– The fraction of the incident laser energy transmitted through vapours and plasma formed during the interaction of the laser radiation with the target (Fig. 3).

– The moment of occurrence of the induced and sustained light signal on the target surface.

A series of measurements were performed, concerning the temperature dependence of target material absorptivity, the measurements being performed for the first time for aluminium (Fig. 4).

A few-correlation were established between the characteristic quantities being studied. The material absorptivity A_{eff} shows a steep encrease from (3–4)% to (15–20)% situated in a peak intensity range between $I_0 = I_1 = 1.2 \times 10^8$ W/cm^2 and $I = 2.4 \times 10^8$ W/cm^2. For larger values of the intensity, the value of A_{eff} begins to decrease.

A common threshold $I_0 = I_2 = 1.7 \times 10^8$ W/cm^2 for the appearance of incident laser radiation absorption in transmission measurements and for the appearance of the light signal, for measurements with balistic pendulum, confirming that the recorded light originates in the vapour jet and plasma evacuated from the irradiated surface, was put into evidence.

The absorptivity is 8–11% for this value of the incident laser intensity.

It follows that the increase of the plasma effective absorptivity does not occur simultaneously with the appearance of plasma luminosity (and of the screening effect).

A theoretical analysis has pointed out that the explanation of this phenomenon is not due to a metal-dielectric laser induced transitions, and can be explained through the temperature dependence of the aluminium absorption coefficient and the common vaporization of the metal.

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Laser Chemical Physics

Deuterium Isotope Separation in the Infrared Multiphoton Dissociation of CF_2HCl and $CFCl_2H$

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PACS: 82.40

Marling et al. [1] have recently shown that the infrared multiphoton dissociation (IRMPD) of CF_3H provides an attractive candidate for possible large scale isotope separation. It appears that we might still improve the economic feasibility of such a photochemical deuterium isotope separation if we can find a system with better isotopic selectivity than CF_3H. Here we wish to report on an investigation of the IRMPD of CF_2HCl and $CFCl_2H$ for this purpose.

We follow the following criteria to optimise the isotope separation: *1*) Relatively high yield for the dissociation of the D isotope at "reasonable" energy fluences. *2*) Negligable yields for the H isotope, and *3*) negligable single photon absorption of the *H* isotope at the wavelength of maximum yield for the D isotope. *4*) The molecule choosen must be small, i.e. must dissociate close to the dissociation limit, and *5*) it must have as low as possible a threshold for unimolecular reaction. *6*) Reaction products should not absorb the ir radiation and be chemically stable. 7) The molecule choosen should be easily redeuterated to natural abundance. *8*) A strong CO_2 laser line should be available.

CF_2HCl appears to obey all these criteria to a large extent as can be shown in the following figures. Figure 1 shows the IRMPD yield as a function of wavelength near 982 cm^{-1}. Yields as high as 5% are obtained at fluences as low as 6 J cm^{-2}. Figure 2 shows that the CF_2HCl molecule absorbs hardly any energy at this wavelength. Figure 3 the selectivity of the IRMPD of 0.3 torr CF_2DCl in 10.5 Torr of CF_2HCl: Fig. 3a shows the total ir spectrum in the region of interest prior to irradiation, Fig. 3b shows the scale expanded peaks due to CF_2HCl near 3 μm and CF_2DCl near 9.85 μm, and Fig. 3c the mixture after 500 laser pulses of 6.3 J cm^{-2} at 10.19 μm. The selectivity measured in these experiments (defined as the ratio of the fraction of CF_2DCl dissociated per pulse in the irradiated volume/the fraction of CF_2HCl dissociated per pulse in the irradiated volume) exceeds 10^5.

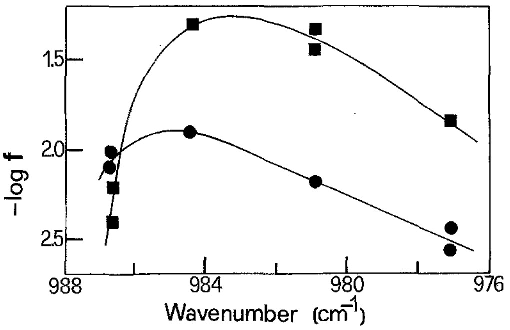

Fig. 1. IRMPD spectrum of CF_2DCl taken with a 30 ns FWHM pulse of 6 J cm^{-2}, ● and ■ are measurements at, respectively, 298 and 473 K. The CF_2DCl pressure is 0.4 Torr

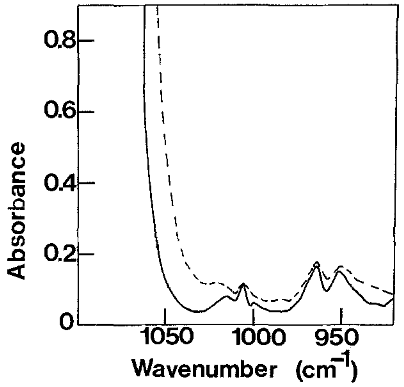

Fig. 2. The low intensity absorption spectrum of 760 Torr of CF_2HCl at room temperature (———) and 200 °C (– – – – –). Optical path = 10 cm

Redeuteration to natural abundance of the depleted CF_2HCl could not be carried out by direct exchange with water using the

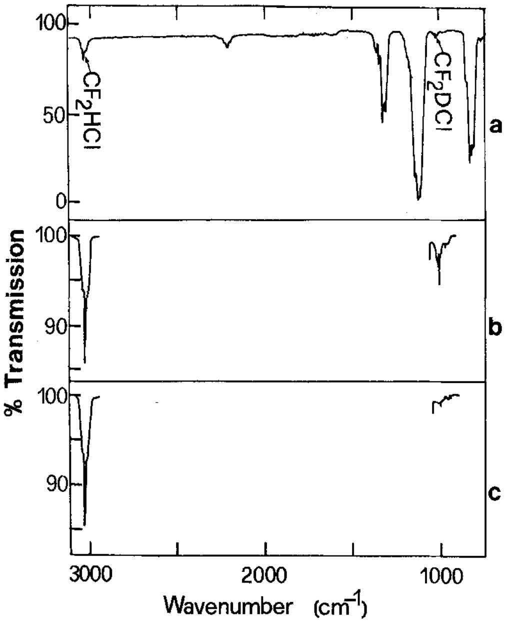

Fig. 3. (a) Low intensity spectrum of 0.3 Torr CF_2DCl with 10.5 Torr CF_2HCl. (b) The bands characteristic of both isotopes have been expanded 5×. (c) The same as in (b) after 500 laser pulses (70 ns FWHM) of 6.3 J cm^{-2} at 10.19 μm, at room temperature. Whereas CF_2DCl has completely disappeared, CF_2HCl is not diminished at all

NaOH/DMSO catalyst as in most freons. CF_2HCl appears to hydrolyse faster than it exchanges in a basic medium. Thus we developed the following scheme: First the CF_2HCl (depleted from D) is heated to about 500 °C with excess HCl (natural abundance D) according to

$$CF_2HCl \xrightarrow[\Delta]{} :CF_2 + HCl$$

$$:CF_2 + HCl\ (\text{excess, natural abundance D}) \longrightarrow CF_2HCl$$
$$\begin{pmatrix}\text{nearly natural}\\ \text{abundance in D}\end{pmatrix}$$

after which the somewhat depleted HCl is exchanged with water at natural abundance containing added H^+ or Cl^- to decrease the HCl solubility.

Experiments with $CFCl_2D$ also showed very little optical absorption due to $CFCl_2H$ at the wavelength were $CFCl_2D$ has its maximum IRMPD yield (about 930 cm^{-1}). The yields themselves in this region are quite high, near 10% at 6 J cm^{-2}. The redeuteration of the depleted $CFCl_2H$ with water using NaOH/DMSO catalyst works well. It appears however that in this substance a chemical reaction, possibly of thermal nature, leads to a decrease in the $CFCl_2H$ concentration when mixtures of the two isotopes are irradiated. We are presently investigating this interesting phenomena, and are trying to establish if it leads to a decrease in the isotopic selectivity.

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Infrared Laser-Induced Photodissociation of Fast Sulfur Dioxide Ions

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The frequency dependent single and multiple photon dissociation of initially highly vibrationally excited two- and polyatomic ions under collision free conditions has been reported recently, e.g. HD^+ [1] and CF_3X^+ (X=Cl, Br, I) [2].

In the following a home-built laser-ion-beam apparatus for studying laser-induced ir photodissociation and uv fragmentation of fast molecular ions is described briefly. Positive ions formed in a hollow cathode discharge of the parent gas in a duoplasmatron ion source at pressures around 2×10^{-1} mbar extracted and accelerated to final kinetic energies between two and seven keV. After deflection and mass separation by a 90° magnetic sector field laser excitation of the ions can be obtained in coaxial or crossed beams configurations, the intersection angle between laser- and ion beam being 45°, 90°, and 180°, respectively. The kinetic energies and masses of fragment ions are determined using a 90° electrostatic spherical condenser. The ions are detected by a channeltron electron multiplier using lock-in technique, the photon beam is mechanically chopped at about 95 Hz.

First results are reported on the collision free photodissociation of fast SO_2^+ ions via the two channels

$$SO_2^+ + \hbar\nu \rightarrow SO^+ + O \qquad (1)$$

and

$$SO_2^+ + \hbar\nu \rightarrow S^+ + O_2 \qquad (2)$$

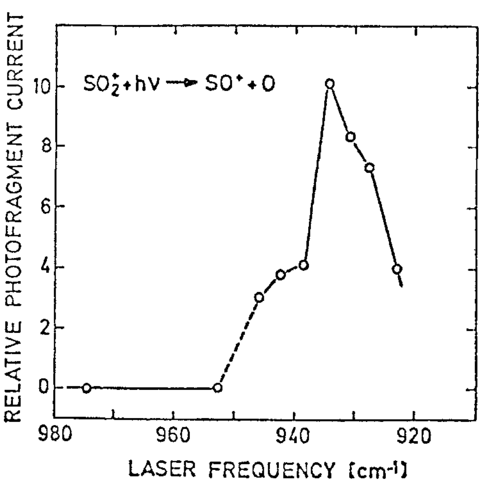

Fig. 1

after excitation of the ν_1 symmetric stretching mode of the parent SO_2^+ ions with a low power cw CO_2 laser, $P \leq 20$ W, coaxial beams configuration.

Process (1) shows a distinct frequency dependence of the SO^+ ion yield peaking around 935 cm^{-1} (Fig. 1) with a FWHM of about 25 cm^{-1}. In the other wavelength region spanned by the CO_2 laser (9.15–10.91 μm) no dissociation has been observed, in contrast to channel (2) exhibiting dissociation across the CO_2 laser wavelength region but relatively little variation in the S^+ ion yield. The observation of two dissociation channels indicates that the SO_2^+ ion beam formed in the duoplasmatron probably consists of internally excited ion species in various electronic and vibrational states.

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