

MOLECULES IN ISOLATION AND IN COLLISION AFTER PUMPING WITH NARROW BAND LASERS

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Narrow line excitation (ca., 0.1 cm^{-1}) is being used to explore both collision-free and collisional processes of S_1 polyatomic vapors. In some cases these lines pump molecules with well-structured absorptions so that single rotational level (SRL) excitation is achieved. However, narrow line pumping proves also advantageous for larger molecules with crowded rotational structure that precludes pumping of single lines.

Collision-free dissociation after pumping SRLs in various vibrational levels of S_1 glyoxal occurs with high quantum yield (0.5). The dissociation yields only molecular products (CO , HCHO , and H_2), with radicals being precluded by energetics. The dissociation also appears to be remarkably clean. We have been unable to detect changes in the kinetic parameters of the dissociation even when 90 percent of the glyoxal is destroyed. Thus the dissociation is potentially an ideal candidate for learning about the dependence of photochemical dissociation upon single rotational and single vibronic level excitation. It may also be useful for isotope separation. However, the most pressing unresolved question still concerns the mechanism. Is it a direct predissociation of the S_1 state or does dissociation follow from a hot ground state after internal conversion? Experiments designed to study this issue as well as some details of the rotational and vibrational dependence of the dissociation will be discussed.

Rotational relaxation studies in S_1 states of glyoxal and, more recently, in benzene have been made possible by narrow line excitation. Relaxation cross sections for both gases are in the range 1 to 10 times gas kinetic. These are similar to those seen with ground electronic states. Selection rules on J and K changes seem minimal for these gases. S_1 glyoxal relaxation with over 20 collision partners shows that the relative cross sections can be related simply to the intermolecular potential well-depth between S_1 glyoxal and the collision partner.

Intramolecular vibrational redistribution in a variety of molecules is being studied as part of our work on mode-to-mode vibrational energy flow in S_1 polyatomics. We are exploring this problem by looking at the time evolution of $S_1 \rightarrow S_0$ fluorescence spectra after narrow band excitation to S_1 vibrational domains where the density of levels is greater than about 100. By a simple technique of chemical timing we are able to observe the transformation of a spectrum which is largely unresolved congestion 10 ns after excitation to a reasonably well-structured spectrum when emission times are restricted to only the first 10 ps. While this change is strongly suggestive of an intramolecular vibrational flow from the restricted distribution established by excitation, the method has sufficient opportunity for speculative maneuver so that some uncertainty yet remains.

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