MOLECULAR DISSOCIATION OF SF_6 BY ULTRA-SHORT CO_2 LASER PULSES*

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We have measured the absolute dissociation probability of SF_6 gas irradiated by CO_2 laser pulses varying in duration from 0.5 nsec to 100 nsec. We find a threshold for dissociation of ≈ 1.4 J/cm^2, independent of pulse duration. For fixed energy density, the dissociation probability increases as the pulse duration decreases, but not nearly to the degree expected from theory. We have also determined the dissociation probability in the $\nu_2 + \nu_6$ combination band and find it to be 10^3 times less than in the ν_3 band, in contradiction to some conclusions recently reported by Ambartzumian et al. The dissociation mechanism takes place without collisions, and if collisions occur, they tend to be detrimental to the dissociation rate.

The isotopically selective [1] dissociation of SF_6 and other molecules by intense CO_2 laser radiation has recently aroused considerable attention [2]. The physical mechanism [3] which permits a molecule to absorb 40 or more infra-red quanta in reaching the dissociation limit is of fundamental interest. Therefore, it is this physical aspect which we emphasize.

In this paper we study the dissociation efficiency as a function of laser intensity as well as laser pulse duration. Although some of the broad qualitative features of the dissociation effect are known [3], quantitative data are lacking. This is because previous investigators generally used a focused beam geometry, in which the intensity varies greatly from point to point in the gas cell. Therefore, the dependence of dissociation efficiency on intensity is convoluted with the beam geometry, and most of the key experimental information is lost. By contrast, in the experiment reported here collimated beam geometry was used whereever possible.

In addition, earlier investigators have been unable to vary the laser pulse duration significantly. We have had access to the Harvard CO_2 oscillator-amplifier system [4], which generates 0.5 nsec pulses by optical free induction decay [5] (OFID). Thus we were able to vary the pulse duration from 0.5 nsec to 100 nsec, a wide enough range to see important effects.

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The experiment was performed by laser irradiation of a brass cell containing pure SF_6 at a pressure of 0.2 torr. The cell was 4.5 cm long and 2 cm in diameter, with sodium chloride end windows. The partial pressure of SF_6 before and after CO_2 laser irradiation was measured on an ir spectrometer by the size of the transmission dip in the ν_3 band. The size of the dip was independently calibrated against an absolute pressure gauge. The partial pressure of SF_6 was always low enough so that the cell could be regarded as optically thin.

In a typical run only 10% of the gas was dissociated, thereby avoiding possible problems associated with the build-up of reaction products. Depending on the dissociation efficiency, this might require as few as 25 laser shots or as many as 10,000.

It was very important to bake the cell during evacuation before filling it. Otherwise there was a slow build-up of background pressure during the experiment due to outgassing from the cell walls. On a long run the background pressure would build up sufficiently to have a strong effect on the dissociation efficiency, invariably reducing it. (This is strong evidence for the collisionless nature of the dissociation process.) To avoid this difficulty, the pressure at which these experiments were run, 0.2 torr, was low enough that reducing it further had no effect on dissociation efficiency.

Two types of laser systems were used for these experiments: (a) A conventional multi-mode TEA CO_2

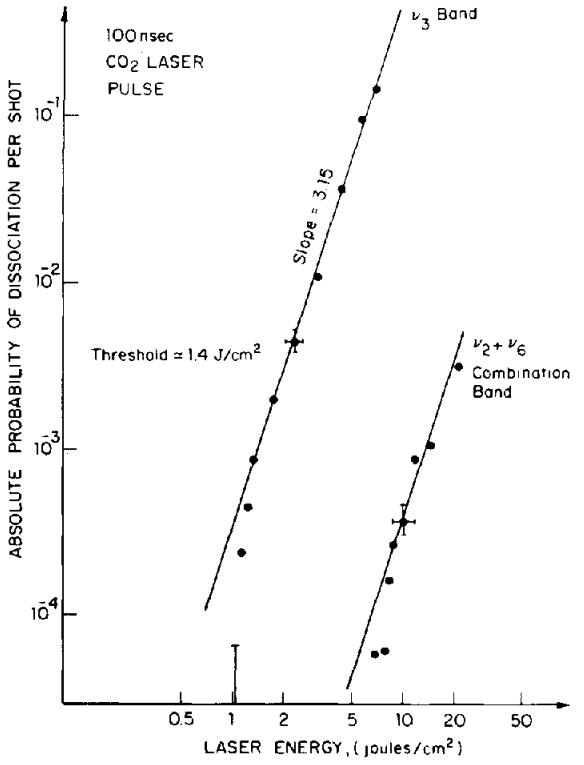

Fig. 1. The absolute probability of dissociation per irradiated SF_6 molecule per laser shot as a function of energy density. The laser was a conventional multimode TEA CO_2 laser, tuned to P20 for the ν_3 band and to R20 for the $\nu_2 + \nu_6$ combination band. The error bar coming out of the bottom of the graph represents a null result for dissociation below threshold, $E_{th} \approx 1.4$ J/cm^2. Notice that the probability approaches unity near the top of the graph. Collimated beam geometry was exclusively employed for all these data points. The combination band has 10^3 times less dissociation probability at a given energy density.

laser and (b) a single-mode oscillator-amplifier system based on an OFID pulse shaper. The system could be adjusted to deliver pulses of 0.5 nsec, 10 nsec and 100 nsec durations.

Fig. 1 shows some experimental results which were produced with system (a), the conventional multimode TEA laser. The output was focused by a long focal length lens, producing a long, narrow collimated region of light at the sample cell. Since the depth of focus was much greater than the thickness of the cell, the beam geometry could be regarded as collimated. In fact, the beam area could be varied by moving the cell back and forth along the focal region.

The absolute dissociation probability per irradiated molecule per shot, α, was calculated from the following formula:

$$\alpha = \frac{A}{aN} \ln \frac{p_i}{p_f},$$

where p_i and p_f are the initial and final partial pressures of SF_6, A and a are the cell and beam areas, respectively, and N is the number of laser shots of irradiation.

Measurements extended up to an energy density of 20 J/cm^2, the window damage threshold for 100 nsec pulses. The laser was tuned to P20 for irradiation of the ν_3 band and to R20 for irradiation of the $\nu_2 + \nu_6$ combination band. The dissociation probability had a cubic dependence on energy density for both bands.

At a given energy density, the combination band was weaker by a factor 10^3. This disagrees with Ambartzumian et al. [6], who claim that the combination band is only 10 times weaker. Their conclusion is applied to a beam geometry where the laser is focused inside the cell. The dissociation fraction is then a weighted average over a wide range of intensities, with most of the effect coming from the very high intensity region where the probability is 100% in either case. Therefore, experimental results based on focused beam geometry require some form of spatial de-convolution before they can be interpreted. When properly deconvoluted, the experimental result of Ambartzumian et al. can be made consistent with fig. 1.

The other important experimental information in fig. 1 is the threshold energy density $E_{th} \approx 1.4$ joules/cm^2 below which the dissociation efficiency quickly fell to zero, as indicated by the error bar coming out of the bottom of the graph. This feature is strong evidence for the two-step dissociation model [3] in which the second step, linear absorption in the continuum of molecular states, requires a finite energy density to reach the dissociation limit:

$$E_{th} = I_{diss}/\sigma,$$

where I_{diss} is the dissociation energy and σ is the absorption cross section in the continuum. For $I_{diss} \approx 5$ eV and E_{th} as measured, $\sigma \approx 5 \times 10^{-19}$ cm^2, a cross section which is consistent with the oscillator strength sum rule [3].

The curves in fig. 1 were all taken at a pulse dura-

tion of 100 nsec. Unfortunately, it was not possible to repeat the experiment with the 0.5 nsec CO_2 laser pulse. The windows would already be damaged by the ultra-short pulses at the dissociation threshold of 1.4 J/cm^2 in the collimated beam geometry. Consequently, no measurements could be taken at any higher energy density. At least it was possible to confirm that dissociation was not occurring below 1.4 J/cm^2, for the ultra-short CO_2 laser pulses. Therefore, the threshold is certainly energy dependent and not power dependent.

In order to study the pulse duration dependence further, it was necessary to revert to focused beam geometry. Then the intensity in the cell could be very high even while the windows were kept below damage threshold. As already discussed, this geometry presents some problems in regard to data interpretation. The approach taken here was to vary only the pulse durations, keeping all other experimental factors as constant as possible. The pulse energy, spatial structure and geometry of illumination were unchanged, even though the pulse duration was varied from 0.5 nsec to 100 nsec.

The laser system (b) was operated in three different modes: (*i*) The OFID mode generated 0.5 nsec pulses. (*ii*) With the OFID cell evacuated, the plasma shutter [7] was triggered to transmit only the initial rising portion of the TEA laser pulse. This had a width of 10 nsec. (*iii*) With the plasma shutter not triggered, the full 100 nsec-long laser pulse was transmitted. Linear attenuators insured that the beam energy was the same, 0.1 joules, in each of the three different modes.

The laser, tuned to the P20 rotational line at 10.6 μ, was focused into the cell with an *f*/2.5 germanium lens. Due to the focused beam geometry the absolute probability of dissociation could not be measured. Fig. 2 plots merely the fraction of molecules in the cell dissociated per shot.

The most unexpected aspect of the results is the relatively small increase in dissociation fraction for the short pulses compared to the long pulses. In going from 100 nsec to a 0.5 nsec pulse of equal energy, the dissociation fraction increased only 30%, despite the greatly increased peak power. Pulse energy seems to be more important than peak power in determining the dissociation probability.

At the threshold energy density of 1.4 J/cm^2, the peak power in a 0.5 nsec pulse is 2.8 × 10^9 W/cm^2.

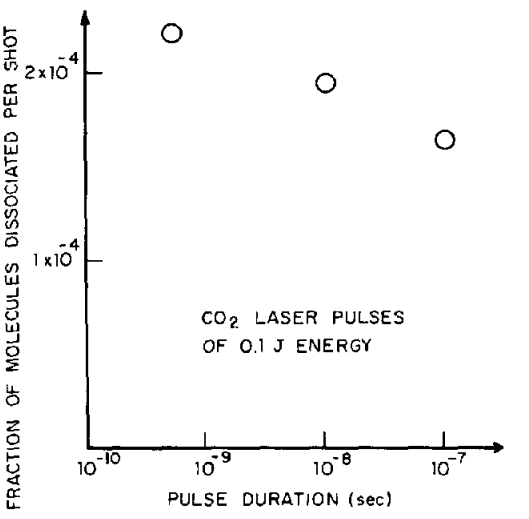

Fig. 2. Comparison of the fraction of molecules dissociated by three varying pulse durations, but with fixed pulse energy, irradiation geometry and spatial structure of the beam. The laser was tuned to P20, and a focused beam geometry of aperture ratio *f*/2.5 was used. The surprising result is that the ultra-short pulse dissociated only 30% more molecules in spite of its hundred-fold increase in peak power.

The electric field is 10^6 volts/cm, and the Rabi precession frequency is 7 cm^{-1}. Most theoretical concepts imply that 100% dissociation efficiency should be expected at that intensity. But if the entire volume in which threshold was exceeded had experienced 100% dissociation, then the observed dissociation fraction for the 0.5 nsec pulse in fig. 2 would have been fourteen times higher. This then is the surprising aspect of the results. Short pulse irradiation is more efficient than long pulse irradiation, but not nearly to the degree expected.

These experiments permit us to draw several conclusions about the dissociation mechanism. In the first place collisions are certainly not necessary for dissociation. At 0.2 torr pressure only ≈ 0.1% of the molecules undergo collisions during the ultra-short laser pulse. Furthermore, in all cases the dissociation efficiency was reduced when the gas pressure was increased. Additionally, experiments are now being reported of dissociation in a high vacuum molecular beam apparatus. The weight of evidence for the collisionless nature of the mechanism is threrefore overwhelming.

Also on fairly solid ground is the idea that a finite energy density is required to drive SF_6 up the vibra-

tional continuum to the dissociation limit. The integrated power, rather than the peak power, is of importance here, which is indicative of step-wise absorption. The cross-section of 5×10^{-19} cm^2 seems reasonable for this type of process, and it agrees with estimates based on a oscillator-strength sum-rule.

The relatively weak dissociation on the $\nu_2 + \nu_6$ combination band shows that the dipole matrix element plays quite an important role. The dipole moment of $\nu_2 + \nu_6$ is weaker than ν_3 by a factor 10, yet the dissociation is weaker by a factor 10^3. This ratio would probably be even larger, but for the close proximity of the two bands in frequency. This probably permits the combination band to "borrow" oscillator-strength from the ν_3 band, especially in the higher vibrational levels.

The most puzzling conclusion drawn from these experiments is that the dissociation probability depends mostly on the energy density of the pulse and very little on the power density. This dependence on time integrated power seems to indicate that sequential absorption of photons is playing an important role in determining dissociation probability. On the other hand, theory [3] claims that peak power should be the important factor, provided that the energy threshold is exceeded. Clearly there is much yet to be learned about the interaction between intense infrared radiation and polyatomic molecules.

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