

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

R VENKATASUBRAMANIAN and S L N G KRISHNAMACHARI  
Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

MS received 5 February 1988

**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  $\approx 2000$  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.

PACS Nos 32.20; 34.50

### 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

freezing and thawing cycles before its vapour was admitted into the absorption cell; spectra were obtained with an absorption path length of 12 m and with a time delay of 5  $\mu$ s between the photolysis and monitoring flashes. A grating spectrograph (1.3 m Ebert) using a holographic grating with 2400 lines/mm with a reciprocal dispersion of 2.5  $\text{\AA}/\text{mm}$  in the first order was employed to record the spectra.

### 3. Results

The spectrum recorded when thiazole alone was flash-photolysed at 150 m torr showed an intense (0, 0) band of the CN violet system with a prominent head at 3883.4  $\text{\AA}$ ; the heads of the (0, 1) and (1, 1) bands were also seen, however, with low intensity (figure 1a). From the ratio of the intensities of the 1, 1 and 0, 0 band heads, which was 0.09, the vibrational temperature was estimated to be  $\approx 1300$  K. The rotational structure of the 0, 0 band consisted of R and P branch lines extending to high  $K$  values; the R branch was found to extend up to  $K = 35$  while the P branch formed an intense head at  $K = 25$  (figure 1a). The R branch lines showed an intensity maximum corresponding to  $K_{\text{max}} = 19$  and from this the rotational temperature was  $\approx 2000$  K which is different from the vibrational temperature thus showing that the equilibrium has not been established between the vibrational and rotational degrees of freedom. Thus in the absence of argon and at low pressure (150 m torr) of thiazole, vibrational levels up to  $v'' = 1$  and the rotational levels up to  $N'' = 35$  in the  $v'' = 0$  level were populated in the CN ( $X^2\Sigma^+$ ) radical. This situation is similar to the case of CN radicals produced in the ( $X^2\Sigma^+$ ) state as a result of the photolysis of low pressure of  $\text{C}_2\text{N}_2$  (0.012 torr) with radiation of  $\lambda = 160$  nm (Cody *et al* 1977). These CN radicals were vibrationally and rotationally excited as in the present studies; vibrational level up to  $v'' = 1$  and rotational levels up to  $N'' = 55$  in the  $v'' = 0$  level were populated. Also an intense head of the P branch of the CN (0, 0) band was formed at  $K = 25$  as observed in the present investigation. The non-thermal excitation of CN ( $T_{\text{rot}}(0, 0) \approx 1400$  K) is attributed to the formation of CN in excited state during the u.v. photodissociation of  $\text{C}_2\text{N}_2$ .

### 4. Effect of addition of argon and thermal excitation of CN

When thiazole (150 m torr) was flash-photolysed in the presence of argon (200 torr), NCS bands at 3820  $\text{\AA}$  and HCCS bands at 3825  $\text{\AA}$  and 3880  $\text{\AA}$  appeared with good intensities and at the same time the CN radical got relaxed rotationally and vibrationally (figure 1b). As can be seen from this figure, the (0, 0) head of CN violet system is absent or extremely weak. With the addition of argon, the rotational intensity distribution of (0, 0) band of CN got altered in such a way that  $K_{\text{max}}$  occurred at  $K = 8$ ; the temperature corresponding to this intensity distribution was  $\approx 350$  K which is close to the ambient temperature. The spectrum obtained with the addition of argon to thiazole is similar to the rotationally relaxed spectrum obtained in the photodissociation of  $\text{C}_2\text{N}_2$  at relatively higher pressure (0.12 torr) (Cody *et al* 1977) or that obtained with active nitrogen flame (Broida and Golden 1960).

Thus in the absence of argon and at low pressure (150 m torr) of thiazole, non-thermal rotational and vibrational excitation of CN has resulted while rotationally equilibrated spectrum of CN radical was observed with the addition of argon.

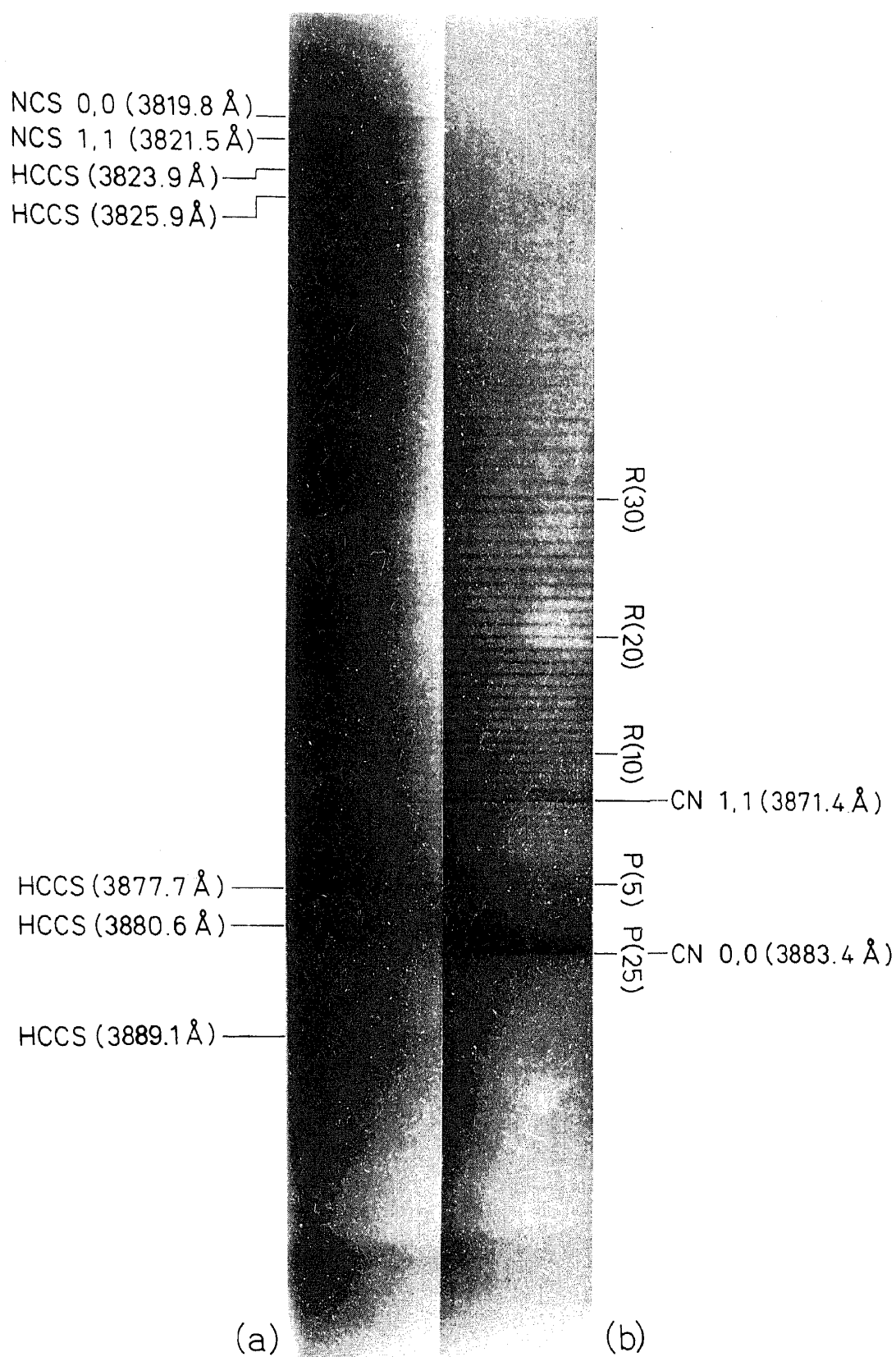


Figure 1. Absorption bands due to NCS and CN produced in the flash photolysis of thiazole ( $C_3H_3NS$ ). (a) Thiazole 150 m torr pressure. (b) Thiazole 150 m torr + argon 200 torr pressure.

Having observed that the addition of argon to thiazole relaxes the CN rotationally and vibrationally, experiments were conducted to study the effect of addition of different amounts of argon on the decay of the intensity of the CN (0,0) band head; the results are presented in figure 2. As can be seen from this figure, the relaxation occurs faster with increased pressure of argon.

### 5. Discussion

As mentioned earlier, the non-thermal excitation of CN in the u.v. photodissociation of  $C_2N_2$  (Cody *et al* 1977) is attributed to the formation of CN in excited state. A similar situation occurs in the present investigation. The fact that NCS bands are absent or extremely weak in the absence of diluent gas and appear with good intensity when argon is added shows that this radical is initially formed in the photodecomposition of thiazole in a highly excited state which, in the absence of rapid relaxation by a diluent gas, would dissociate to produce CN and S; during this dissociation process the excess energy of NCS would be transferred to CN to excite it non-thermally to high rotational and vibrational levels. The present observations are in conformity with the theoretical predictions (Kimura and Nishitani 1975) regarding the formation of rotationally and vibrationally excited diatomic species split from an excited triatomic complex.

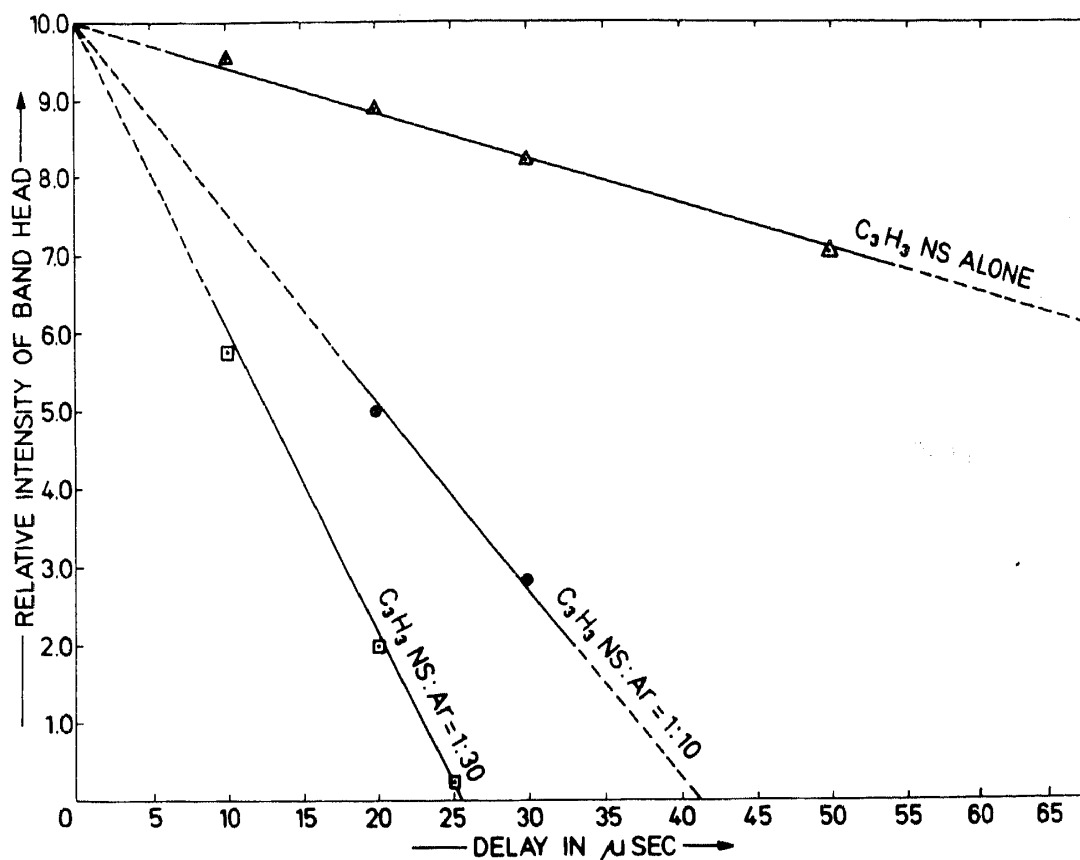
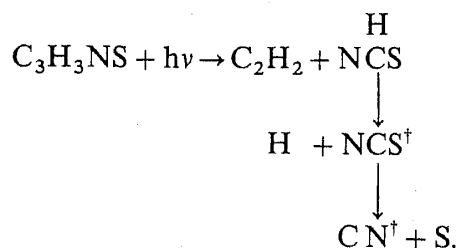


Figure 2. Effect of addition of argon on the variation of the intensity of CN (0,0) band head with time.

According to Kimura and Nishitani, the angular momentum possessed by the triatomic complex (ABC) exerts considerable influence upon the initial and non-thermal distribution of populations in the vibrational and rotational levels of diatomic AB. In the present investigation, the energy difference between the photon energy supplied (6 eV) and the energy required to dissociate the thiazole molecule (5 eV) goes to excite the NCS fragment formed as a result of the photolysis of thiazole. This excited triatomic NCS fragment acted as a precursor to the rotationally and vibrationally excited CN radical as shown in the following equation.



This CN radical could not have been formed as a result of the autodecomposition of the transient species HNC which was also observed in the present experiment since the latter was seen in both the conditions under which the spectra shown in figure 1 were recorded.

The fact that the addition of argon rotationally and vibrationally relaxes CN shows that a similar relaxation process should occur to NCS when argon is added which would stabilize the radical and enable it to appear with appreciable intensity.

Just as in NCS, addition of argon also stabilizes the HCCS radical soon after it is formed as a result of the photodecomposition of thiazole molecule. The band heads belonging to HCCS could therefore be seen when the spectra were recorded after the addition of argon (figure 1b).

## References

- Broida H P and Golden S 1960 *Can. J. Chem.* **38** 1666  
 Cody R J, Sabety-Dzvonik M J and Jackson W M 1977 *J. Chem. Phys.* **66** 2145  
 Dixon R N and Ramsay D A 1968 *Can. J. Phys.* **46** 2619  
 Kimura M and Nishitani T 1975 *J. Phys. Soc. Jpn.* **39** 759  
 Krishnamachari S L N G 1974 *Photochem. Photobiol.* **20** 33  
 Krishnamachari S L N G and Ramsay D A 1981 *Faraday Disc. No.* **71** 205  
 Krishnamachari S L N G and Venkatasubramanian R 1986a *Indian J. Phys.* **B60** 37  
 Krishnamachari S L N G and Venkatasubramanian R 1986b *Spectrosc. Lett.* **19** 55  
 Krishnamachari S L N G and Venkitachalam T V 1978 *Chem. Phys. Lett.* **55** 116  
 Krishnamachari S L N G and Venkitachalam T V 1979 *Chem. Phys. Lett.* **67** 69