

Short Communication

Mode selective collisional energy transfer and its influence on the relaxation properties of UF_6

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Laser isotopic separation of UF_6 may be achieved by a two photon process: the first IR photon only excites the $^{235}\text{UF}_6$ molecules vibrationally while the second, a UV photon of suitably chosen wavelength, takes these molecules to a dissociative or pre-dissociative state. It is therefore of primary importance to understand the intermolecular and intramolecular relaxation processes that may be involved in the final dissociation. In this communication we analyse some features of collision-induced relaxation in UF_6 that are relevant to the more general field of collisional energy transfer in fairly large molecules.

To probe the collision-induced intramolecular dynamics we detected both the dissociation of UF_6 by a UF_5 "laser snow" method described previously [1] and the visible fluorescence emission, both following excitation within the A-X band, where collisions at relatively high pressure have been proved [2] to enhance the emission and dissociation yield. Details of the experiment were given in ref. 1. Since then, we have extended the investigation of the dissociation yield as a function of the mass and the kind of collision partners to include vibrationally inelastic collisions with SF_6 and UF_6 itself. The effect of inelasticity can be clearly seen in Fig. 1 and may be related to the near resonance between some vibrational modes of UF_6 and SF_6 , as seen in Table 1.

Further information can be obtained by detecting the visible fluorescence, which is another deactivation channel. Time-resolved fluorescence spectra, which show the influence of collisional inelasticity on the emission yield, are shown in Fig. 2. It can be seen from a comparison of the upper and lower parts that collisions with SF_6 greatly enhance the emission yield (upper part), while collisions between UF_6 molecules are a very inefficient mechanism for relaxation of the radiative state; indeed the emission from 1 Torr UF_6 in an SF_6 bath is comparable with that from eight times the amount of UF_6 molecules (lower part). Furthermore, normalization of the intensity of the 8 Torr UF_6 fluorescence at zero time shows a decrease with

TABLE 1

Vibrational frequencies (in wavenumbers) of SF₆ and UF₆ [3]

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
SF ₆	773.5	641.7	939.0	614.0	525.0	347.0
UF ₆	667.1	532.5	624.0	186.2	202.0	142.0

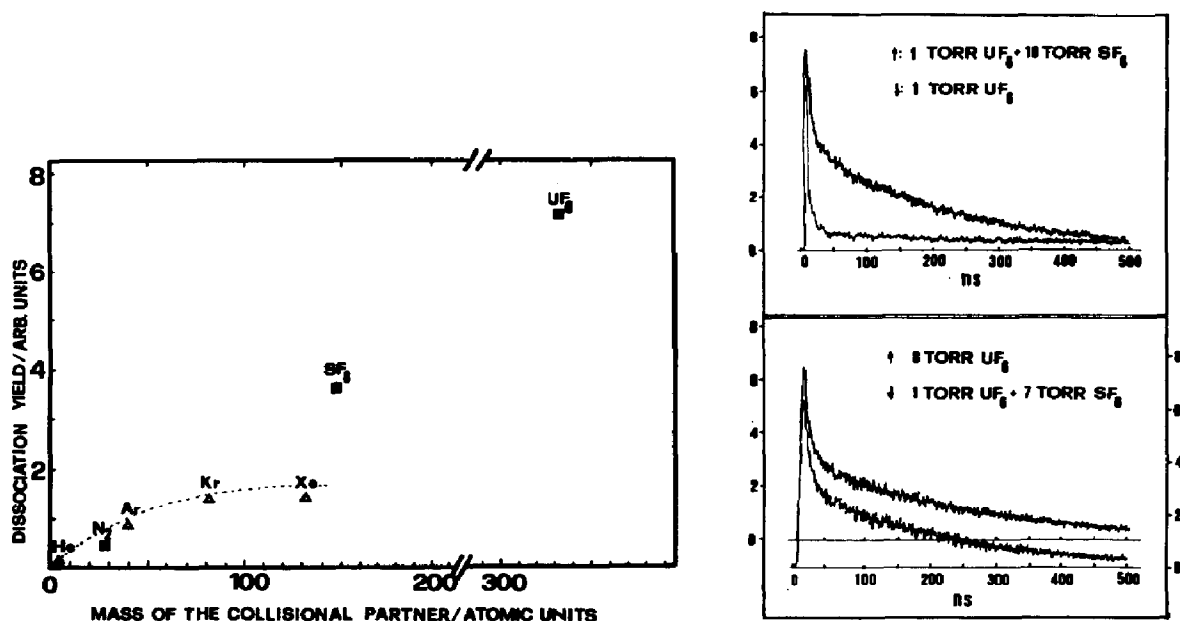


Fig. 1. Dissociation yield vs. mass of the collision partner (1 Torr UF₆, 20 Torr collision partner). The experimental error is estimated to be about $\pm 15\%$ of the point. For clarity an $M^{1/2}$ curve is drawn through the monatomic-gas points, assuming an SSH model for resonant collisional relaxation for the dissociation.

Fig. 2. Time-resolved emission at $\lambda = 421$ nm for pure UF₆ and UF₆-SF₆ mixtures with excitation at 390 nm (the peak in the fluorescence excitation spectrum). See text for further details.

respect to the 1 Torr intensity. Time-resolved emission spectra have been fitted to simple exponentials and the fit parameters are reported in Table 2 for collisions of 1 Torr UF₆ with helium, argon and SF₆ at pressures of 40 Torr. Zero-time emission rates show an enhancement of energy transfer in the order He < Ar < SF₆ which could be accounted for simply on the basis of a mass effect [4, 5]. Therefore energy exchange in the UF₆-SF₆ resonant modes does not strongly affect the relaxation of the radiative states. On the contrary, dissociation is always enhanced by collisions that are partially (SF₆) or totally (UF₆-UF₆) vibrationally resonant.

This seems to prove that energy exchange in the ν_1 , ν_4 , ν_5 and ν_6 modes of UF₆ affects the relaxation path differently from energy flow in

TABLE 2

Best-fit parameters for fluorescence decays assuming a single-exponential shape $F(t) = I_0 \exp(-t/\tau)$

	SF_6	Ar	He
τ (ns)	57	120	135
I_0 (V)	6.51	4.95	3.80

the other modes. At the high level of excitation involved in this experiment (about 3 eV) it is often quoted that energy levels form a true continuum and, owing to the coupling between different modes caused by anharmonicity, it would be expected that the molecules will display a random internal motion with little memory of their low-energy normal-mode frequencies. It is therefore somewhat surprising that different relaxation paths can be selected by using an appropriate choice of normal-mode resonances in collisions.

These data may suggest that an incomplete randomization of intramolecular motion exists even under our experimental conditions.

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