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ARTICLE TYPE

Investigation on ultrafast excited state dynamics of 2,2',4,4',6,6'-hexanitrostilbene using femtosecond transient absorption spectroscopy

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Study on dynamics and structures of the excited states of 2,2',4,4',6,6'-hexanitrostilbene shows equilibrium between vibrationally hot S_1 (S_1*) and S_1 states with lifetimes of 0.8 and 6 ps, respectively. The T_1 state has a lifetime of about 4 ns. It advances understanding of energetic materials ignition.

Excited states play a crucial role in the energy conversion of energetic materials[1, 2], and these excited states could be initiated by a number of different ignition processes such as photons, sparks, or shocks[3, 4]. Moreover, fast non-radiative transitions of excited states can lead to local heating effect called "hot spots" in liquids or crystals, which can accelerate chain reactions of energetic materials[2]. Excited state decomposition can convert chemical energy into mechanical energy in the sub-picosecond (ps) timescale, which has been extensively investigated by ultrafast pump-probe techniques[1, 5-9]. Representing the crossing of multidimensional electronic potential energy surfaces, conical intersections (CIs) are well established as controlling factors in the excited state decomposition of energetic material molecules[1]. The response to ultrafast laser shock loading of liquids has been monitored to reveal the existence of excited states occurring in the first 350 ps following the shock front[10]. To the best of our knowledge, however, the dynamical and spectral behaviours of the excited state of energetic materials have been rarely observed.

Stilbene is a prototypical molecule showing isomerization in the lowest excited state (S_1)[11] and its rotational mechanism has been explained using CIs at the perpendicular configuration, which can be accessed from either the *trans*- or *cis*- side on the S_1 potential surface[11]. Isomerization dynamics have also been observed for azobenzene and its derivatives in the $n\pi^*$ (S_1) and $\pi\pi^*$ (S_2) states[12, 13]. Such processes may be quenched by strong intramolecular steric hindrance by increasing multiple nitro functional groups in the molecule. As a derivative of nitrostilbene, 2,2',4,4',6,6'-hexanitro-stilbene (HNS, Figs. 1) is a well-known explosive for good performance with excellent thermal stability, impact and shock insensitivity.

To continue the effort on understanding the energy transfer process of energetic materials, we present an experimental investigation on the excited states of HNS using femtosecond (fs) transient absorption spectroscopy. We establish a cascading de-excitation $S_2 \rightarrow S_1^* \rightarrow S_1 \rightarrow T_1$ model to interpret the dynamical and structural behaviours of the HNS excited states. The results show equilibrium between S_1* and S_1 states, which have lifetimes of 0.8 and 6 ps, respectively. The T_1 state has a long lifetime of about 4 ns. The results of this study advance the understanding of energetic materials ignition.

In the steady-state absorption spectrum of HNS in CH_3CN in Fig. 1, there is a wide band centred at 266 nm, which extends to the 400 nm range[14]. After identifying the effects of the solvent, the wide band can be assigned to $\pi \rightarrow \pi^*$ (S_2 state) and $n \rightarrow \pi^*$ (S_1 state) transitions. The vertical transition energies of the S_2 and S_1 states are calculated to be 4.75 eV (~261 nm) and 3.55 eV (~358 nm), respectively, at the level of B3LYP/6-311++G(d,p), which are consistent with experimental results. The oscillator strengths of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are computed to be 0.17 and 0.20, respectively. These two states are the Franck-Condon states accessible from the ground electronic state configuration. According to the steady-state absorption spectrum and theoretical calculations, HNS molecules primarily populate lower vibrational manifolds of the S_2 surface by ultraviolet excitation at 266 nm.

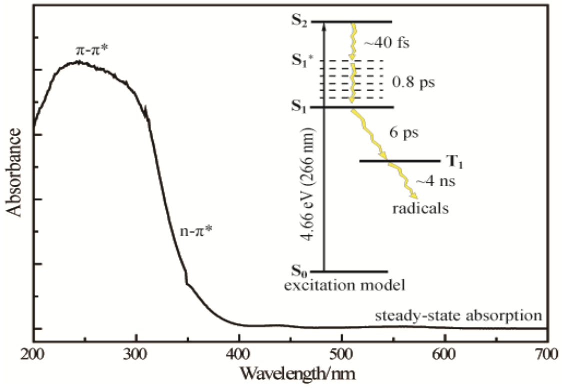

Fig. 1 Steady-state absorption spectrum of HNS in CH_3CN. The inset dynamical scheme describes the HNS excited state processes upon excitation.

The distinct excited state absorption of HNS is exhibited from femtosecond-resolved absorption spectra in Fig. 2. The peaks of the S_1 fluorescence and T_1 phosphorescence of HNS are located at 421 and 412 nm in Figs. 2, respectively. There have been no reports on S_2 fluorescence and higher-energy T_n phosphorescence of HNS, and the quantum yields of such radiative transitions may be beyond the detection limit. Thus, ground state absorption and stimulated emission are not evident in the transient absorption spectra of HNS.

A particularly long-lived state is observed to have a timescale on the order of hundreds of picoseconds, which could be assigned

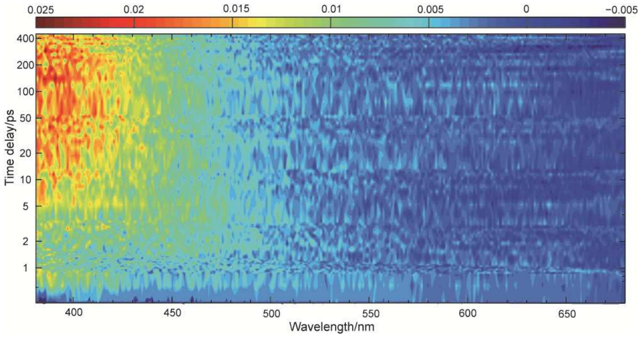

Fig. 2 Two-dimensional transient absorption spectra of HNS in CH_3CN from 380–680 nm with a time delay up to 450 ps following excitation at 266 nm.

to the T_1 state. The T_1 state has been recognized as a prominent feature in the energy conversion of energetic materials[14]. The lifetime of the T_1 state may be greatly reduced by the strong steric hindrance of molecular planarity in HNS molecule. Moreover, the T_1 state of HNS has been observed via nanosecond-resolved transient absorption spectroscopy, where HNS primarily populates the S_1 state at an excitation of 355 nm before undergoing intersystem crossing to the T_1 state for investigation. The T_1 state is further decomposed into radicals. The observable decay rate difference between N_2 and O_2 ambience in Figs. 3 is due to radical absorption rather than T_1 state as Ref. 14. The two peaks at 340 and 520 nm are assigned to radical absorption, with born-lifetimes of 10–30 ns. These results indicate that the lifetime of the T_1 state of HNS is shorter than 10 ns. When the HNS solution does not sufficiently flow, a nearly non-decay transient product with lifetime more than 1 ms is observed by the femtosecond absorption method before the overlap of pump-probe pulses (Figs. 4). This point is consistent with radical absorption of HNS from the T_1 state using the nanosecond-resolved absorption method.

From the Jablonski energy level model, the T_1 state is primarily populated from the minimal intersystem crossing of the lowest excited single state (S_1 state). This process usually relaxes in the timescale of several picoseconds. From this point of view, the S_1 state and its exponential decay to T_1 state are expected to be observed in the transient absorption spectra. Furthermore, an ultrafast internal conversion from the initial S_2 state to S_1 state can be also expected in the time scale of 0.1–1 ps.

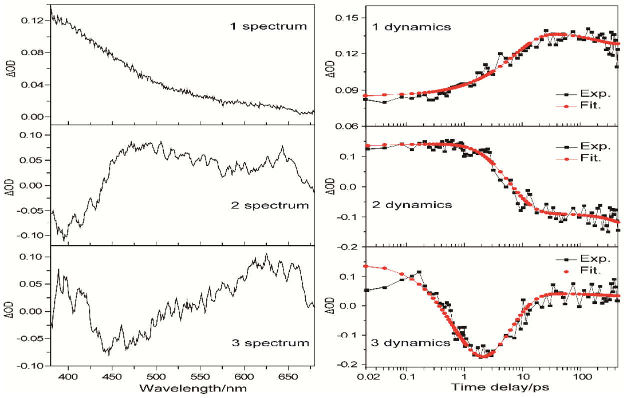

Fig. 3 Spectra and dynamics of the three species obtained using SVD.

To analyse the spectra, the singular value decomposition (SVD) method is presented to illustrate the spectra and dynamics of different species. The first three species have reasonable signal-to-noise ratios and are utilized for further investigation, as shown in Fig. 3. The first spectrum is very broad with one band at 400 nm. The dynamical behaviour shows that it increases exponentially after excitation, and then decays slightly in the range of 20–450 ps. Furthermore, this behaviour indicates that there are primarily two processes for this species. Two bands at 480 and 650 nm are observed in the second spectrum, and its dynamics show a major exponential decay. The third spectrum has peaks centred at 400 and 625 nm, respectively. Moreover, its dynamics show a fast decay after excitation and an exponential increase later. Based on the above discussion, we propose a typical three cascading de-excitation model, where $S_2 \rightarrow S_1 \rightarrow T_1$ fits the SVD results and a global fitting is performed, as shown in Fig. 3. The obtained lifetimes for S_2 and S_1 are 0.8 and 6 ps, respectively. The 0.8-ps lifetime is explicitly assigned to the decay of the S_1^* state to S_1 state involved in the $S_2 \rightarrow S_1$ transition, as discussed below. The T_1 state is established to have a long lifetime of 1000 ps, exceeding the experimental range of 450 ps. Associated with nanosecond-resolved absorption spectra (Figs. 3) and sub-picosecond-resolved spectroscopy by Rajchenbach et al.[2], we determine that its lifetime is about 4 ns here. The dynamics for the three excited states are exhibited in Fig. 4. The corresponding spectra are present on basis of the de-excitation model and the obtained decay rate (1/lifetime). There are two peaks at 400 and 625 nm in S_1^* spectrum, and one at 450 nm in S_1 spectrum. A band is centred at 400 nm in the T_1 spectrum.

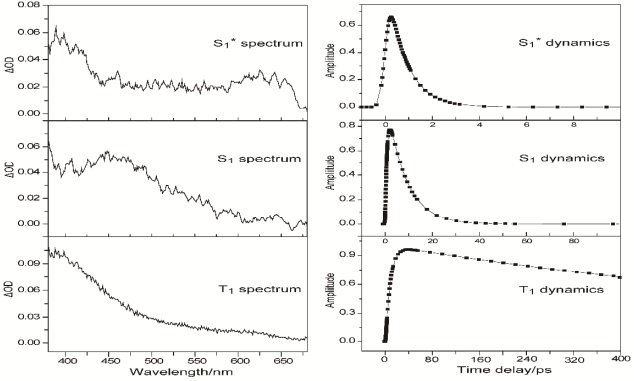

Fig. 4 Spectra and dynamics of the three HNS excited states.

We now examine the de-excitation process of the $S_2 \rightarrow S_1$ transition of HNS. The timescale for this excitation is usually between 0.1–0.2 ps for some kinds of aromatic hydrocarbons in gas phase, such as benzophenone[15]. The lifetime of 0.8 ps for this transition of HNS in CH_3CN is much larger than that in the gas phase[15]. There should be an observation of one particular state assigned to a vibrationally hot S_1 state (so-called S_1^* state) in the de-excitation $S_2 \rightarrow S_1^* \rightarrow S_1$ processes. The evolution from the initial S_2 state leads to the S_1^* state, which indicates that the electronic excitation energy is converted into thermal energy through vibrational and translational energy motion. Such states have been commonly observed in various kinds of photochromic reactions[12]. The de-excitation of $S_2 \rightarrow S_1^*$ is fast on the order of ~40 fs for carotenoid[16] and 70 fs for trans-4-aminoazobenzene[17]. The rapid process is probably due to the S_2-S_1 conical intersection zone, which is close to the steep slope in Franck-Condon region on the S_2 surface[15, 18]. However, the ultrafast lifetime of the $S_2 \rightarrow S_1^*$ transition for HNS is not observed in this work. For some energetic materials such as nitromethane, there may be also S_1^* state involvement in the lifetime. The excitation of nitromethane at 271 nm could be assigned to the S_2 state according to the results by Arenas et al.[19]. The lifetime of the nπ* state at the excitation of 271 nm was determined to be 36 fs through femtosecond-resolved mass spectrometry by Guo et al.[20]. The 36-fs lifetime could be assigned to the $S_2 \rightarrow S_1^*$ transition rather than to ground state transition through internal conversion.

The relaxation of the S_1^* state undergoes through an intermolecular energy transfer to the surrounding solvent. The cooling process of the initial S_1^* state of chrysene in solution has been suggested to lead to the relaxed S_1 state[21]. Moreover, the lifetimes of the $S_1^* \rightarrow S_1$ transition for carotenoid[16] and trans-4-aminoazobenzene[17] are determined to be 0.9 and 0.7 ps, respectively. The relaxation process of such transition is established to be 0.8 and 1.0 ps for HNS in CH_3CN and 1,4-dioxane (Figs. 5) in this work, respectively, in agreement with the above results. The increase of lifetime in solution can be ascribed to the viscosity of solvent, which slows the spread of the wavepacket on the S_1 surface from the S_2 surface[15]. In addition, the vibrational cooling dynamics of azobenzene in the vibrationally hot ground electronic state has been determined to be on a time scale of approximately 20 ps via time-resolved IR spectroscopy with femtosecond time resolution[13, 22, 23]. In the gas phase, the photoexcitation of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) primarily populates the upper vibrational manifolds of the S_1 surface (S_1^* state) at the photon energy of 4.8 eV (258 nm) [1, 5-9, 20]. The NO product from S_1^* state via CIs is observed to be vibrationally hot (1600 K) and rotationally cold (20 K), which is similar behaviour to NO dissociated from S_2 surface (5.5 eV at 226 nm). The overall process should be faster than 180 fs[1].

Our results reveal new classification of excited states of energetic materials introduced by Rajchenbach et al.[2]. First, we observe equilibrium among the S_1^* state, the rapidly populated S_1 state, and the long-lived T_1 state. We then obtain the absorption spectra for the three states and demonstrate that the S_1 spectrum is similar to that given in Ref. 2. Second, the 6-ps lifetime for the non-radiative $S_1 \rightarrow T_1$ process of HNS is consistent with the related 4.7-ps lifetime for $S_1 \rightarrow X$ transition of CH_3NO_2 obtained by the coherent anti-Stokes Raman scattering (CARS) technique. Finally, we determine that more excited states should be involved in the fast non-radiative transition, other than $S_1 \rightarrow T_1$ transition. Despite the fast local heating effect and the acceleration of decomposition in liquid or crystal due to the excited states, vibrational cooling dynamics[24] and other effects may be important factors for further understanding the ignition of energetic materials.

Conclusions

The dynamics and structures of the HNS excited states have been investigated using femtosecond transient absorption spectroscopy. Via SVD and the global fitting method, three species are analysed, and a cascading de-excitation model ($S_2 \rightarrow S_1^* \rightarrow S_1 \rightarrow T_1$) is established. An equilibrium between the S_1^* state, rapidly populated S_1 state and the long-lived T_1 state is acquired, and the spectrum for each state is exhibited. The lifetimes of S_1^* and S_1 are about 0.8 and 6 ps, respectively. The T_1 state has a lifetime of about 4 ns. This study reveals new recognition of excited states and understanding of energetic materials.

Notes and references

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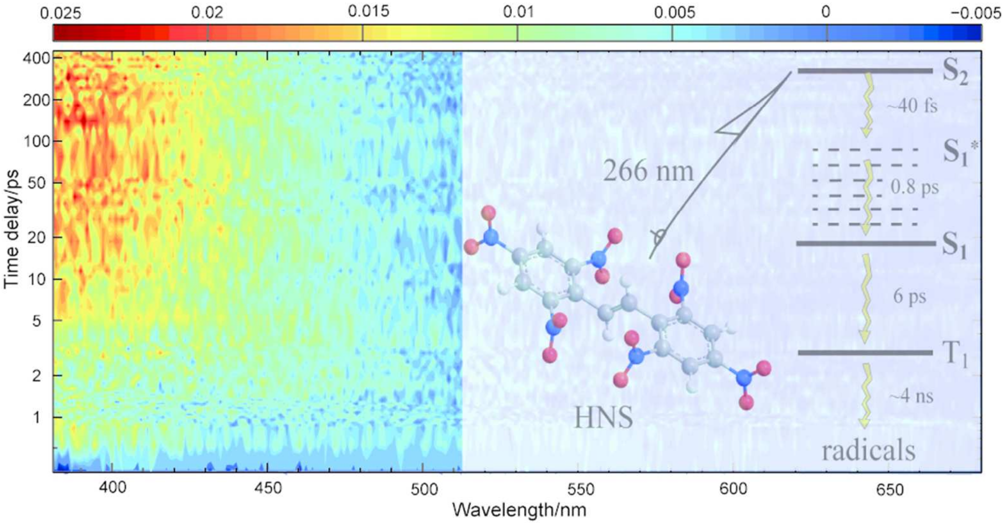

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