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Non-thermal rotational and vibrational excitation of CN produced in the flash photolysis of thiazole

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Abstract. In the flash photolysis of thiazole at low pressure without any diluent, the 0–0, 1–1 and 0–1 bands of the CN violet system were observed in absorption; the 0–0 band at 3883·4 Å showed a high rotational excitation corresponding to a temperature of $\simeq 2000$ K. The addition of argon makes the NCS bands appear with good intensity and at the same time relaxes the CN rotationally and vibrationally. These observations suggest that highly excited NCS is initially formed in the photodecomposition of thiazole which acted as a precursor to the rotationally and vibrationally excited CN radical. This paper deals with studies on the effect of argon on the relative intensities of CN and NCS and on the non-thermal rotational and vibrational intensity distribution of the CN violet system. The mechanism of formation of rotationally unrelaxed CN in the flash photolysis of thiazole has been proposed.

Keywords. Flash photolysis of thiazole; non-thermal excitation of CN; vibrational excitation; rotational temperature.

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1. Introduction

As a part of our general programme of spectroscopic studies on the transient species produced in the flash photolysis of heterocyclic compounds (Krishnamachari and Venkitachalam 1978, 1979), flash photolysis of thiazole (C_3H_3NS) has been recently studied. In this case, the absorption spectra of several transient species have been observed, viz., SH (1, 0 and 0, 0 bands of the $A^2\Sigma^+ - X^2\pi_i$ system), S_2 ($B^3\Sigma_u - X^3\Sigma_g^-$) system with $v'' = 0$ to 4, CN ($B^2\Sigma^+ - X^2\Sigma^+$ system), NCS ($A^2\pi_i - X^2\pi_i$ and $B^2\Sigma^+ - X^2\pi_i$) system lying in the region 3700–3850 Å (Dixon and Ramsay 1968), HCCS (Krishnamachari and Ramsay 1981), CCSH (Krishnamachari and Venkatasubramanian 1986a) and HNC (Krishnamachari and Venkatasubramanian 1986b). The relative intensities of the absorption bands of the different species vary with experimental conditions i.e. the pressure of thiazole, the presence or absence of diluent gas and the time delay between the photolysis and monitoring of flashes. The present paper deals with studies on the effect of argon on the relative intensities of CN and NCS and on the rotational intensity distribution of the 0, 0 band of the CN violet system. Also, the mechanism of formation of non-thermally excited CN in the flash photolysis of thiazole has been proposed.

2. Experimental

The flash photolysis apparatus used was described earlier (Krishnamachari 1974). The thiazole was from M/s. Fluka Chemicals, Switzerland; the sample was subjected to