAVE ECHO EXPERIMENT*

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Experimental observation of a new nonlinear plasma phenomenon, the plasma wave echo, is reported.

A recent theory[1-3] predicts that there are echo phenomena associated with electron plasma waves. We report here an experiment which demonstrates existence of second- and higher-order echoes. The echoes appear at the predicted position in the plasma. The frequency of the echo wave and the dependence of its amplitude on the amplitude of the initial waves are correctly predicted by theory. Observation of plasma echoes is of fundamental interest, since it experimentally verifies the reversible nature of Landau damping. In addition, it provides an experimental test of the perturbation method used to calculate the nonlinear behavior of plasmas in a wide variety of other situations.

If an electric field of frequency f_1 is continuously excited at one point in a plasma and an electric field of frequency f_2 is continuously excited at a distance l from this point, and each Landau damps in space as it propagates away from its point of origin, then the theory predicts that a spatial echo of frequency

$$f_3 = mf_2 - nf_1 \tag{1}$$

will appear at a distance

$$l^* = (nf_1/f_3)l \tag{2}$$

from the point where the second field is excited, provided that

$$mf_2 > nf_1. \tag{3}$$

In general echoes will appear on both sides of the pair of transmitting antennas, but the situation is *not* symmetric: The echoes in opposite directions will differ in frequency, position, and amplitude unless $f_1 = f_2$. The integers m and n are associated with the order of the perturbation theory predicting the particular echo, and for small-amplitude initial waves

$$A_3 \sim A_1^n A_2^m, \tag{4}$$

where A_1, A_2, and A_3 are the amplitude of the wave of frequency f_1, the wave of frequency f_2, and of the echo, respectively.

These experiments were performed with an apparatus[4] previously used to test experimentally[5-7] the Landau damping and dispersion theory.[8] These prior experiments guarantee that the plasma meets the assumptions of the echo theory, i.e., that the plasma is "collisionless" in the sense of the theory, that the electron velocity distribution is Maxwellian, that the waves are properly identified, and so on. The experimental geometry is a long column of plasma bounded in the radial direction by a good conductor. For the data reported here, the cylindrical plasma column has a length of 180 cm and a central density of 1.5×10^8 electrons/cm^3, and a temperature of 9.4 eV. It is immersed in a magnetic field of 305 G, which is large enough to be considered "infinite" in the sense of the theory to be tested. The background pressure is 1.5×10^{-5} Torr (mostly H_2).

Three radial probes are used as antennas. Two of the probes are connected by coaxial