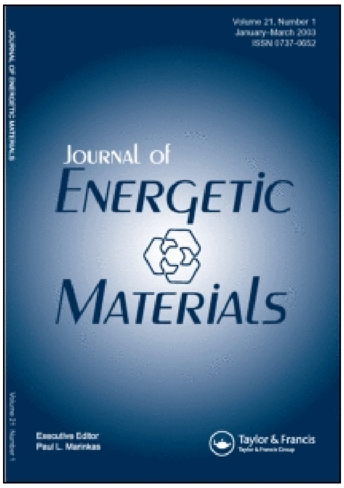

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Ultraviolet and visible absorption spectroscopy of some energetic molecules in the solid state

K. J. Smit[a]
[a] Explosives Division, DSTO Materials Research Laboratory, Ascot Vale, Victoria, Australia

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ULTRAVIOLET AND VISIBLE ABSORPTION SPECTROSCOPY OF SOME ENERGETIC MOLECULES IN THE SOLID STATE

K.J. Smit

Explosives Division, DSTO Materials Research Laboratory,
PO Box 50, Ascot Vale, Victoria, Australia, 3032

ABSTRACT

The solid state absorption spectrum in the range 190 to 550 nm has been obtained for four common high explosives; HNS, RDX, HMX and PETN. Studies were performed with HE crystals embedded in potassium chloride disks and compared to spectra in acetonitrile solution. It was observed that the solid state spectra generally have red shifted absorption maxima and extended red edge absorption compared with the solution phase spectra. These effects are attributed to intermolecular stabilization of the energetic molecules in the solid phase.

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INTRODUCTION

Since lasers first became readily available their ability to initiate detonation of high explosives (HE) has been extensively investigated. Using short pulses of high energy both primary and secondary explosives can be detonated directly [1-3]. The lasers used for this purpose have tended to be high power visible and infrared lasers, although HE generally absorb only weakly at these wavelengths. Often addition of light absorbing graphite or a thin coating of aluminium is used to increase energy transfer to the energetic molecules [3,4]. Alternatively it is possible to irradiate at ultraviolet (UV) wavelengths [4-8] where there is strong absorption of light, but where the laser pulse energies available are lower. It has recently been recognised that excitation in the UV can markedly reduce the power requirements for detonation of some secondary explosives [4,8]. Initiation in the lower UV range may become more readily accessible as high power UV excimer lasers become more widely available.

In order to facilitate more efficient use of UV radiation in initiating detonation of HE it is desirable to have accurate UV absorption spectra. Previous spectral measurements have involved monitoring the transmission of light through thin single crystals [9,10], or the reflectance of light from single crystals [4,10-12] and powdered samples [11]. However the techniques used often present difficulties at short wavelengths (< 250 nm) where the HE absorb most strongly [9,11].

The study of thin crystalline films provides an alternative method of obtaining the absorption spectra of solid HE. The transmission of light is monitored through these thin films which are formed by solution evaporation on quartz plates [13]. However absorption by thin films may be strongly influenced by crystal defects [10] and polarization effects arising from crystal orientation [14]. Generally solution rather than solid state studies have been undertaken to obtain precise electronic spectral data on energetic molecules [11,13,15-18]. HE are often produced as precipitated powders and for the practical application of laser initiated detonation it is of greater relevance to investigate the absorption spectra of these powders rather than the absorption spectra of HE single crystals, films or solutions.

In the study reported here the absorption spectra have been obtained by a pressed potassium chloride (KCl) disk technique, analogous to that using KBr which is commonly used in infrared spectroscopy. The use of KCl disks for electronic spectroscopy was first applied by Dale [19] and is discussed in detail by Suzuki [14]. Using this method the dual beam absorption spectrometer automatically corrects for KCl absorption by passing the reference beam through a blank KCl disk. Light scatter from the sample disk is also cancelled out in this process, although the reference disk scatters less light and this results in a non-zero baseline. An advantage of using KCl instead of KBr is the lower chemical reactivity and higher heat stability of the former [20]. As a basis for further excited state studies it will also be desirable to reduce heavy-atom effects on the excited state properties of the HE by choosing the lower atomic weight halide. The energetic molecules chosen for this study are four of the most commonly used high explosives; HNS, RDX, HMX and PETN. Each of these solutes was also studied in acetonitrile solvent in order to compare the absorption spectra in the solid and solution phases.

EXPERIMENTAL

The high explosives studied were: 2,2',4,4',6,6'-hexanitrostilbene (HNS), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and pentaerythritol tetranitrate (PETN). The HNS is considered to be entirely trans isomer since no cis isomer was observed by proton nmr analysis. The HNS-IIB (batch X580, Naval Surface Warfare Center, Whiteoak, MD), RDX Grade A (Albion Explosives Factory, Vic., Australia) and PETN (ICI Australia) were supplied as high quality graded powders. The HNS-IIB and RDX were further recrystallised two and three times respectively from acetonitrile (BDH, Far UV HPLC grade). The HNS recrystallised to form fine pale yellow needles, the colour having remained after boiling with charcoal. The RDX readily formed large translucent orthorhombic crystals , but the final recrystallisation was used to produce small white crystals . PETN was recrystallised twice from methanol (BDH, AR grade) to give thick translucent needles, while β-crystalline HMX was used as supplied (research grade, MRL, DSTO Melbourne).

Finely divided KCl crystals were produced by the procedure described by Hales and Kynaston [20]. A filtered saturated solution of KCl (Ajax, AR grade) was added dropwise with stirring to an equal quantity of concentrated HCl (May and Baker, AR grade) in an ice bath. The precipitated KCl was washed twice with saturated KCl solution, dried for 1 h at 110°C and 8 h at about 450°C. The KCl disks were prepared by grinding 4 to 8 mg of HE in a mortar with about 140 mg KCl to dilute the HE. Additional dilutions were sometimes necessary before grinding the final mixture, 153 mg of which was used in a 13 mm diameter die. This mixture was pressed under vacuum at 10 tonne pressure to obtain a transparent disk of about 0.58 mm width, assuming a disk density of 1.988 Mg/m^3 [14]. The final proportions of HE in the disks were approximately 0.03, 0.18, 0.08 and 0.11 w/w % for HNS, RDX, HMX and PETN respectively, producing absorbances in the range 0.4 to 0.8. All KCl disks were stored in a vacuum desiccator to reduce moisture adsorption.

For all measurements on pressed disks a blank KCl disk was used as a reference, and new reference disks were prepared shortly prior to each set of measurements. Both the sample and reference disks were contained in specially constructed cardboard holders matched for aperture and height. These were attached to the cell holders of a UV-visible absorbance spectrophotometer (Varian, Superscan 3). Solutions of the HE were also prepared in acetonitrile at a concentration of about 50 μM and studied in 1 cm quartz cuvettes.

RESULTS AND DISCUSSION

1. Studies on HNS

The absorption spectrum for HNS in acetonitrile is shown in Figure 1(a), indicating unstructured absorption peaking at 221 nm. This represents a substantial blue shift in wavelength from that of trans-stilbene, the base chromophore of HNS, which has a long wavelength A-band at 294 nm in n-heptane solution [21,22a]. It should be noted that there is little effect of solvent on the absorption spectrum of t-stilbene [22a,23]. An important factor contributing to the blue shift is the substantial amount of steric hindrance to molecular planarity in HNS. The bulky nitro groups distort the ground and excited state molecular configurations of HNS in a similar way to the methyl groups in 2,2',4,4',6,6'-hexamethylstilbene [21,22b]. Relief of steric strain in these molecules is more difficult in the excited state, and this results in a 31 nm absorption band blue shift for the latter molecule relative to t-stilbene in n-heptane solution [22b,24]. However it is unlikely that steric strain alone can account for a blue shift of over 70 nm. It is therefore proposed that the long wavelength A-band for HNS in acetonitrile is hidden in the extended red tail of the principal absorption band, the latter absorption at 221 nm being attributed to the B-band which for t-stilbene appears at about 230 nm [22b]. The presence of the A-band in the acetonitrile solution spectrum is discernible also by the inflection in the spectrum at 270 to 290 nm.

Since both HNS and hexamethyl stilbene are sterically crowded molecules, the ratio of their lower to upper absorption band intensities are likely to be more similar than when HNS is compared to t-stilbene. For HNS the molar absorptivity (ϵ) at 221 nm is 41,300 M^{-1} cm^{-1}, while that of the submerged A-band is much lower. This may be compared to data on hexamethylstilbene in n-heptane in which the lower and upper wavelength bands, for excitation into the second and first excited electronic states, have molar absorptivities of 35,700 M^{-1} cm^{-1} (214 nm) and 16,000 M^{-1} cm^{-1} (263 nm) respectively [21]. This contrasts with t-stilbene in which the B-band has a molar absorptivity (ϵ = 16,200 M^{-1} cm^{-1} at 228.4 nm) which is less than that for the A-band (ϵ = 27,950 M^{-1} cm^{-1} at 294 nm) in n-heptane solution [22a]. For HNS $\pi \rightarrow \pi^*$ transitions are expected to dominate the absorption spectrum, as they do for t-stilbene and its hexamethyl derivative, however it is also possible that lower intensity $n \rightarrow \pi^*$ transitions associated with the NO_2 groups occur in the extended red tail for HNS. Unlike t-stilbene the absorption spectrum of HNS has no vibrational fine structure. This observation can be attributed to the non-planar ground state of the HNS molecule [25]. Many stilbene compounds undergo trans-cis photoisomerisation, however preliminary UV lamp irradiation studies on the photodegradation of HNS in acetonitrile did not indicate the formation of a spectrally resolved cis isomer. This may be due to the large intramolecular steric hindrance to photoisomerisation in HNS molecules [26].

In pressed KCl disks the absorption maximum of HNS is at 238 nm (Figure 1b), 17 nm to the red of that in acetonitrile solution. The extended absorption tail now stretches into the blue region of the visible spectrum resulting in the yellow colouration of the crystals. In Figure 1b the molar absorptivity is normalized to the solution peak value due to poor reproducibility in absolute intensity measurements for KCl disks. This problem is associated with the degree of grinding of the HE in KCl, which is difficult to regulate. It may be noted that in absorption studies reported for pressed KCl disks of t-stilbene a red shift of only about 5 nm was obtained for the A-band in KCl relative to n-heptane solution [14]. However this red shift was also accompanied by significant intensity redistribution between vibrational bands. The red shift was attributed to either intermolecular interactions within the t-stilbene crystals or between t-stilbene molecules and KCl. In Suzuki's study [14] the sterically hindered stilbene derivatives had even smaller red shifts in KCl disks than did t-stilbene itself. However the study by Goedicke et al [27] showed no correlation between the amount of red shifting of the absorption band of diarylethylenes in the crystalline phase and the degree of molecular coplanarity in the ground and excited states. In this latter study the transmission spectra of diarylethylene crystals sandwiched between quartz plates could be studied for wavelengths greater than 350 nm and compared to hydrocarbon solution spectra. The crystalline phase showed marked broadening and red shifting of the long wavelength absorption band from 5 to 70 nm [27]. However the emission spectrum was also red shifted resulting in little net Stokes shift. No theoretical explanation was advanced for these effects which appear similar to those observed in our absorption studies. Reflection spectra of HNS measured by Paisley [4] similarly show strong absorption in the UV and blue regions of the visible spectrum, but they also report a shoulder in the spectrum at about 270 nm which may be due to the A-band of HNS.

2. Studies on RDX

The absorption spectrum of RDX in acetonitrile is given in Figure 2a. Its features include an absorption maximum at 193 nm of molar absorptivity $\epsilon = 16{,}000\ M^{-1}\ cm^{-1}$, with a longer wavelength peak at approximately 234 nm ($\epsilon = 11{,}000\ M^{-1}\ cm^{-1}$). This compares to results reported by Orloff et al [17] in which absorption bands are reported at 195.5 nm ($\epsilon = 16{,}400\ M^{-1}\ cm^{-1}$) and at 236.0 nm ($\epsilon = 11{,}000\ M^{-1}\ cm^{-1}$). The small differences observed between the present results and literature values is attributed to Orloff et al's identification of band positions in their higher resolution spectrum at wavelengths slightly longer than that for the absorption maximum. Stals [16] reports the longer wavelength peak to be at 235 nm. This absorption peak has been attributed to absorption by $N\text{-}NO_2$ moieties and is often referred to as the nitramine band [10,12].

In ethanol, a solvent more polar than acetonitrile, the absorption maximum is reported at 202 nm ($\epsilon = 13{,}100\ M^{-1}\ cm^{-1}$) with a shoulder at 236 nm [16], while in methanol, which is even more polar, the absorption wavelengths reported are at 204 nm ($\epsilon = 13{,}100\ M^{-1}\ cm^{-1}$) and 234 nm (shoulder) respectively [16]. The high molar absorptivity and small positive solvent polarity effect on the lower wavelength absorption band are consistent with the contention that the absorption arises principally from $\pi \rightarrow \pi^*$ transitions [16,17]. The longer wavelength band for RDX absorption appears less sensitive to solvent polarity, and there may be a contribution to this band from weak $n \rightarrow \pi^*$ absorption [17].

The absorption spectrum for RDX in pressed KCl disks (Figure 2b) changes markedly from the spectrum in acetonitrile; the absorption shoulder at 234 nm in solution is now the dominant feature, absorbing at 243.5 nm. The lower wavelength absorption appears to peak near 190 nm. The ratio of the upper to lower absorption intensities is 1:0.96. Increasing the proportion of RDX in KCl six fold from an absorbance of 0.4 to 2.4 at 243.5 nm did not alter the relative peak heights or the relative intensity of the extended long wavelength tail.

A study of thin RDX films by Maycock et al reported absorption maxima at about 248 nm and 209 nm (ratio of intensities 1:0.89) with considerable absorption in an extended red tail [13]. This compares to values of 255 nm and 220 nm (intensities 1:0.53) for the absorption spectra calculated from single crystal reflectance studies [10]. These latter studies also show significant absorption at wavelengths above 300 nm, which was further examined using thin crystal transmission measurements [10]. Marinkas et al report that at approximately 365 nm an absorption band of maximum molar absorptivity 2 M^{-1} cm^{-1} is observed, which may be due to intermolecular charge transfer within the solid RDX [10,12]. A similar absorption band at about 340 nm was also observed in reflectance studies reported by Stals [11]. An absorption band of such low molar absorptivity is understandably indiscernible in our study, although we do observe significant absorption in the region 300 - 400 nm, the origin of which we are unable to identify. Absorption in this region was reported for thin RDX films, and it may arise from excitonic absorption [13], in which excited state electron delocalization is achieved through strong intermolecular interaction.

A common feature of all the above techniques used to determine the solid state absorption spectrum of RDX is the increase in the relative amount of absorption at longer wavelengths compared to solution spectra. The extent of these changes appear most pronounced in single crystals, but are however evident in the pressed disks of ground crystalline RDX.

3. Studies on HMX

The absorption spectra of HMX in acetonitrile solution and in pressed KCl disks are shown in Figures 3a and 3b respectively. In solution the absorption maximum is at 227 nm with molar absorptivity 21,000 M^{-1} cm^{-1}. This is in reasonable agreement with the results of Stals et al who obtained values of 226 nm and 18,000 M^{-1} cm^{-1} for acetonitrile solution [16]. Stals did not show the position of the lower wavelength band in acetonitrile which we found occurred at about 190 nm. However in ethanol this band is reported to occur at about 201 nm [16]. The longer wavelength nitramine band for ethanol solution is reported to occur at 228.5 nm (ϵ = 21,000 M^{-1} cm^{-1}) [15] which is very similar to that in acetonitrile.

Stals et al suggested that for HMX the absorption bands derived most of their intensity from $\pi \rightarrow \pi^*$ transitions, in particular that of $^1A_1$ to $^1B_2$.

When HMX is studied in pressed KCl disks the long wavelength absorption band becomes more prominent than in acetonitrile solution. The absorption maxima of the solid HMX are at 194 and 233 nm, with an extended tail to the red of the longer wavelength band. Thin films of β -HMX on quartz similarly showed the longer wavelength absorption peak at about 247 nm to be more prominent than the lower wavelength nitramine peak at 224 nm [13]. By comparison, reflectance studies indicated that the peak and shoulder absorption bands were at 245 and 202 nm respectively [10]. Both reported studies show significant absorption above 300 nm, and a band at about 355 nm is attributed to charge-transfer (CT) interaction [10,12]. This CT band was also reported by Stals, but its molar absorptivity is expected to be much too low to allow it to be observed in pressed KCl disks. There are many similarities between the absorption spectra of HMX and RDX, suggesting that similar chromophores are responsible for absorption in each molecule. A possible explanation for the observed increase in red edge absorption is the cooperative excitation of molecules paired together by resonance interaction [28a,28b,29]. Singlet excitonic absorption often occurs in organic crystals, of which anthracene provides a well known example [28b,29]. However the low degree of structure apparent on the red edge of the principal absorption band for HMX makes it difficult to ascribe this region of the spectra to a definite absorption transition.

4. Studies on PETN

In acetonitrile PETN appeared to have an absorption maximum at a value less than or equal to 192 nm, the limits of accuracy for our spectrophotometer. Using a vacuum scanning spectrometer Mullen and Orloff [18] reported the absorption maximum to be at 193.5 nm (ϵ = 20,400 M^{-1} cm^{-1}) with further bands assigned to inflections occuring at 260 nm (ϵ = 75) and 290 nm (ϵ = 22). Molecular orbital calculations suggested that this absorption transition has principally $\pi \rightarrow \pi^*$ character localised on the nitro group, but it may also have a significant contribution from intramolecular charge transfer [18]. The weaker long wavelength bands were attributed to $n \rightarrow \pi^*$ transitions [18].

When embedded in pressed KCl disks the absorption maximum of PETN was at 193 nm with an extended tail at longer wavelengths (Figure 4, Table 1). Data concerning the UV absorption spectra of PETN is particularly relevant given the recent interest in initiating detonation of PETN by UV lasers. Studies by Paisley [4] suggest that exciting PETN at 266 nm to initiate detonation requires significantly less energy than at 355 nm and the saving in energy is even more pronounced when compared to 1.06 μm laser radiation. Studies by Renlund et al [8] similarly indicate that there is less need to confine PETN when using 308 nm radiation to initiate detonation than when exciting at 355 nm. It may however be noted that, even at 266 nm, PETN does not absorb very strongly.

Table 1. Absorption Maxima (λ) and Molar Absorptivities (ϵ) for High Explosives in Acetonitrile Solution and Pressed KCl Disks

HE	In Acetonitrile				In KCl	
	λ(nm)		$\epsilon(M^{-1}\ cm^{-1})$		λ(nm)	
	λ_1	λ_2	ϵ_1	ϵ_2	λ_1	λ_2
HNS	221		41300		238	
RDX	193	234	16000	11000	≤190	243.5
HMX	≤190	227	-	21000	194	233
PETN	193.5$^{(a)}$		20400$^{(a)}$		193	

$^{(a)}$ Obtained from Reference 18

DISCUSSION AND CONCLUSION

It is observed that the ultraviolet absorption spectra of HE in the solid state are substantially different from those in acetonitrile solution. The main difference is that the solid state absorption is relatively greater at longer wavelengths. This is particularly noticeable for RDX and HMX, where the longer wavelength nitramine bands become more prominant and are red shifted in the pressed disk spectra relative to the solution spectra. The extended absorption tail to the red of the absorption maximum appears to be the result of spectral broadening rather than the occurrence of a new absorption transition. However each of the tails may hide weak $n \rightarrow \pi^*$ or charge transfer bands. The former bands should also then be present in the solution spectra, while the latter bands have previously been reported for both RDX and HMX [10, 12]. Spectral broadening is also apparent in the pressed disk PETN spectrum, although the non-zero baseline absorption attributed to light scattering dominates the tail of the spectrum.

For HNS the absorption maximum is significantly broadened and red shifted in pressed KCl disk. An absorption transition appears to be present in the tail of the acetonitrile solution spectrum of HNS at 270 to 290 nm which may correspond to the upper electronic transition to the first excited state. This transition may also be partly responsible for HNS crystallite absorption between 300 and 360 nm.

An effect that may contribute to the pressed disk spectra is the loss of crystal structure by the incorporated crystallites, resulting in a distortion of their absorption spectra. This can occur when grinding of the HE with the KCl is excessive, or when the crystal lattice energy of the HE or matrix is low, leading to the formation of amorphous particles; this has been observed in infrared absorption studies [30]. However, in the study reported here the extent of manual grinding used was kept to a minimum and, with the exception of PETN (M.P. 140°C), all the HE have melting points exceeding 200°C, indicating that their crystal lattice energies are likely to be high enough to avoid loss of crystallinity [30]. The use of KCl instead of KBr matrix also favours retention of crystal structure of the HE due to the higher lattice energy of KCl [30]. The observations recorded here for HE crystallites are in broad agreement with absorption spectra obtained on thin films of RDX and HMX, as well as absorption spectra derived from reflectance studies on single crystals of HE. The differences between solid state and solution spectra are more pronounced for single crystals with the KCl disk spectra being intermediate.

The red shifts observed for the absorption spectra of HE crystallites are attributed to strong intermolecular interaction between HE molecules following excitation. This interaction lowers the excited state energy level relative to the ground state. The large degree of variability in the strength of the interaction may be responsible for the broadness of the absorption bands. A distinct charge transfer or excitonic absorption transition is not observed for the HE spectra, however the possibility that these transitions may contribute to the red shift is not ruled out. The extent of involvement by KCl matrix in the excited state stabilisation of the HE is expected to be much less than the interaction between HE molecules.

Laser initiated detonation of high explosives (HE) has generally involved the use of high powered visible and infrared lasers. Previous studies have however established that HE absorb most strongly in the UV, and it has been shown recently that laser excitation in this region reduces the laser power requirements for HE initiation. The study presented here is particularly useful in providing absorption spectra for solid HE in the form it is most often produced and used in, ie, the precipitated powder form, as opposed to thin films or single crystals.

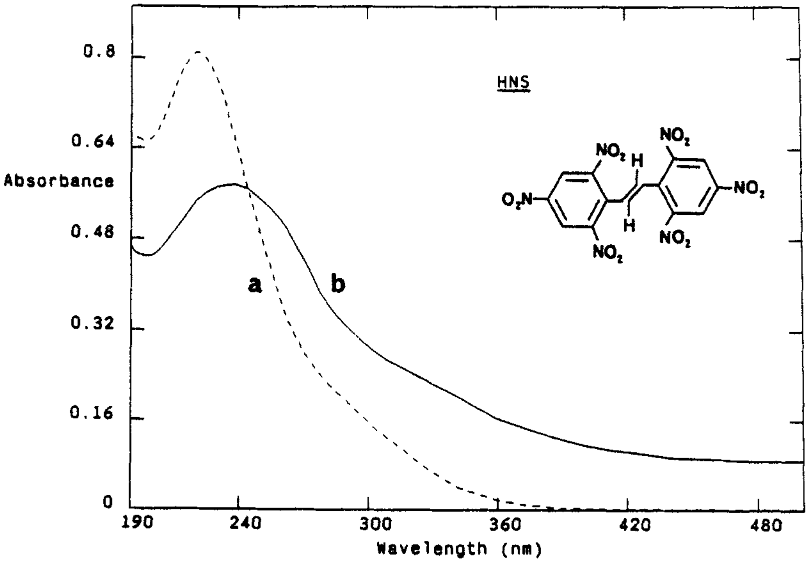

FIGURE 1. Absorption spectrum of HNS in; (a) acetonitrile, (b) KCl.

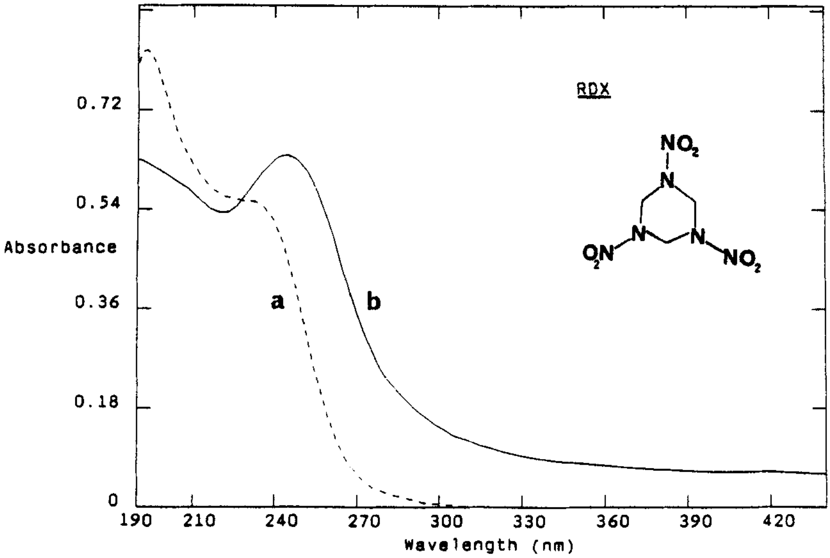

FIGURE 2. Absorption spectrum of RDX in; (a) acetonitrile, (b) KCl.

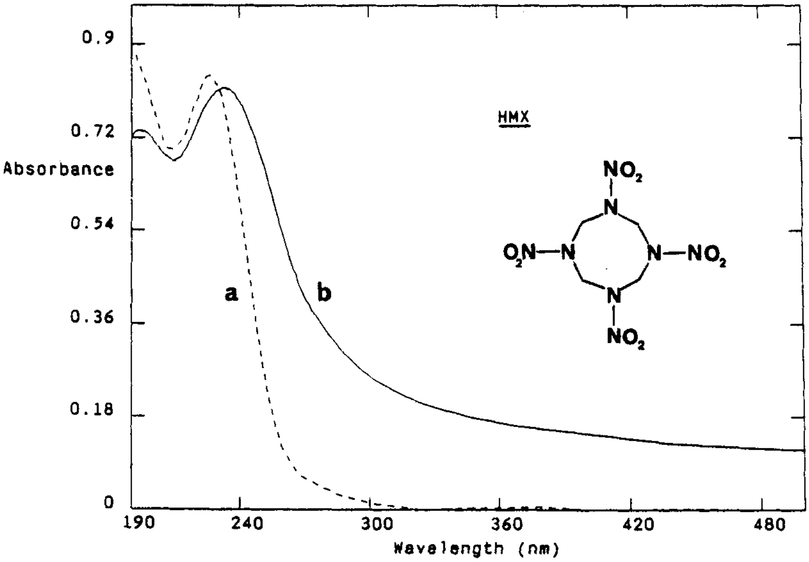

FIGURE 3. Absorption spectrum of HMX in; (a) acetonitrile, (b) KCl.

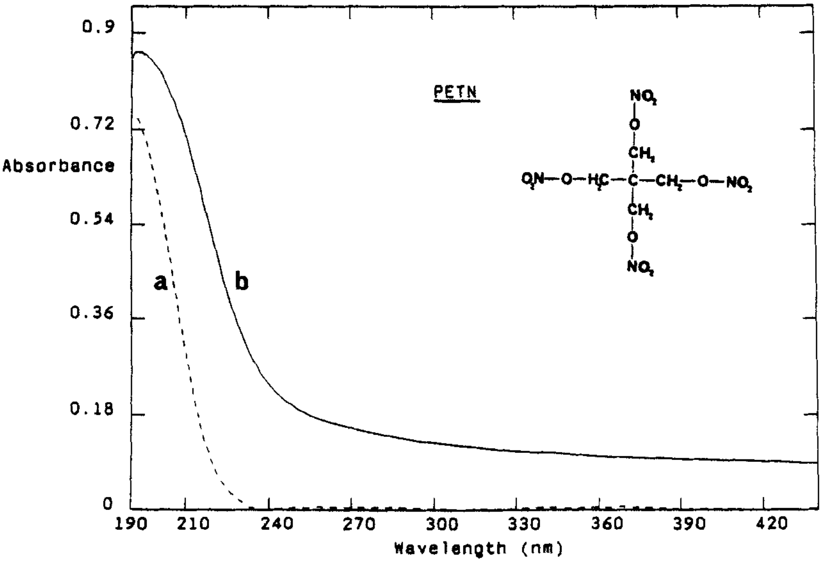

FIGURE 4. Absorption spectrum of PETN in; (a) acetonitrile, (b) KCl.

REFERENCES

1. L.C. Yang and V.J. Menichelli, "Laser Initiation of Insensitive High Explosives", Proc. 6th Symp. (Int.) on Detonation, Coronado, CA, (1976), p. 612.
2. H. Ostmark, "Laser as a Tool in Sensitivity Testing of Explosives", Proc. 8th Symp. (Int.) on Detonation, Alberquerque, NM, (1985), p. 46.
3. M. Brochier, "Contribution a l'etude de l'initiation de substance pyrotechniques par laser", Proc. 19th Int. Ann. Conf. of I.C.T., Karlsruhe, FRG, (1988), p. 78.
4. D.L. Paisley, "Prompt Detonation of Secondary Explosives by Laser", Preprint 9th Symp. (Int.) on Detonation, Portland, OR, (Aug./Sept. 1989), p. 492.
5. J.F. Eloy and A.E. Delpuech, "Experimental Study of Photon-phonon Interactions in an Explosive by Laser Probe Mass Spectrography (LPMS-2S)", in Shock Waves in Condensed Matter 1987, S.C. Schmidt and N.C. Holmes, eds., Elsevier, Amsterdam, (1988), p. 557.
6. B.J. van der Meer and M.W. Leeuw, "Laser-Initiated Decomposition Reactions of Explosives", Proc. 13th Int. Pyrotech. Sem., (1988) p. 823.
7. A.E. Delpuech, "The Use of Time-Resolved Spectrometries in the Study of Initiation of Explosives at the Molecular Level", Preprint 9th Symp. (Int.) on Detonation, Portland, OR, (Aug./Sept. 1989), p. 73.

8. A.M. Renlund, P.L.Stanton and W.M. Trott, "Laser Initiation of Secondary Explosives", Preprint 9th Symp. (Int.) on Detonation, Portland, OR, (Aug/Sept. 1989), p. 781.

9. F.P. Bowden and A.D. Yoffe, "Fast Reactions in Solids", Academic Press, New York, 1958, p. 107.

10. P.L. Marinkas, J.E. Mapes, D.S. Downes, P.J. Kemmey and A.C. Forsyth, Mol. Cryst. Liq. Cryst. 35, 15 (1976).

11. J. Stals, Trans. Far. Soc. 67, 1739 (1970).

12. P.L. Marinkas, J. Luminescence 15, 57 (1977).

13. J.N. Maycock, V.R. Pai Verneker and W. Lochte, Phys. Stat. Sol. 35, 849 (1969).

14. H. Suzuki, Bull. Chem. Soc. Japan. 33, 944 (1960).

15. W.A. Schroeder, P.E. Wilcox, K.N. Trueblood and A.O. Dekker, Anal. Chem. 23, 1740 (1951).

16. J. Stals, C.G. Barraclough and A.S. Buchanan, Trans. Farad. Soc. 65, 904 (1969).

17. M.K. Orloff, P.A. Mullen and F.C. Rauch, J. Phys. Chem. 74, 2189 (1970).

18. P.A. Mullin and M.K. Orloff, J. Phys. Chem. 77, 910 (1973).

19. J. Dale, Acta Chem. Scand. 11, 650 (1957).

20. J.L. Hales and W. Kynaston, Analyst 79, 702 (1954).

21. H.Suzuki, Bull. Chem. Soc. Japan. 33, 406 (1960).

22. H.H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, 1962; (a) p. 276, (b) p. 424.

23. L.A. Brey, G.B. Schuster and H.G. Drickamer, J. Am. Chem. Soc. 101, 129 (1979).

24. H.H. Jaffe and M. Orchin, J. Chem. Soc. 1078 (1960).

25. I. Berlman, J. Phys. Chem. 74, 3085 (1970).

26. G. Fischer, K.A. Muscat and E. Fischer, J. Chem. Soc. B, 156 (1969).

27. Ch. Goedicke, H. Stegemeyer, G. Fischer and E. Fischer, Zeit. Phys. Chem. (NF) 101, S. 181 (1976).

28. (a) H.W. Offen, "Absorption and Luminescence of Aromatic Molecules at High Pressures", in "Organic Molecular Photophysics", Vol. 1, J.B. Birks, ed., Wiley, London, 1973; p. 140. (b) C.E. Swenburg and N.E. Geacintov, "Exciton interactions in organic solids", ibid; p. 489.

29. J. Jortner, S.A. Rice and R.M. Hochstrasser, "Radiationless Transitions", in "Advances in Photochemistry", Vol. 7, J.N.Pitts, Jr., G.S. Hammond and W.A. Noyes, Jr., eds., Wiley, New York, 1969; p. 226.

30. A.W. Baker, J. Phys. Chem. 61, 450 (1957).