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[14] The theory of Ref. 4 has been shown[15] to be inconsistent with the observed variation of oscillator strength and ground-state splitting through the isoelectronic series V^{2+}, Cr^{3+}, Mn^{4+}. Anisotropy of spin–orbit coupling is calculated by the Helmholz–Wolfsberg molecular orbital method in Ref. 6. The results are in quite good agreement with experiment. However, it is doubtful if this method, which among other approximations neglects the important three-center integrals, is really applicable to transition-metal ions[16] particularly in the calculation of fine spectral details.

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Iodine-Atom Laser Emission in Alkyl Iodide Photolysis*

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LASER emission at 7603 cm^{-1} due to the atomic iodine $^2P_{\frac{1}{2}}\rightarrow{}^2P_{\frac{3}{2}}$ transition, first observed in the photolysis of CF_3I and CH_3I,[1] has been studied in more detail. Moreover, this same laser emission has been found in the photolysis of six other alkyl iodides. We present here a preliminary account of these experiments, all conducted with the confocal laser cavity and In–Sb detector described earlier.[1]

Flash energy was varied, and inert gases were added to test the hypothesis given earlier[1] that the abrupt CF_3I laser quenching prior to flash termination is due to a temperature rise. When quenching is observed, such as that shown in Trace A of Fig. 1, no emission is obtained if the same sample is exposed to a second flash. Trace B_1 shows the emission that results if the flash energy is lowered to 320 J. Now the laser emission continues throughout the first flash (B_1) and it occurs again on a second flash (B_2). In fact, many successive laser emissions have been obtained from a single CF_3I sample at low energies, each delayed a few microseconds and weaker than its predecessor. The quenching can also be prevented merely by adding an inert gas, such as Ar or C_2F_6 (Traces C, D, and E). Again, this results in laser emission on successive flashes.

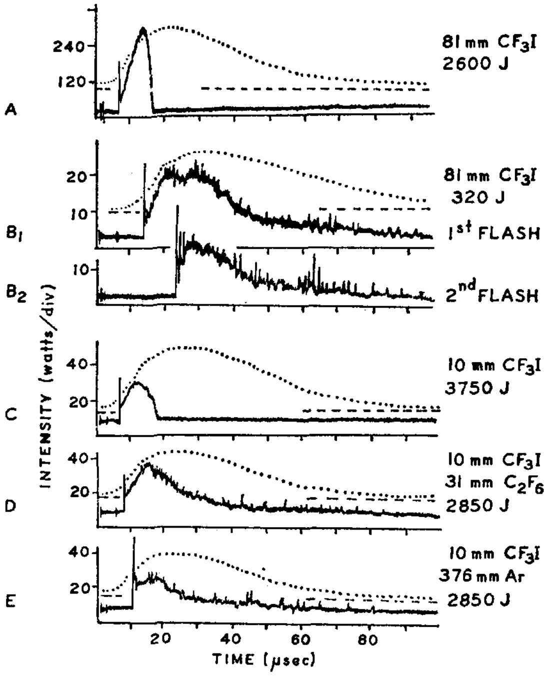

FIG. 1. Effect of flash energy and inert gases on CF_3I laser emission. Dotted lines show flash duration (arbitrary intensity scale).

The behavior shown in Fig. 1 clearly shows that the quenching is caused by a temperature rise. Infrared analysis of the gases remaining after a single flash showed that quenched laser emission (Traces A and C) is accompanied by over 75% decomposition of the CF_3I. When quenching is eliminated (Traces B, D, and E), the percent decomposition is very much smaller (e.g., 3% decomposition with a 320-J flash). These data are probably to be explained in terms of accelerated reaction of $I(^2P_{\frac{1}{2}})$ atoms with CF_3I or, less probably, pyrolytic decomposition of CF_3I to give ground-state iodine atoms.

Figure 2(a) compares the CF_3I laser emission to that from the closely related compounds, C_2F_5I, 1-C_3F_7I, and CH_3I. The quenching evident in the CH_3I case led us to investigate other alkyl iodides in the presence of argon. Figure 2(b) shows laser emission from C_2H_5I, 1-C_3H_7I, 1-C_4H_9I, and isobutyl iodide. The most intense laser emission is obtained from the fluorinated compounds, and the intensity diminishes among the hydrocarbons as molecular complexity increases. Interestingly, no laser action was obtained in the photolysis of 2-C_3H_7I, HI, or I_2.[2]

The absence of emission from I_2 is surprising; its electronic spectrum furnishes a convincing basis for expecting equal numbers of $^2P_{\frac{1}{2}}$ and ^2P atoms,[3] an inverted population in view of the degeneracies. This contradiction suggests that I_2 acts as a quencher, by catalyzing the deactivation of ^2P atoms and/or the

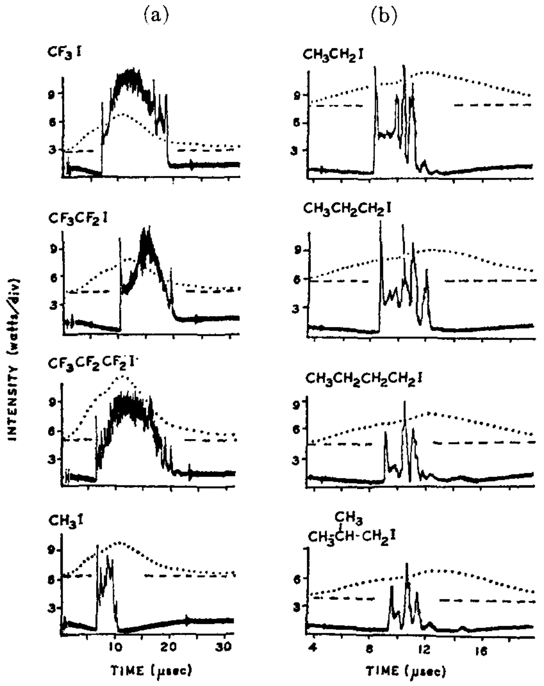

FIG. 2. Laser emission from various alkyl and perfluorinated alkyl iodides. Flash energy, 1070 J. (a) 15-mm iodide; (b) 7.5-mm iodide, 50-mm argon.

recombination of iodine atoms. The latter effect has been observed for $I(^2P_{\frac{1}{2}})$ atoms.[4] To explore this quenching action, mixtures of CF_3I and I_2 were photolyzed. With 29-mm CF_3I and flash energy 684 J, laser emission was delayed and weakened as I_2 vapor pressure was raised to about 1 mm (~40°C) and it was quenched completely at 1.5-mm pressure and higher.[5] The small amount of I_2 needed identifies its role as a quencher rather than a photolytic source of ground-state atoms.

Similar experiments with mixtures of CF_3I and 2-C_3H_7I show that an 8-mm partial pressure of 2-C_3H_7I is needed to quench laser emission from 29-mm CF_3I (684-J flash). In this case, the quenching could be due to photolytic production of $I(^2P_{\frac{1}{2}})$ atoms from 2-C_3H_7I or to preferential reaction of $I(^2P_{\frac{1}{2}})$ atoms with 2-C_3H_7I.

The results suggest that free-radical reactions, probably those of abstraction, play important roles in the observed laser behavior. Thus the study of chemical lasers furnishes a new avenue for the study of such rapid reactions, as well as of energy distribution in bond rupture.

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[2] Conditions explored included 2-C_3H_7I, $p=0.4$ to 11 mm; C_2F_6, $p=0$ to 190 mm, 684–3600 J; HI, $p=7$ or 10 mm, 1600 J; I_2, $t=110$°C, v.p.$=75$ mm; Ar, $p=0$ or 200 mm, 684 J.

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[5] This pressure of CF_3I gives almost unchanged laser emission at temperatures up to 70°C with the same flash energy, 684 J, and no I_2 present.

Notes

Confirmation of Phase Change in Solid Adamantane by NMR

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PROTON NMR spin–lattice relaxation times (T_1) for solid adamantane. have been measured by McCall and Douglass.[1] They observed a minimum in T_1 which they interpreted to be of the type predicted by the theory of Bloembergen, Purcell, and Pound.[2] At about the same time Chang and Westrum[3] measured heat capacities for solid adamantane, which clearly revealed a phase change at 208.62°K, which is in the region of the T_1 minimum found by McCall and Douglass. No obvious discontinuity in T_1, which would clearly indicate a phase change, is to be found in the data of McCall and Douglass, perhaps because it is masked in the scatter of the data points. Questions have been raised as to the cause of this discrepancy.[4,5]

The point of this letter is to show that the phase transition is indeed observable by NMR. Figure 1 shows the proton spin–lattice relaxation times measured at 29.6 Mc/sec by the spin-echo technique. There is a discontinuous change in T_1 at the transition tem-

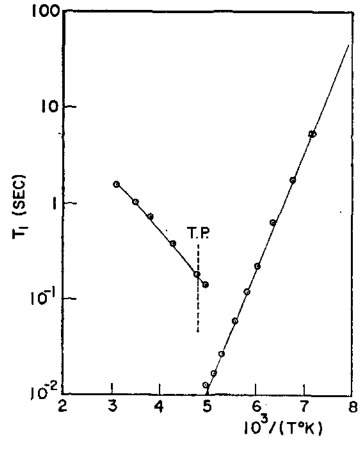

FIG. 1. Spin–lattice relaxation time T_1 vs reciprocal temperature for solid adamantane. The phrase transition temperature is indicated by T. P.