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Geometrical Effects on the Isotopically Selective Photodissociation of SF_6 Under CO_2 Laser Pulses

P. Fettweis and *M. Nève de Mévergnies*

C.E.N./S.C.K., B-2400 Mol, Belgium

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Abstract. A linear relationship is found between the ^{34}S isotopic enrichment factor per pulse and the focal distance of the lens used to concentrate the laser beam. From this, one derives a threshold power of 26 MW/cm^2 for photodissociation, a mean absorption of 100 photons of 10.59 μm wavelength per $^{32}SF_6$ dissociation, and a dependence of the enrichment factor on the 3/2 power of the laser pulse energy.

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It is known [1, 2] that isotopically selective photodissociation of SF_6 occurs under CO_2 laser pulses, when the pressure is sufficiently low so as to have a collisionless regime within the duration of the pulse, and when the radiation power (or energy) exceeds a given threshold value. It has also been shown theoretically [3–5] that the dissociation results most probably from a cascade excitation along the vibrational manifold of the SF_6 molecule.

A better understanding of the physics of this interesting phenomenon requires first an adequate knowledge of simple geometrical effects, if any.

We have investigated the relationship between the focal distance of the lens used to concentrate the laser beam, and the ^{34}S enrichment factor per pulse w. The relation between w and the enrichment factor β after N pulses (i.e. the ratio of the final to the initial value of $^{34}S/^{32}S$ in the SF_6 gas) is: $\beta = \exp(wN)$. Our TEA-CO_2 laser (Lumonics Mod. 203) delivered multimode, line-selected pulses of about 1 Joule energy and 80 ns FWHM, 200 ns FW duration. The irradiation cell had NaCl windows of 3 cm diameter, a total length of 46 cm and a total gas volume of 440 cm^3. Mass spectrometric analysis of the irradiated gas was based on the 129/127 peak ratio of the SF_5^+ ion of the residual SF_6 gas.

Our results are shown on Fig. 1. It is seen that, for a given set of experimental conditions, a linear relationship is found between w and f.

This result is easily explained if it is assumed that the photodissociation occurs exclusively inside a "reaction volume" with a shape, as shown schematically in Fig. 2a, the power density inside the volume being larger than the threshold value for photodissociation. Such a volume is approximately proportional to f. A

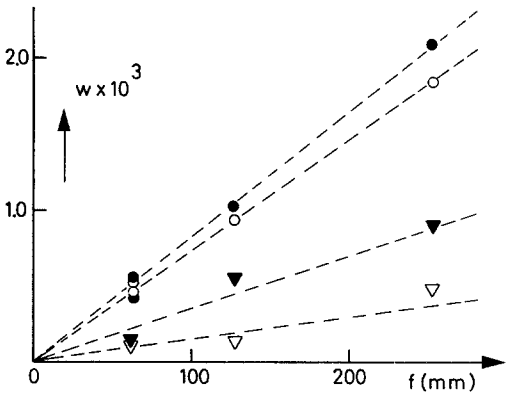

Fig. 1. Enrichment factor per pulse w vs focal length f. The CO_2 laser was adjusted on the $P(20)$ line of the (00°1–10°0) band. ●: 0.5 Torr SF_6; ○: 1.0 Torr SF_6; ▽: 1.0 Torr SF_6 and 10 Torr H_2; ▼: 0.5 Torr SF_6 and 5 Torr H_2

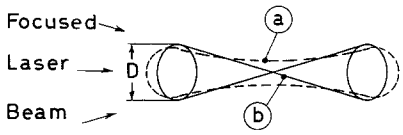

Fig. 2 (a) Surface (schematic) where the energy density in the laser beam equals the threshold value for photodissociation; the volume enclosed by this surface is called the "reaction volume". (b) Biconical approximation for the reaction volume

similar shape has been demonstrated experimentally by Isenor et al. [6] in the case of SiF_4. It implies that, within the reaction volume, the photodissociation rate per unit volume is constant. This is probably a fairly good assumption if the laser photons interact with isolated SF_6 molecules, i.e. in a collisionless regime.

It was not possible to make an exact calculation of the shape of this reaction volume, as the mode distribution within our laser beam was unknown. However, for the f-lengths used in our experiments, the focal volume is at most of the order of a few 10^{-3} cm^3, i.e. more than 10^2 times smaller than our estimated reaction volume (see below). Thus, the biconical shape shown in Fig. 2b should be approximately correct.

We have used this simplification for evaluating the reaction parameters in the ($f=254$ mm; $P=0.5$ Torr; pure SF_6) case, where 0.2% of the total number of $^{32}SF_6$ molecules are dissociated per pulse. The existence of the reaction volume defined above implies that inside it, all the SF_6 molecules able to absorb the 10.59 μm photons of the $P(20)$ laser line are dissociated. The ν_3 absorption bands of $^{32}SF_6$ and $^{34}SF_6$ are well separated (isotopic shift of 17 cm^{-1}) [7]. It can thus be assumed that the $^{32}SF_6$ species dissociates almost exclusively, yielding a reaction volume of 0.9 cm^3.

Taking into account the transmission of the $f=254$ mm, 28 mm diam. Ge lens and of the NaCl entrance window, the incident laser energy amounts to 0.67 J, of which 3.3% was found to be absorbed by the SF_6 gas between the entrance window and the reaction volume, and 4.3% within this volume. Supposing that the laser energy decreases linearly along the optical axis of the reaction volume, we conclude that the threshold energy amounts to 2.4 J/cm^2. According to the time shape of our laser pulse this would yield a threshold power of 26 MW/cm^2.

Using the 4.3% absorption quoted above, it is found that each $^{32}SF_6$ molecule dissociates after a mean absorption of about 100 photons, i.e. 3.4 times the minimal value of 29 photons needed to break an S-F bond.

The geometrical effect described here implies that, for a given f-length, w varies linearly with D^3 (see Fig. 2). As D^2 is proportional to the energy density, one concludes that w varies as the 3/2 power of the laser pulse energy. A similar relation has been found by Isenor et al. [6] for the dissociation rate of SiF_4.

Additionally, our experiments show (see Fig. 1) that, in the $f=254$ mm case, the w-value for pure SF_6 is about 1.5 times larger than for a SF_6+H_2 (1/10) mixture.

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