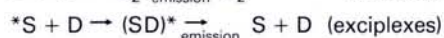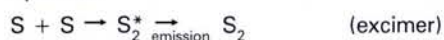Fig. 2 — Transient absorption spectrum of the luminescent charge transfer excited state of the metal complex, Tris-bipyridyl ruthenium(II), $Ru(bpy)_3^{2+}$ in water at room temperature recorded at the end of laser pulse. (a) difference absorption spectrum, (b) absorption spectrum after correction for the ground state absorption.
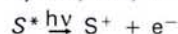
The forward reaction can be followed either by monitoring the enhanced decay of luminescence of $^3Ru(bpy)_3^{2+*}$ at $\lambda = 615$ nm (trace (a)) or by the rate of formation of the products, e.g. MV^+, optically monitoring its growth at its absorption maximum in the visible (at $\lambda = 600$ nm), (trace (b)). The redox products of the photoreaction $Ru(bpy)_3^{3+}$ and MV^+ recombine slowly in the dark and the rate constant for the back reaction measured by monitoring the decay of MV^+ absorptions at $\lambda = 600$ nm or of $|Ru(bpy)_3^{3+} - Ru(bpy)_3^{2+}|$ at $\lambda = 457$ nm (curve (c)). Kinetic analysis of the curves yields the rate constants for forward and reverse transfer as $4.0 \times 10^8 M^{-1} s^{-1}$ and $2.0 \times 10^9 M^{-1} s^{-1}$, respectively. The quantum yield of the excited state $^3Ru(bpy)_3^{2+}$ and of the redox products MV^+, $Ru(bpy)_3^{3+}$ can be shown to be 1.00 and 0.30 respectively in water.

(b) *Formation of the excited state associated dimers or complexes (excimers and exciplexes):*

$$S + S \rightarrow S_2^* \xrightarrow{emission} S_2 \qquad (excimer)$$
$$*S + D \rightarrow (SD)^* \xrightarrow{emission} S + D \quad (exciplexes)$$

To explain some experimental results, Th. Forster postulated the possible formation of these excimers and exciplexes in 1955. By quantitative studies of their absorption spectra, lifetimes and yields by pulsed laser techniques, especially due to Mataga and Ottolenghi, these associated excited species are now as well characterized as their parent species: singlets and triplets. Typical examples are excimers of hydrocarbons such as pyrene and exciplexes derived from aromatic hydrocarbon amines.

(c) *Photoionization from the excited state by one, two, ... multiphoton processes:*

$$S* \xrightarrow{h\nu} S^+ + e^-$$

The photoionization process is monitored by following the growth and decay of the cations and electrons by optical absorp-

tion. An equivalent and elegant method in use is *pulsed laser conductivity* studies, where instead of absorptions, changes in the conductivity of the solutions upon laser light excitations are monitored on very fast scales. By this means, extensive information has been obtained on the mechanisms of mono, biphotonic processes as well as on the dynamical behaviour of electrons in liquids (mobility, trapping, etc.).

Application to Photochemistry and Photobiology

In addition to their routine use to monitor the kinetic behaviour of singlet and triplet excited states, the technique of laser flash photolysis has been exploited to assimilate extensive information on several areas of organic and inorganic photochemistry as well as in photobiology. Particular attention here can be paid to the recent advances in the chemistry of singlet oxygen, photoreactivity of carbonyl compounds, photochemistry of transition metal complexes, especially those with bipyridine or phenanthroline ligands, fluorescence probe analysis of aggregate systems such as micelles, vesicles, polymers and polyelectrolytes, primary processes of photosynthesis and photochemistry of visual pigments such as retinals and rhodopsin. Space limitations preclude any detailed discussions of these.
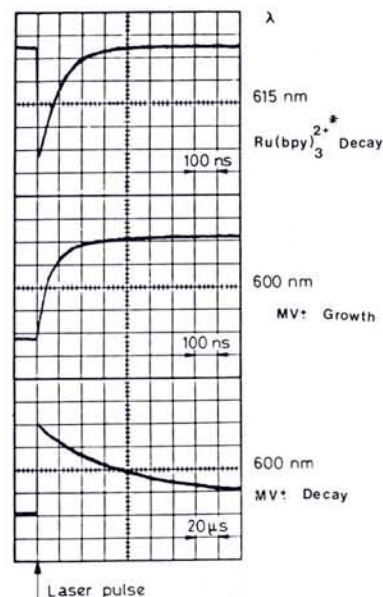

Fig. 3 — Oscilloscope traces showing the kinetic behaviour of the transients following electron-transfer quenching of $^3[Ru(bpy)_3^{2+}]^*$ excited state by methylviologen (MV^{2+}).
a) decay of $^3[Ru(bpy)_3^{2+}]^*$ emission monitored at $\lambda = 615$ nm.
b) growth of MV^+ radical, monitored at $\lambda = 600$ nm.
c) decay of MV^+ radical at longer time scale (back transfer).

Isotope Separation

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Isotope separation is today one of the most actively pursued areas of laser application. The advent of laser excitation sources at many different wavelengths, with high spectral purity and high energy density has revolutionized concepts of photophysical or photochemical isotope separation, which were, in principle, known long ago but could never be put into practice because of the limited source quality of conventional lamps. Many isotopes have been separated successfully to date in laboratory experiments, but much still remains to be done to extend the results to an industrial scale, where the process is optimized for economy.

There are many problems in science which can be tackled if high quality pure isotopes are available, while the enrichment of uranium in the isotope ^{235}U is of considerable importance to nuclear technology.

The most important differences between the isotopic constituents of an atomic or molecular mixture are spectral, which opens the possibility of directing the energy needed for separation, to the isotope that is to be extracted. In any

isotope separation scheme the following requirements must be satisfied:
1) The absorption spectrum must exhibit an isotope shift, sufficiently large in relation to the spectral line or band contours.
2) A laser light source or combination of sources must be available with appropriate wavelengths, monochromaticity and intensity.
3) The selective excitation of the desired species must lead to an irreversible separation process via a physical/chemical follow-up procedure.
4) The selectivity of the entire sequence of excitation and separation steps must not significantly be impaired by inter-isotope energy transfer and scrambling.

Spectral isotope shifts are found in both atomic and molecular spectra. We shall concentrate in the following on the latter and, in particular, on the use of infrared laser induced multiphoton absorption to dissociate the desired isotopic compound.

Basic Spectroscopic Prerequesites

In 1975 it was discovered by several groups that the incidence of high power infrared laser radiation on molecular gases,
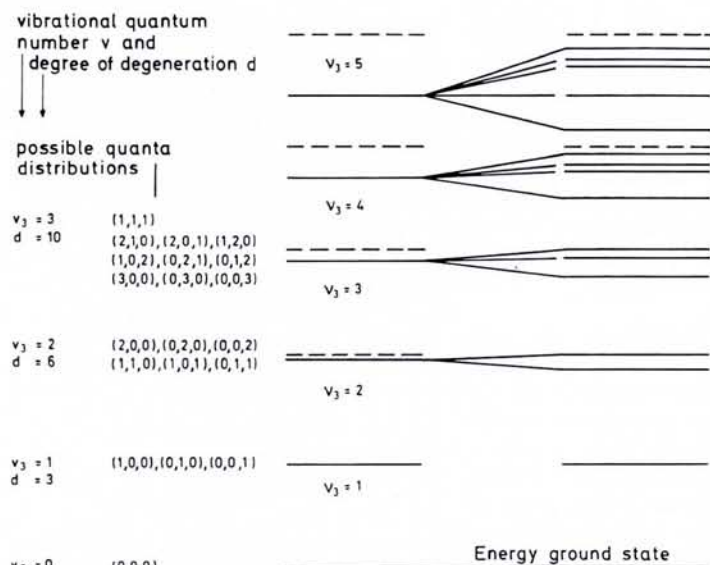
Fig. 1 — Schematic representation of quantum levels and degeneracies in the v_3-mode of SF_6. On the right hand side the anharmonic splitting of the levels is shown while the levels on the left represent the unperturbed terms (after Ref. 1).

Fig. 2 — Dependence of the dissociation yield and the isotope selectivity on the CO_2 laser frequency for the v_3 SF_6 band. It can be seen in the lower part of the figure that the maximum of the dissociation yield is shifted by about 8 cm^{-1} towards lower frequencies with regard to the small signal absorption spectrum (after Ref. 2).

can lead to the absorption of a large number of photons and induce chemical changes. This appeared surprising at first sight, since anharmonicity effects in vibrational absorption spectra are expected to cause loss of resonance for laser absorption of a single frequency as higher energy vibrations are populated. SF_6 and UF_6 are highly symmetrical molecules, in which the heavy atom is positioned in the centre of the octahedron formed by the six fluorine atoms. Fig. 1 shows the energies and degeneracies of the first few excited v_3 levels. Only the v_3 and v_4 vibrations are infrared active and exhibit pure rotational-vibrational spectra. Other vibrations, however, are involved in combination modes. Fig. 1 shows the increased level density in the v_3 mode due to multiple level splitting effects[1], which increases the chances for resonant absorption steps.

As more energy is accumulated in the molecule, a transition from the individual level structure to a quasicontinuum of states is expected, when coupling phenomena between the different modes of vibration will increase in importance. In the language of molecular trajectories this is accompanied by a transition from periodic to ergodic molecular motion. If the energy content increases still further to reach, and exceed, the dissociation limit, molecular fragmentation will occur. It should be stressed that this dissociation occurs without the influence of collisions, which indeed must be avoided because they will give rise to isotopic scrambling. For this reason, laser isotope separation experiments have to be done at low pressure.

The isotopic shift between ^{32}S and ^{34}S in SF_6 is about 17 cm^{-1} and is thus large compared with the anharmonic splittings and band shifts shown in Fig. 1. Results for the selective dissociation of SF_6 for different laser frequencies are exemplified in Fig. 2[2].

UF_6 is a natural choice for any uranium isotope separation scheme because of its high vapour pressure of about 100 Torr at 300 K. In addition, the element fluorine occurs only in one isotopic modification. Furthermore, being the process gas in the existing uranium enrichment plants, a vast body of information about the properties of UF_6 has been collected, although detailed spectroscopic data became available only recently. In Fig. 3 the v_3 absorption spectrum of both the rare $^{235}UF_6$ and the common $^{238}UF_6$ is depicted, showing the small isotope shift of only 0.65 cm^{-1} (Ref. 4).

As multiphoton experiments on SF_6 do not permit the conclusion that this small shift could be conserved in a single frequency dissociation, various authors have proposed the decoupling of the first selective step from the dissociative ones by means of a two frequency dissociation. In practice, it has been shown that the absorption of various molecules, including UF_6, can be altered in the UV as well as in the IR regime by IR laser excitation (for a more extensive discussion, see Ref. 5). The UV second step would have the advantage of greater simplicity because a single photon would suffice to furnish the energy necessary to reach the dissociation limit. The published experiments, however, are not very encouraging because it has been shown that the energy necessary to induce a change in the UV spectrum is comparatively high. In addition, the process governing the UF_6 UV dissociation seems to be a collision-induced predissociation, whereas such collisions are detrimental for the selective IR step.

The available data for the IR-IR two laser combination show better prospects. Using an appropriate time delay between the exciting and the dissociation pulse, a considerable lowering of th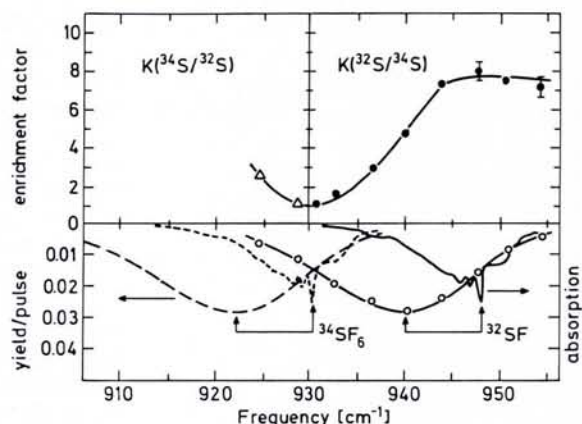e threshold as well as an enhanced yield can be obtained. Experiments with UF_6 have shown that a CO_2 laser operating in the 1080 cm^{-1} region[6] can be used to enhance significantly the dissociation yield of a CF_4 laser (q.v.) operating at 615 cm^{-1}.

Up to now, none of the published UF_6 dissociation experiments have been able to reproduce the selectivity deducible from the two small signal absorption curves (Fig. 4). Recently, however, opto-acoustic measurements[7] have hinted that for moderate excitations of about three (16 µm) quanta per molecule, the obtainable absorption difference could be even greater than the expected value; the reasons for this effect are still not clear.

To clarify the prospects for a uranium isotope separation scheme based on UF_6, it would be very desirable to learn to what extent, and with what yield, the absorption selectivity observed at low intensities, could be transformed by means of a two frequency process into a permanent dissociation. The requirement for working in the collisionless domain, limits the working pressure to around 0.2 Torr. This permits the static cooling of the UF_6 down to about 230 K, which should result in an appreciable increase of the small signal

Fig. 3 — Small signal absorption of the $^{235}UF_6$ and the $^{238}UF_6 v_3$ bands. Due to the relatively small mass difference, the bands are shifted only about 0.65 cm^{-1}. The dashed curve shows the frequency dependent absorption ratio for room temperature (after Ref. 5).