

# Dissociation of Cyclotrimethylenetrinitramine Under 1064-nm Laser Irradiation Investigated by Time-of-Flight Mass Spectrometer

Wei Zhang,  
Ruiqi Shen,  
Yinghua Ye,  
Lizhi Wu,  
Yan Hu,  
and Peng Zhu

School of Chemical Engineering,  
Nanjing University of Science and  
Technology, Nanjing, China

**ABSTRACT** Laser-induced dissociation pathways of cyclotrimethylenetrinitramine have been investigated with a focused laser of 1064 nm by use of a time-of-flight mass spectrometer. The ions produced from the cyclotrimethylenetrinitramine surface were detected and the mass spectra of both positive and negative ions were obtained. According to the possible distribution of the decomposition products, possible dissociation paths of cyclotrimethylenetrinitramine were proposed. The influence of the intensity and the delay time of the laser beam to the decomposition have also been studied. The results may possibly throw some light on our understanding of the reactions taking place in laser ignition.

**KEYWORDS** cyclotrimethylenetrinitramine, dissociation mechanism, laser initiation, time-of-flight mass spectrometer

## INTRODUCTION

Laser initiation of energetic materials is one of the most promising methods of initiating combustion, deflagration, or detonation in energetic materials.<sup>[1,2]</sup> Optical initiation with a laser beam offers several potential advantages, such as high safety, precisely timed release, easy-to-realize multipoint ignition and initiation, no requirement to sensitivity of explosives, and more efficient energy coupling.<sup>[3,4]</sup> Understanding the mechanism of the interaction of laser and energetic materials is important to the reliability and safety of laser initiators and firing systems. Cyclotrimethylenetrinitramine (RDX) is a highly symmetric, energetic compound often used as a secondary explosive, which has been the subject of a number of studies regarding the sensitivity and mechanism of decomposition in energetic materials.<sup>[5,6]</sup> There have been studies on decomposition of RDX initiated by infrared lasers, which is utilized as a versatile heating source. Earlier work done on molecular gas-phase RDX exposed to CO<sub>2</sub> laser pulses were carried out by Zuckermann and Zhao et al. The results of Zuckermann<sup>[7]</sup> from laser-induced fluorescence experiments showed the existence of OH radicals. Studies from Zhao<sup>[8]</sup>

Received 11 July 2013;  
accepted 12 August 2013.

Address correspondence to  
Ruiqi Shen, School of Chemical  
Engineering, Nanjing University of  
Science and Technology, Nanjing,  
China. E-mail:  
rqshen@mail.njust.edu.cn

suggested that the N-N bond rupture and ring scission are two competing reaction pathways, with the latter one being the primary channel. Wight and Botcher carried out experiments in which a pulsed CO<sub>2</sub> laser (wavelength 944 cm<sup>-1</sup>) was used to dissociate condensed-phase RDX. The Fourier transform infrared spectra of the products showed the presence of N<sub>2</sub>O<sub>4</sub>, an NO<sub>2</sub> dimer molecule. Therefore, they proposed that N-N bond fission is the initial reaction step. They also suggested that no ring scission mechanism took place.<sup>[9]</sup> Capellos et al.<sup>[10]</sup> studied the decomposition of molecular gas-phase RDX induced by an unfocused KrF excimer laser beam. Electronically excited NO<sub>2</sub> and OH were observed in the emission spectra and were postulated to derive from N-N bond rupture and a loss of HONO group, respectively. More recently, Bernstein's group carried out a series of studies on ultraviolet laser-induced decomposition of isolated gas-phase RDX, which is produced from a combination of matrix-assisted laser desorption (MALD) and supersonic molecular beam techniques.<sup>[11]</sup>

The dissociation process of RDX under 532 nm was studied in our previous work.<sup>[12]</sup> A 1064-nm laser is also used as an ignition source of energetic materials, yet the reaction mechanism is still not very clear. To gain a better understanding of the various reactive transient species and intermediates and the processes involved in ion formation and occurring after 1064-nm laser irradiation, in this article, we describe a study in which RDX is heated photothermally by irradiating solid samples with a 1064-nm pulsed laser and the ablation products contain a lot of ion fraction, which is tested by a time-of-flight mass spectrometer (TOFMS).

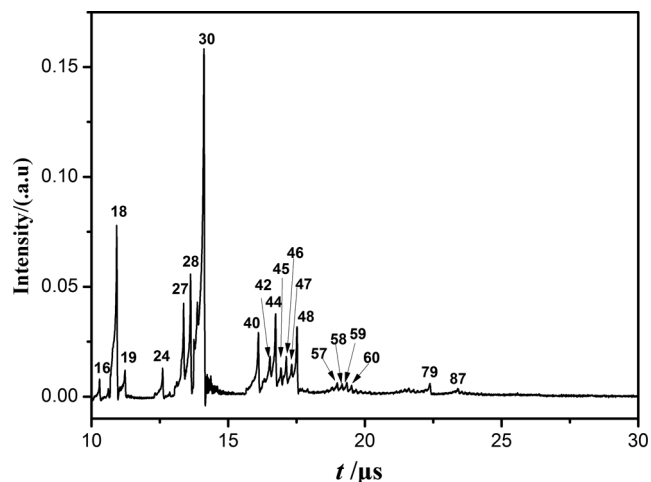
## EXPERIMENT

The solid RDX sample was synthesized by ourselves and the purity is above 99%. It was compressed in a small aluminum cylindrical cup (inner diameter = 6 mm; depth = 11 mm) under a pressure of about 80 MPa. The experimental setup has been introduced in our previous study.<sup>[13]</sup> It was a home-made reflectron time-of-flight mass spectrometer; the length of the extraction field and acceleration field is 20 mm, the distance between the acceleration field and the reflectron field is 512 mm, and the distance between the reflectron field and the detector (MCP) is 328 mm. The time-of-flight mass spectrometer was combined with a vacuum chamber, pumping down

to  $4 \times 10^{-4}$  Pa with two turbomolecular pumps. The fundamental 1064-nm output from a Q-switched Nd:YAG laser (LOTIS TII [Minsk, Belarus], LS-2147, 800 mJ @ 1064 nm/15 ns) was focused by a quartz lens ( $f = 500$  mm) to the sample surface, with a spot size of about 0.8 mm<sup>2</sup>. The energy of the laser pulse was measured with an energy meter (Ophir, Model 30A, Jerusalem, Israel). The time delay was monitored via an adjustable time delay generator. The sample was located outside the extraction electrodes of the time-of-flight (TOF) spectrometer, and the laser beam passed through the extraction zone in a direction perpendicular to the acceleration field. After ionization, the laser-generated plasma diffused into the extraction zone by its initial kinetic energy and then was accelerated by a pulsed electric field, reflected by the reflectron field and finally detected with a dual microchannel plate (MCP). For the positive mode, the direct current (DC) voltages on the extraction plate, the acceleration plate, the reflectron plate, and the detector were +1100 V, +900 V, +2700 V, and -2100 V, respectively. For the negative mode, the DC voltages were -1300 V, -1100 V, -1900 V, and +2100 V, respectively. The ions were mass analyzed by their flight time. The TOF signals were accumulated 128 times by a digital oscilloscope (Tektronix, DPO7140, Beaverton, OR, USA) to improve the signal-to-noise ratio.

## RESULTS AND DISCUSSION

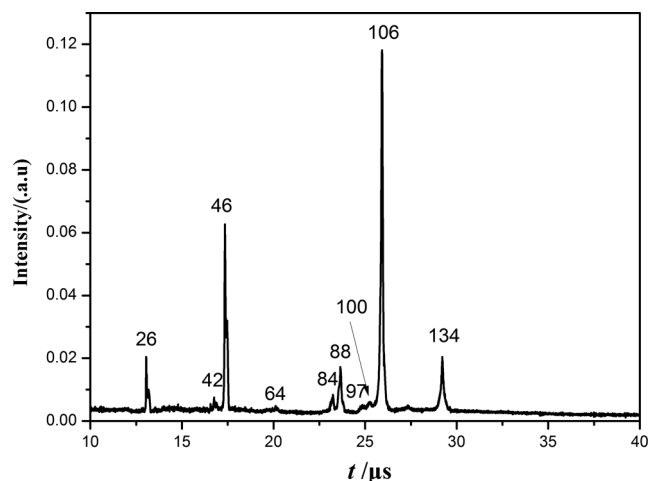
The typical mass spectrum of positive ions is shown in Fig. 1. The peaks with the highest intensity in the positive ion spectrum are at  $m/z = 30$ , corresponding to the NO or CH<sub>2</sub>O fragments. Another relatively strong peak appears at  $m/z = 18$  and can be assigned to H<sub>2</sub>O or NH<sub>4</sub>. A series of peaks are observed at  $m/z = 40, 42, 43, 44, 46$ , and  $47$  and can be assigned to CN<sub>2</sub> [or C<sub>2</sub>H<sub>2</sub>N], N(CH<sub>2</sub>)N [or (CH<sub>2</sub>)<sub>2</sub>N], NCOH, N<sub>2</sub>O [or CO<sub>2</sub>, CH<sub>2</sub>NO], NO<sub>2</sub> and HONO, respectively. The results from the thermal decomposition of the isotopically labeled RDX showed that the formula for the ion signal at  $m/z = 45$  is H<sub>2</sub>NCHO and is probably formamide. Likewise, the results also showed that the formula that corresponds to  $m/z = 59$  is CH<sub>3</sub>NHCHO and is most likely N-methylformamide.<sup>[14]</sup> A series of small peaks appear in  $m/z = 57, 58, 59$ , and  $60$ , and these ions could be ascribed to (CO)NH(CH<sub>2</sub>) or N(COH)N; CNO<sub>2</sub> or (COH)NH(CH<sub>2</sub>); CHNO<sub>2</sub>; and



**FIGURE 1** Typical TOF mass spectrum of positive ions of RDX produced by laser ablation.

$\text{CH}_2\text{NO}_2$  or  $\text{NNO}_2$ , respectively. Some other peaks can be seen at  $m/z=16$ , 19, 24, 27, 28, 74, 79, and 86, which may be due to  $\text{CH}_4$  or O,  $\text{H}_3\text{O}$ ,  $\text{C}_2$ ,  $\text{C}_2\text{H}_3$  or  $\text{CHN}$ ,  $\text{N}_2$  or CO or  $\text{C}_2\text{H}_4$  or  $\text{CH}_2\text{N}$ ,  $\text{CH}_2\text{NNO}_2$ ,  $(\text{HC})\text{N}(\text{CN})_2$  and  $(\text{CH}_2)\text{NNO}_2$ , respectively.

The position of the peaks of the negative ion mass spectrum under 1064 nm is similar to that under 532 nm.<sup>[12]</sup> The difference is the intensity of the main peaks. Figure 2 shows the mass spectrum of negative ions of the pure RDX sample. The peak with the highest intensity in this sequence of spectrum is at  $m/z=106$  and corresponds to the  $\text{CH}_2(\text{NO}_2)_2$  fragment. Unlike at 532 nm, two small new peaks appear in  $m/z=98$  and 100, and these two peaks can be ascribed to  $(\text{CH}_2)_3\text{N}_2(\text{NN})$  and  $(\text{CH}_2)_3\text{N}_2(\text{NO})$ , respectively. Some relatively strong peaks at  $m/z=26$ , 46, 88, and 134 are ascribed to CN or  $\text{C}_2\text{H}_2$ ,



**FIGURE 2** Typical TOF mass spectrum of negative ions of RDX produced by laser ablation.

$\text{NO}_2$ ,  $(\text{CH}_2)\text{NNO}_2$ , and  $\text{H}_2\text{C}(\text{N}-\text{NO}_2)_2$ , respectively. Finally, some low-intensity peaks are observed at  $m/z=42$ , 64, and 84 and are most likely the  $\text{CNO}$  or  $(\text{CH}_2)_2\text{N}$ ,  $\text{CH}_2\text{N}_2$ , and  $(\text{CH}_2\text{N})_3$  species, respectively.

The fragment ions are yielded gradually with increasing laser energy (Fig. 3). Moreover, it is clear that fragmentation processes are highly dependent on the laser energy. Higher values result in an excess of internal energy and more efficient dissociation. The different types of spectra can also be accessed by the appropriate choice of delay time between initiation of a laser pulse and extraction of ions into the TOFMS system (Fig. 4). In a certain range, with the increase of delay time, the ion signal intensity gradually increased, but when the delay time increased to 90  $\mu\text{s}$ , the signal peaks became very wide, and part of the ion peaks disappeared; this may be due to the high-voltage pulse valve being closed before these ions entered the accelerating electric field.

The products assigned in the positive and negative spectra reflect the partial chemical structure of RDX ( $m/z=222$ ) and can be viewed as direct fragments. The RDX ( $m/z=222$ ) ring lost an  $\text{NO}_2$  ( $m/z=46$ ) group to form  $(\text{CH}_2)_3(\text{NNO}_2)\text{N}$  ( $m/z=176$ ). Although  $m/z=176$  was not detected, reaction (I) might exist. Two C-N bonds of the  $(\text{CH}_2)_3(\text{NNO}_2)\text{N}$  ( $m/z=176$ ) ring broke up to give two fragments  $\text{CH}_2(\text{NNO}_2)$  ( $m/z=134$ ) and  $(\text{CH}_2)_2\text{N}$  ( $m/z=42$ ); the observed peaks at  $m/z=134$  and 42 supported reaction (II). After the rearrangement and the fracture of the bonds, the  $\text{CH}_2(\text{NNO}_2)$  ( $m/z=134$ ) decomposed to form two small fragments,  $\text{N}_2$  ( $m/z=28$ ) and  $(\text{CH}_2)(\text{NO}_2)_2$ . The peak corresponding to  $m/z=106$  was strong, and the peak of  $m/z=28$  was obvious; this gave evidence for reaction (III), seen in Scheme 1.

An oxygen atom transferred from the nitramino group to a neighboring carbon to form an eight-member ring oxadiazole intermediate; it can ring-open and lose  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NNO}_2$ , and  $(\text{CH}_2)_2\text{NO}_2$  to give  $m/z=44$ , 30, 60, and 88, respectively (reaction IV and V), seen in Scheme 2.

The  $m/z=74$  peak with the possible formula of  $\text{CH}_2\text{N}-\text{NO}_2$  was most likely from concerted triple dissociation of the RDX molecule as shown in reaction (VI). Reactions (VIII), (V), and (XI) can be a reason for  $m/z=30$  and 44, corresponding to  $\text{H}_2\text{CO}$  and  $\text{N}_2\text{O}$ , respectively. Behrens et al proposed the similar reactions.<sup>[14]</sup> The  $m/z=47$  and 27 peaks

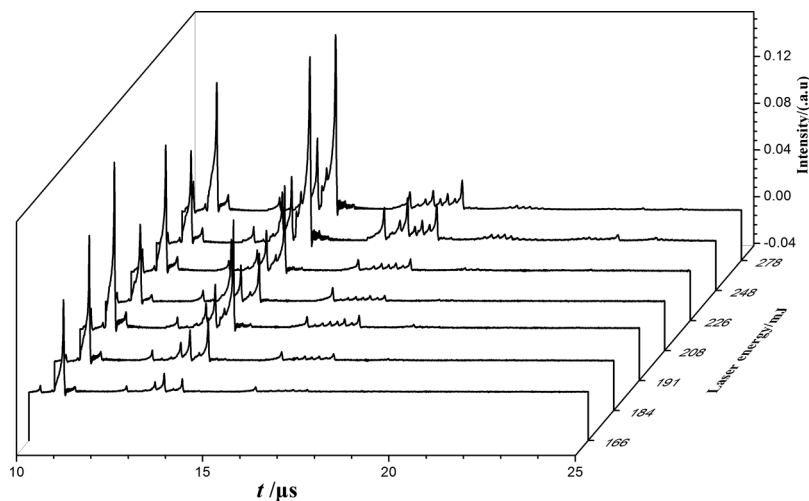


FIGURE 3 TOF mass spectra of positive ions obtained at the laser delay of 70  $\mu$ s as a function of laser energy.

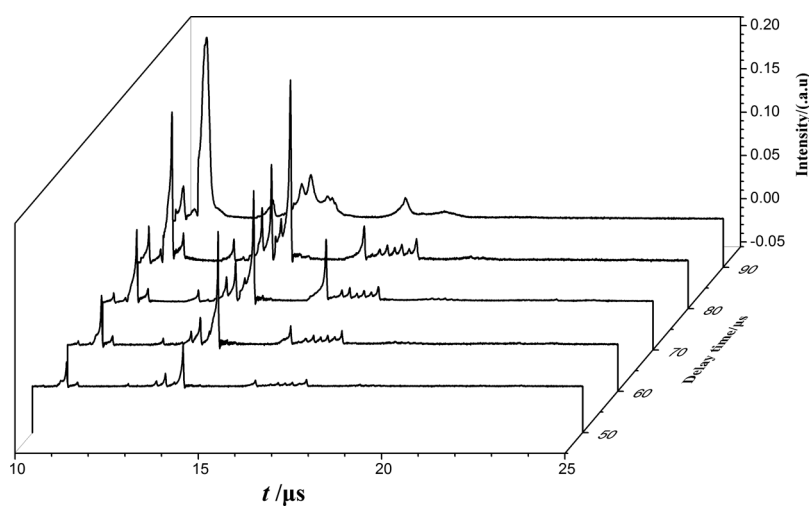
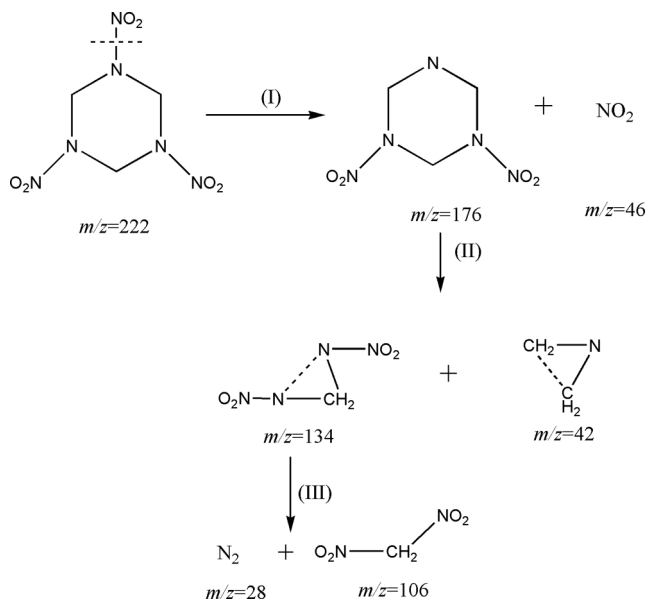
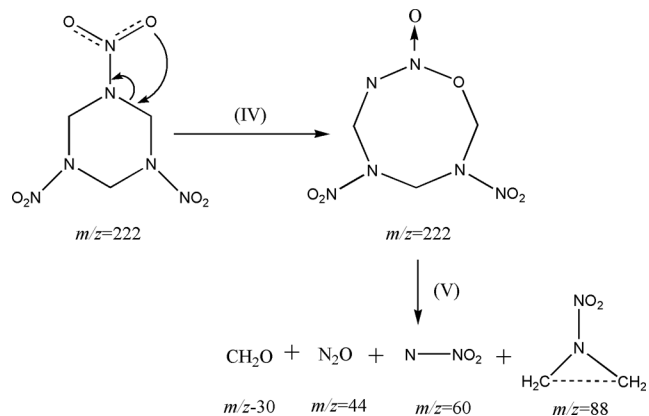
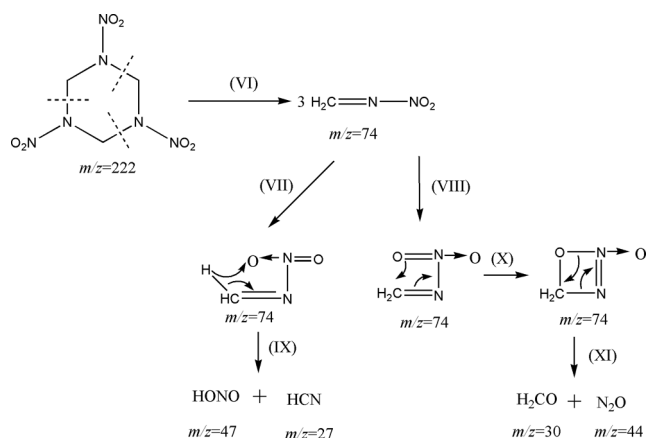


FIGURE 4 TOF mass spectra of positive ions obtained at the laser energy of 226 mJ as a function of laser delay.



indicated reaction channels (VII) and (IX), which could produce HONO and HCN, respectively seen in Scheme 3.





**SCHEME 3**

## CONCLUSIONS

TOFMS with its unique advantage has been successfully used to study the dissociation process of RDX under 1064-nm irradiation. Both positive and negative ions were detected, and possible distribution of the ions was analyzed. A lot of reaction can lead to these ions, and some possible reactions were proposed to give a reason for their formation. Of course, some other reaction may exist, and other methods could be used to confirm the most possible reaction. The laser energy and the delay time will affect the dissociation process. It is worthwhile to pay more attention to these dissociation mechanisms both experimentally and theoretically due to their importance in understanding the mechanisms of laser initiation.

## FUNDING

This work was supported by the Program for Postgraduates Research Innovation at University of Jiangsu Province (Grant No. CXZZ13\_0224).

## REFERENCES

- Zhang, X.; Hikal, W. M.; Zhang, Y.; Bhattacharia, S. K.; Li, L.; Panditrao, S.; Wang, S.; Weeks, B. L. Direct laser initiation and improved thermal stability of nitrocellulose/graphene oxide nanocomposites. *Appl. Phys. Lett.* **2013**, *102*(14), 141905.
- Picard, Y. N.; McDonald, J. P.; Friedmann, T. A.; Yalisove, S. M.; Adams, D. P. Nanosecond laser induced ignition thresholds and reaction velocities of energetic bimetallic nanolaminates. *Appl. Phys. Lett.* **2008**, *93*(10), 104104.
- Monat, J. E.; Gump, J. C. Decomposition products of RDX and TNT after resonant laser excitation. *Proceedings of the American Physical Society Topical Group on Shock Compression of Condensed Matter*, Nashville, Tennessee, June 28–July 3, 2009; AIP: America, **2009**, *1195*(1), 1309–1312.
- Sun, H. *Investigations of Laser Ablation and Laser-Induced-Plasma Ignition of Cyclotrimethylenetri-nitramine (RDX)*. Auburn University, Auburn, 2011.
- Swadley, M. J.; Li, T. Reaction mechanism of 1,3,5-trinitro-s-triazine (RDX) deciphered by density functional theory. *J. Chem. Theory Comput.* **2007**, *3*(2), 505–513.
- Gershnik, A. P.; Zeiri, Y. Sublimation rate of energetic materials in air: RDX and PETN. *Propell. Explos. Pyrot.* **2012**, *37*(2), 207–214.
- Zuckermann, H.; Greenblatt, G. D.; Haas, Y. Hydroxyl radical formation in the infrared multiphoton decomposition of jet-cooled cyclic nitroamines. *J. Phys. Chem.* **1987**, *91*(20), 5159–5161.
- Zhao, X.; Hints, E. J.; Lee, Y. T. Infrared multiphoton dissociation of RDX in a molecular beam. *J. Chem. Phys.* **1988**, *88*(2), 801–810.
- Botcher, T. R.; Wight, C. A. Explosive thermal decomposition mechanism of RDX. *J. Chem. Phys.* **1994**, *98*(21), 5441–5444.
- Capellos, C.; Papagiannakopoulos, P.; Liang, Y. The 248 nm photodecomposition of hexahydro-1,3,5-trinitro-1,3,5-triazine. *Chem. Phys. Lett.* **1989**, *164*(5), 533–538.
- Greenfield, M.; Guo, Y. Q.; Bernstein, E. R. Ultrafast photodissociation dynamics of HMX and RDX from their excited electronic states via femtosecond laser pump-probe techniques. *Chem. Phys. Lett.* **2006**, *430*(4–6), 277–281.
- Zhang, W.; Shen, R.; Wu, L.; Ye, Y.; Hu, Y.; Zhu, P. Dissociation of RDX at 532 nm laser. *Chin. J. Explos. Pyrot.* **2012**, *35*(1), 39–42.
- Zhang, W.; Shen, R.; Wu, L.; Ye, Y.; Hu, Y.; Zhu, P. The formation mechanism of clusters produced by laser ablation of solid sodium azide. *Laser Phys. Lett.* **2013**, *10*(2), 026002.
- Behrens, R.; Bulusu, S. Thermal decomposition of energetic materials. 3. Temporal behaviors of the rates of formation of the gaseous pyrolysis products from condensed-phase decomposition of 1,3,5-trinitrohexahydro-s-triazine (RDX). *J. Phys. Chem.* **1992**, *96*(22), 8877–8891.

Copyright of Spectroscopy Letters is the property of Taylor & Francis Ltd and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.