

Experimental section

HNS powder (purity > 99.5%) was synthesized at Institute of Chemical Materials of China Academy of Engineering Physics. CH₃CN (99% purity) was used as solvent. The concentration of HNS in CH₃CN was 1 mmol/L at room temperature. The solution was flowed by a slow-flow device, to avoid strong decomposition induced by ultraviolet excitation at 266 nm. The geometrical structure and frequency calculations were performed at the B3LYP/6-311++G(d,p) level by using Gaussian09 suite of programs¹.

The typical transient absorption spectrum equipment has been described in many papers². Briefly, the laser system generated fundamental femtosecond pulses at 800 nm, with pulse duration of 35 fs, energy per pulse of 1 mJ and repetition rate of 1 kHz. The third harmonics (266 nm) of fundamental pulses were attenuated to ~5 μJ as pump beam. The white-light-continuum pulses from CaF₂ crystal were used as probe beam, with spectral range of 370-700 nm. The pump-probe pulses were organized as follows: the pump-pulse beam was lead and collimated onto sample cell (1 mm optical pathlength). The probe-pulse beam passed through an optical delay line, and then was split into two parts by a metallic beamsplitter. One part was collimated and overlapped with the pump-pulse in the sample cell. The other was collimated into the sample cell at a different spot for the reference signal, in order to improve sensitivity. The polarization plane of probe pulses was rotated by a λ/2 plate and magic angle (54.7°) configuration between the pump and probe pulses was adopted in all the measurements. Given the speed of light (3 × 10⁸ m/s), the delay time was varies up to 500 ps with a minimum interval of 2.08 fs. The probe-pulse beam was dispersed by a grating inside the spectrometer (Princeton, SpectraPro 2500i) and detected by a two-dimensional CCD detector (PI-MAX, 1024 × 256 pixel array). On the CCD surface, they formed two stripes of image, one from the probe and the other from reference. Each of image signals from CCD was sent to a computer through a 16-bit analog-to-digital converter (ADC). The data acquisition and experiment control were performed via Labview program. Low noise level (<2 mOD) could be achieved by averaging approximately 1600 pulses. The instrumental response of the system was determined to be ~200 fs by cross-section measurement between pump and probe pulses. The chirp of WLC was measured at the position of the sample cell by the use of the optical Kerr effect of solvent, and it was used to correct the dispersion of relative delay time in the time-resolved data. The stimulated emission, ground state bleach and dark response were eliminated by the logical collections, by the use of two shutters. The absorption of excited states, transient products, long-lived molecular states such as triplet state would acquire ΔA>0, while the bleaching of the ground state absorption and stimulated emission obtained ΔA<0. Therefore, spectral changes could be sometimes complicated and required special method to accurately analyse the time-resolved data.

Reference

1. M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox D. J., Gaussian, Revision B.01 2010.
2. Y. P. Wang, S. Zhang, S. M. Sun, K. Liu and B. Zhang, *Chin. J. Chem. Phys.*, 2013, **26**, 651.

Tables 1 Born-rate and lifetime of absorption peaks 340 and 520 nm, respectively

		N ₂ ambience	O ₂ ambience
340	Born-rate(M ⁻¹ S ⁻¹)	30.31 × 10 ⁹	24.18 × 10 ⁹
nm	Born-lifetime(ns)	22.87	28.67
520	Born-rate(M ⁻¹ S ⁻¹)	63.97 × 10 ⁹	33.01 × 10 ⁹
nm	Born-lifetime(ns)	10.83	21.00

Fig. S1 Geometrical structure of HNS molecule

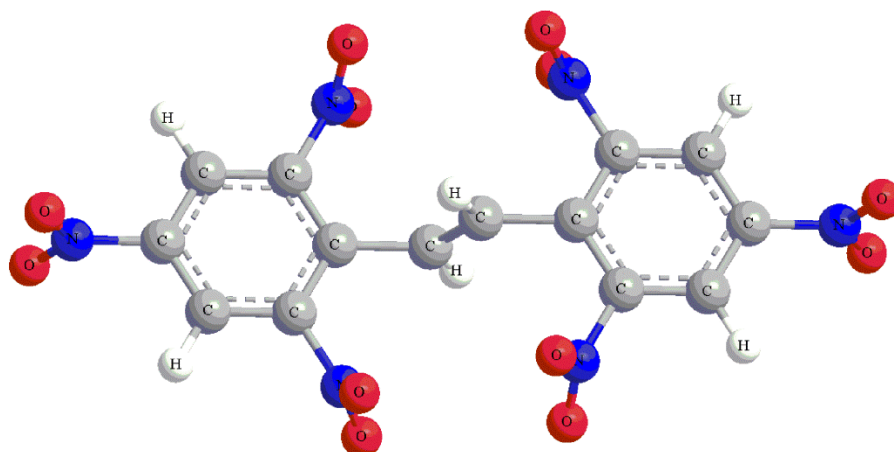


Fig. S2 Spectra of S₁ fluorescence and T₁ phosphorescence of HNS in CH₃CN

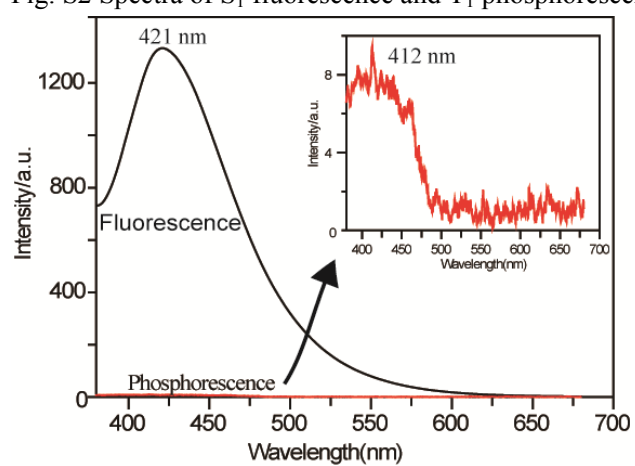


Fig. S3 Transient absorption spectra and decay curves of HNS in CH₃CN in N₂ and O₂ ambience, respectively

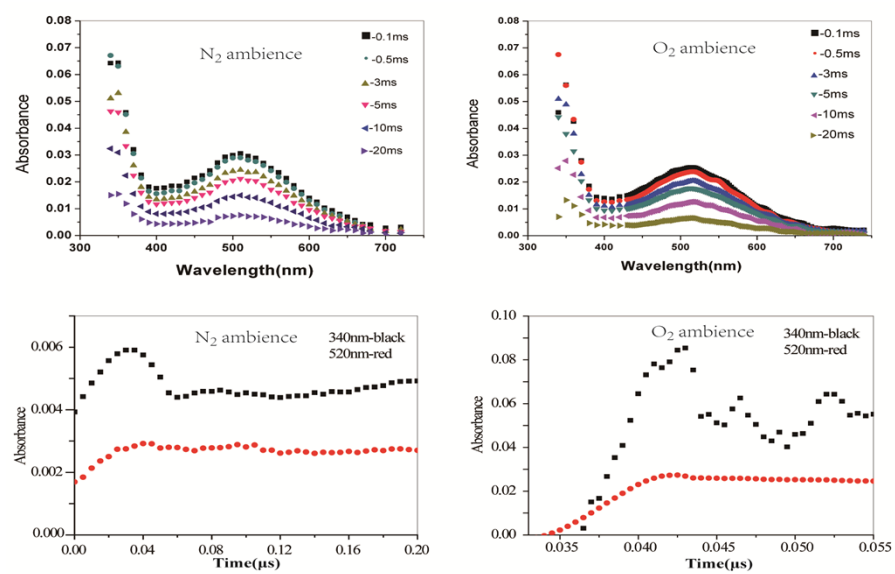


Fig. S4 Transient products with lifetime more than 1 millisecond observed before overlap of pump-probe pulses, when HNS solution is not flowed enough.

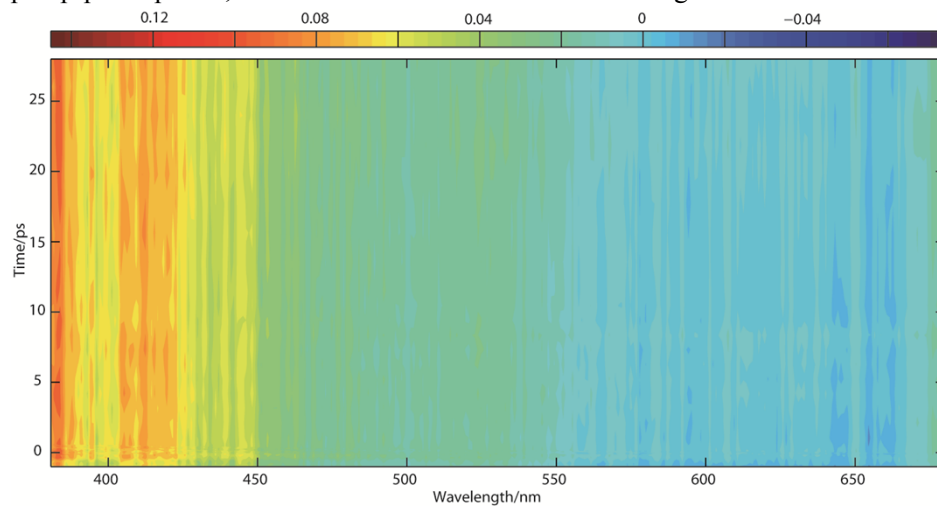


Fig. S5 Time evolution of HNS in 1,4-dioxane at 500 nm, and a lifetime of 1.0 ps assigned to cooling dynamics of S_1^* state

