DYNAMICS OF PHOTODISSOCIATION OF XeF2 IN ORGANIC SOLVENTS

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SUPPORTING INFORMATION

Calculations were performed on the possible charge transfer (CT) states that would exist for solvated F atom or XeF molecules in CD₃CN. These were conducted with a MO62 aug-cc-pVDZ basis set for the F-CD₃CN complex and UB3LYP-DGDZVP for the XeF-CD₃CN complex to model the Xe electron core. Geometries were initially optimised before a time dependent upper state calculation was performed. A SCRF solvent shell was applied to the complex while both the optimisation and upper state calculation were performed. Table S1 displays the absorptions with oscillator strengths greater than 0.1. It is clear from these calculations that no CT absorptions would occur in a region that is observable in our experiments.

F-CD ₃ CN		XeF-CD ₃ CN	
λ / nm	Oscillator Strength	λ / nm	Oscillator Strength
200.8	0.8	286.6	0.362
192.6	2.75		
172.8	2.4		

Table S1. Wavelengths and oscillator strengths of calculated charge transfer absorption bands in $F-CD_3CN$ and $XeF-CD_3CN$ complexes. Transitions with f>0.1 are included.

An RKR analysis was conducted to obtain the *X* and *B* state potentials of the XeF molecule from spectroscopic constants.¹ A Franck-Condon calculation using these modelled potentials simulated the UV absorptions for different initial vibrational and rotational levels of the XeF molecule. FIGURE 10 shows the predicted UV absorption bands of XeF at 293 K for selected initial vibrational levels. Rotational population was treated with a Maxwell-Boltzman distribution at 293 K. A centrifugal distortion component was included in the ground state XeF potential. Under equilibrium conditions, the XeF absorption includes a significant contributions from the XeF v=1 level due to the small vibrational energy gap of 248 cm⁻¹. Figure S1 shows that the highest observed shift is approximately 10 nm from the peak of the thermally equilibrated spectrum to that of the v=10 absorption band. Assignment of the strongly red-shifted feature in Figure 5 to vibrationally excited XeF is therefore discounted.



Figure S1. Simulated XeF (B—X) absorptions for a 293 K sample and from high vibrational levels of the ground electronic state. All spectra have been normalised in intensity and are vertically offset. A rotational temperature of 293 K is used for all states.

1. P. C. Tellinghuisen and J. Tellinghuisen, J. Phys. Chem. A, 2002, 106, 8317–8322.