ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 122 (1999) 1–5

Journal of
Photochemistry
and
Photobiology
A:Chemistry

Photoisomerization of N_2O_3 in an Ar matrix

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Received 3 August 1998; accepted 11 January 1999

Abstract

The photoisomerization of N_2O_3 isomers has been studied by FTIR spectroscopic method in an argon matrix under 632.8, 355 and 266 nm laser irradiations. Photolysis of asym-N_2O_3 leads to the formation of sym-N_2O_3 at 632.8 or 266 nm. Under 355 nm irradiation the asym-N_2O_3 and sym-N_2O_3 can be converted to *trans–cis* isomer, and reversible photoconversion of *trans–cis* N_2O_3 into sym-N_2O_3 occurs at 632.8 nm. The vertical electronically excited states of three isomers have been studied with CIS method and their electronic transitions have also been predicted. A photochemical isomerization cycle of N_2O_3 isomers is proposed to correlate the interconvertions between three different isomers.

Keywords: N_2O_3 isomers; Photoisomerization; Matrix isolation

1. Introduction

NO and NO_2 have long been known to associate into a variety of more complex oxides of nitrogen. The wide variety of their reactions with each other or other small species plays an important role in the chemistry of the earth troposphere (air pollution, acid rain) and stratosphere (ozone destruction). NO mixed with NO_2 produces measurable amount of dinitrogen trioxide which can lead to the formation of different isomers. One of the isomers, the asymmetric $ONNO_2$ (asym-N_2O_3), has been investigated with infrared and Raman spectroscopy in vapor phase [1], liquid phase [2,3], and solid phase [4–8]. The second isomer is a less stable one, symmetric ONONO (sym-N_2O_3). The existence of this isomer has been shown in the pure solid [4], matrices [6,7] and liquefied xenon [3]. Recently our group has studied the infrared spectroscopy of dinitrogen trioxide theoretically [9] and experimentally [10,11] and found convincing evidences for the existence of the third isomer of N_2O_3, *trans–cis* N_2O_3, in an argon matrix, which is the least stable one among the three isomers.

A few photochemical experiments relevant to the formation of N_2O_3 and its isomers were reported previously. The pioneer work on the photochemistry of N_2O_3 in nitrogen matrix reported by Varetti and Pimentel [6] had revealed that asym-N_2O_3 can be converted to sym-N_2O_3 by near infrared irradiation (720 nm) at 20 K, and isomerized back to asym-N_2O_3 by ultraviolet irradiation (370–480 nm). Nour et al. [7] have investigated the similar isomerization process in NO matrix and found that with irradiation in the 568.2–752.6 nm region asym-N_2O_3 could be converted to sym-N_2O_3 but irradiation of 514.5 or 488.0 nm converted the symmetric isomer back to the asymmetric one. Recently we have measured the infrared absorption spectrum of *trans–cis* N_2O_3 after irradiation of asym-N_2O_3 in Ar matrix at 11 K with 355 nm pulsed laser [10]. However, the passways of laser induced photoconversion between various isomers of N_2O_3 in the low temperature matrix remain unclear.

In order to examine the laser wavelength influence on the photochemical interconversions of asym-, sym- and *trans–cis* N_2O_3, in this work we have investigated the photoisomerization of three N_2O_3 isomers in low temperature argon matrix by means of 632.8, 355 and 266 nm laser irradiations. The experimental matrix-isolated FTIR spectra and theoretical calculation were employed to study the vertical absorption and photochemical processes for the conversion of N_2O_3 isomers each other.

2. Experimental

The experimental set-up is similar to that described previously [10]. The gas mixture was deposited onto a surface of a CsI window mounted on a cold tip of a closed-cycle helium refrigerator (Air Products, Model CSW202). The deposition rate was adjusted by needle valves at a rate of ~0.7 mmol/h. The sample temperature

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PII: S1010-6030(99)00012-X

was maintained using a temperature controller (Air Products, Model ADP-E). Infrared spectra were recorded on a Bruker Model IFS 113V Fourier transform spectrometer equipped a Ge/KBr beam splitter, and a Globar source. Happ Genzel apodised and Fourier transformed with a zero filling factor of 4. Spectral resolutions were 0.5 cm^{-1} and the number of scans ranged from 30 to 100. A stainless steel gas inlet, a quartz window, and two KBr windows were mounted on ports along the axes of the rotable sheath to allow for matrix deposition, UV photolysis, and infrared spectroscopic measurements. Three hundred and fiftyfive (355) and 266 nm laser beams were provided by the third and the fourth harmonic frequencies of a Nd:YAG laser (Spectra Physics, GCR-150) with a pulse width of 8 ns, repetition rate of 10 Hz and average laser fluency of 3 mJ/cm^2. A He–Ne laser (Shanghai Laser Technology Institute, 30 mW) was used to provide the cw laser beam at 632.8 nm.

Nitric oxide (99%) was purified by trap to trap distillation until no impurities were detectable in its infrared spectrum. Nitrogen dioxide was prepared by adding an excess of oxygen to NO, freezing the gas mixture at 77 K and pumping off the remaining O_2. Argon (Shanghai BOC gas company, 99.995%) was used without further purification.

3. Results and discussion

3.1. Photoconversion of N_2O_3 isomers

In order to prepare a matrix sample suitable for a photochemical study of N_2O_3, the matrix samples containing NO and NO_2 ($NO:NO_2:Ar=10:1:1500$) were selected to obtain a higher yield of N_2O_3. Fig. 1 presents the infrared absorption spectrum of N_2O_3 argon matrix samples recorded at 11 K before and after laser irradiation at 632.8, 355, and 266 nm, respectively. As shown in Fig. 1(a), the absorption peaks at 1831.5, 1630.1, 1296.4 and 769.5 cm^{-1} (group A) can be easily assigned to asym-N_2O_3, which has been identified previously by many authors [2–8]. The weak absorption bands at 1688.5, 970.1 and 717.4 cm^{-1} (group S) is due to sym-N_2O_3, which are in good agreement with data published in the literatures [6,7,12]. In addition, the set of weak bands at 1704.2, 1666.3, 882.3 and 863.6 cm^{-1} (group T) is also observed. It should be noted that Nakata et al. [13] also observed the N_xO_y absorptions at 881 and 864 cm^{-1} in an Ar matrix, however, these two bands were assigned to precursor of N_2O_4. In nitrogen matrix Varetti et al. [6] found the band at 885 cm^{-1} in N_2O_3 spectra but unidentified properly. Recently ab initio and DFT calculations [9–11] were performed to examine the structure and vibrational spectra of N_2O_3 conformers, and a new isomer of N_2O_3, *trans–cis* N_2O_3 was predicted. The infrared spectra and vibrational assignment of *trans–cis* N_2O_3 were investigated in an argon matrix [10] and isotopic experiments based on ^{18}O-isotopic substitution [11]. Our results confirmed that bands of group T can be assigned to *trans–cis* N_2O_3. The strong bands attributed to NO (1871.8 cm^{-1}), NO_2 (1610.8 cm^{-1}) and *cis*-$(NO)_2$ (1863.4, 1776.4 cm^{-1}) are readily identified. The observed infrared frequencies in Ar matrix for some N_xO_y are listed in Table 1.

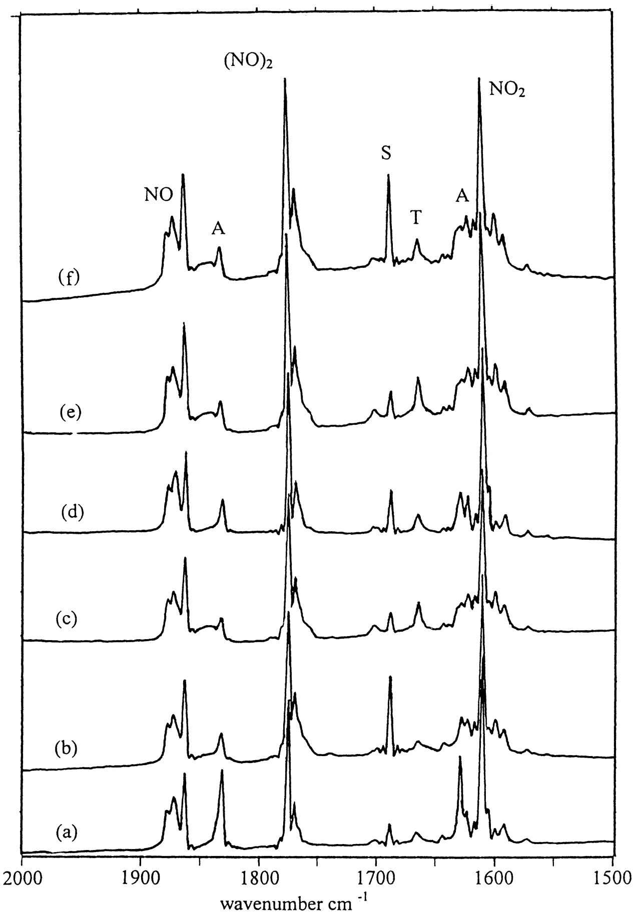

Fig. 1. IR absorption spectra of matrix samples of $NO/NO_2/Ar(10:1:1500)$ before and after irradiation: (a) after deposition; (b) after irradiation at 632.8 nm for 1.5 h; (c) after irradiation of deposition sample at 355 nm for 30 min; (d) after irradiation of deposition sample at 266 nm for 30 min; (e) further irradiation of (b) at 355 nm for 30 min; (f) further irradiation of (e) at 632.8 nm for 1.5 h.

Fig. 1(b)–(d) show absorption spectra obtained for the matrix samples irradiated at 632.8, 355 and 266 nm, respectively. After 632.8 nm laser irradiation, the absorption bands due to sym-N_2O_3 are enhanced obviously as the intensities of the bands attributed to asym-N_2O_3 diminished (Fig. 1(b)). Under 355 nm irradiation of the deposited sample, the *trans–cis* N_2O_3 increases significantly in intensities while bands due to asym-N_2O_3 decrease (Fig. 1(c)). From Fig. 1(d) absorptions of both sym- and *trans–cis* N_2O_3 increase at the expense of asym-N_2O_3 with 266 nm irradiation. These results obviously imply that asym-N_2O_3 is converted into sym-N_2O_3 or *trans–cis* N_2O_3 under irradiation at different wavelength. Fig. 1(e) shows the infrared absorption spectra obtained after sym-N_2O_3 matrix sample (Fig. 1(b)) irradiated with a 355 nm laser. The absorption bands due to sym-N_2O_3 are reduced significantly after

Table 1
Observed infrared frequencies[a] for some N_xO_y in an Ar matrix

This work	Literature data	Ar matrix	Assignment
1871.8 m	1868.5[b]	1872[d]	NO
1863.4 s	1859.1		*cis*-$(NO)_2$
1831.5 vs	1830.0	1830	asym-N_2O_3
1776.4 s	1773.3		*cis*-$(NO)_2$
1704.2 w			*trans–cis* N_2O_3
1688.5 s	1685.9	1689	sym-N_2O_3
1666.3 s	1663.4[c]		*trans–cis* N_2O_3
1630.1 s	1630.0	1631	asym-N_2O_3
1610.8			NO_2
1296.4 s	1298.0	1297	asym-N_2O_3
970.1 vw	968.4		sym-N_2O_3
882.3 vw	878.9[c]	873[e]	*trans–cis* N_2O_3
863.6 w		864[e]	*trans–cis* N_2O_3
769.5 m	769.2	771	asym-N_2O_3
717.4 w			sym-N_2O_3

s=strong, m=medium, w=weak, v=very.
[a] All frequencies are given in cm^{-1}.
[b] Ref. [12].
[c] Observed but not assigned in [12].
[d] Ref. [13].
[e] Observed but assigned to precursor N_2O_4.

irradiation, whereas the bands of *trans–cis* N_2O_3 are enhanced. It was also noted that with 632.8 or 266 nm irradiation no obvious changes occur for sym-N_2O_3 matrix sample. However, after further irradiation of this sample at 632.8 nm, bands for *trans–cis* N_2O_3 (Fig. 1(e)) become less intense whereas peaks for sym-N_2O_3 are observable (see Fig. 1(f)). These results indicate that sym-N_2O_3 is converted into *trans–cis* N_2O_3 by 355 nm laser irradiation and reversible reaction is induced under 632.8 nm irradiation.

Compared Fig. 1(a) and (b), the intensities of *trans–cis* N_2O_3 are almost unchanged after 632.8 nm irradiation; however, the isomerization from *trans–cis* to sym-N_2O_3 occurs upon 632.8 nm irradiation (Fig. 1(f)). Compared Fig. 1(a) and (c), after 355 nm irradiation sym-N_2O_3 is not diminished completely although 355 nm could induce the conversion from sym- to *trans–cis* N_2O_3. It is noted from our experiment that after 1.5 h (at 632.8 nm) or 30 min (355 or 266 nm) irradiation the intensities of three isomers reach their minima and nearly unchanged afterwards as the irradiation time is prolonged. It seams that there are thermal equilibrium existed among three isomers in photoisomerization process.

3.2. *Theoretical calculations*

Up to now, the characters of electronic spectrum of N_2O_3 isomers are not available, so we try to examine the electronic spectra for each of the isomers theoretically. Due to inhomogeneous, "site" effects, homogeneous lifetime and phonon broadening in matrix isolated condition, it is very difficult to theoretically calculate the electronically excited states for three N_2O_3 isomers in an Ar matrix. Here we only examine the vertical electronic excitation energy for each "isolated" isomer theoretically. Configuration interaction with all singlet excited determinations, CIS, has been shown to be an effective method of surveying the excited states of closed-shell molecules with reasonable experience for polyatomic molecules [14]. Molecular orbital calculations have been carried out using Gaussian 94 program. All equilibrium geometries are fully optimized to better than 0.0001 Å for bond distances and 0.01° for bond angles. B3LYP (Becke's nonlocal three-parameter exchange with Lee–Yang–Parr correlation functional) [15] density functional methods are used with the 6-311G(d) and larger cc-PVDZ basis sets. For estimating the vertical energies of low-lying excited electronic states, configuration interaction with single excitation from an RHF reference determinant (CI-singles, CIS method [14]) is used with the 6-311++G(2df,2pd) basis set using B3LYP/cc-PVDZ geometries.

The optimized structural parameters of three isomers are presented in Fig. 2. For asym-N_2O_3, the calculation results, especially with larger basis set (cc-PVDZ), satisfactorily reproduce the experimental structural features. At the B3LYP/6-311G* level the N–N and N–O lengths are 0.094 and 0.013–0.037 Å, respectively, longer than those obtained from the experiment [16]. With the cc-PVDZ basis sets the discrepancy of N–N and NO lengths are reduced to 0.022 and 0.002–0.02 Å, respectively. The discrepancy between the theoretical and experimental bond angles ranges from 0.2° to 3° at the B3LYP/6-311G* level; however, it is decreased to about 0.4–2.1° by using cc-PVDZ basis set. Thus, it seams that the calculated parameters approach experimental values as the basis set becomes complete. Although the experimental structural parameters of sym-N_2O_3 and *trans–cis* N_2O_3 are not available, it is reasonable to expect that the B3LYP/cc-PVDZ calculations could reproduce the structures satisfactorily. We predicted that three conformers, the asym-, sym-, and *trans–cis* N_2O_3 are stable, with the total energies of the sym- and *trans–cis* conformers lying approximately 3.4 and 5.7 Kcal/mol above that of the asym-N_2O_3, respectively. This result is consistent with our experimental observation, in which the asym-N_2O_3 is found to be more stable than the sym- and *trans–cis* N_2O_3 and the latter two conformers can only be stabilized in an argon matrix at sufficient low temperature.

The CIS vertical excitation energies (ΔE) and oscillator strengths (F) for N_2O_3 isomers, based on the B3LYP/cc-PVDZ structural parameters, are presented in Table 2. For asym-N_2O_3 the first excited state located at 491.1 nm has a 0.0004 relative oscillator strength and the second excited state at 259.1 nm has a greater relative oscillator strength (0.0008). The first and second excited states of sym-N_2O_3 are located closely at 346.3 and 341.5 nm, respectively; however, the first state has greater oscillator strength (F=0.005) than second excited state (F=0.0). For *trans–cis* N_2O_3 the first excited state (376.6 nm) has greater oscillator strength (0.0045), but the second excited state at 329.2 nm has zero oscillator strength and should be very

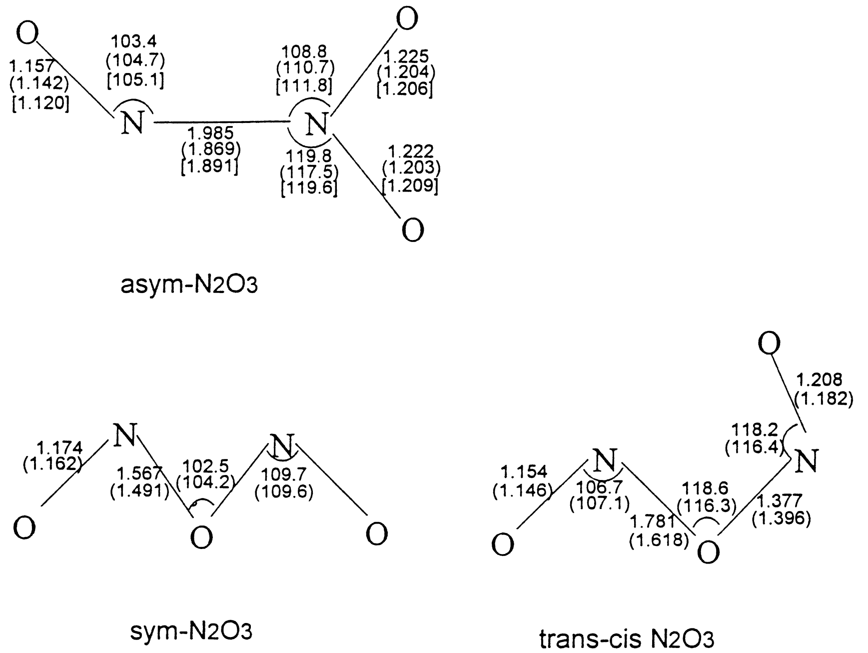

Fig. 2. Geometries of isomers of N_2O_3 calculated at B3LYP/6-311G* level; results obtained using cc-PVDZ basis set are indicated in parentheses and experimental data are given in square brackets.

Table 2

Calculated vertical excitation energies (ΔE) and oscillator strengths (F) for three N_2O_3 isomers[a]

Species	State 1		State 2		State 3	
	ΔE (nm)	F (rel)	ΔE (nm)	F (rel)	ΔE (nm)	F (rel)
asym-N_2O_3	491.1	0.0004	259.1	0.0008	216.6	0.0
sym-N_2O_3	346.3	0.005	341.5	0.0	156.0	0.0026
trans–cis N_2O_3	376.6	0.0045	329.2	0.0	165.2	0.1535

[a] Using B3LYP/cc-PVDZ structural parameters.

weak. The third excited state for *trans–cis* N_2O_3 located at 165.2 nm appears to have a very strong oscillator strength (F=0.1535).

3.3. Discussion

In the vapor phase asym-N_2O_3 is expected to be thermodynamically more stable than sym-N_2O_3 and *trans–cis* N_2O_3, based on the fact that the infrared spectra of N_2O_3 vapors show only the presence of asymmetric isomer. In the matrix case, asym-N_2O_3 is also preferentially produced. The asym-N_2O_3 molecule is well described as a nitric oxide molecule weakly linked to a nitrogen dioxide molecule with a very weak N–N bond. The bond dissociation energy for N–N bond was found to be 9.7 kcal/mol [17] which is more less than the photon energy at visible and ultraviolet region. Other two isomers also have a weak N–O bond [9]. It is reasonable to suggest that the primary step in the photochemical process of N_2O_3 is the absorption of a photon to form an electronically excited state

$$N_2O_3 \rightarrow N_2O_3^* \tag{1}$$

Two possible channels followed by the photoexcitation have to be considered. One is the excited N_2O_3 dissociate to NO and NO_2 fragments, i.e.

$$N_2O_3^* \rightarrow NO + NO_2 \tag{2}$$

then, cage recombination of NO and NO_2 in low temperature matrix could occur to produce the stable conformers of asym-N_2O_3. The other channel is that the electronically excited molecules of $N_2O_3^*$ lead to change its symmetry and induce the intramolecular rearrangement to form another conformer of N_2O_3.

From our theoretical results, the first excited state for asym-N_2O_3 is located at the visible range (491.1 nm). So these N_2O_3 isomers can be photoexcited or photodissociated by visible photon irradiation, then the excited $N_2O_3^*$ or its photofragments of NO and NO_2 preferably rearrange or recombine to form sym-N_2O_3. Since sym-N_2O_3 does not absorb visible photons, the N_2O_3 molecules become "trapped" in this configuration. Nour et al. [7] found that with irradiation in 568.2–752.6 nm region asym-N_2O_3 could be converted to sym-N_2O_3. This result suggested that absorption bands of asym-N_2O_3 at visible region are very

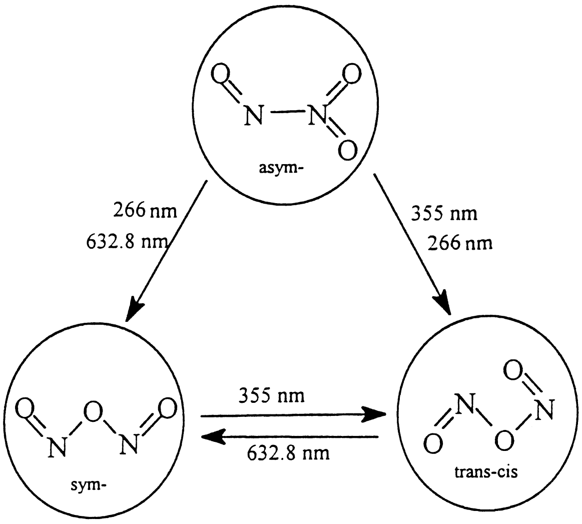

Fig. 3. Formation pathways of N_2O_3 in various conformers.

broad. Theoretically the first excited state of *trans–cis* N_2O_3 is very close to the visible region. The broad absorption is also estimated and 632.8 nm irradiation is possibly matched to absorption shoulders of *trans–cis* N_2O_3. This predication is in agreement to our experimental result we presented above.

Based on the theoretical estimation, it should be noted that the second excited state of asym-N_2O_3 is located at ultraviolet region (259.1 nm) while the first excited state of sym-N_2O_3 is located at 346.3 nm with great oscillator strength. Although the second excited state of *trans–cis* N_2O_3 is located in this region, the oscillator strengths are very weak (F=0.0). This theoretical prediction shows that both asym- and sym-N_2O_3 can be converted into *trans–cis* isomer under 355 nm irradiation. Additionally, asym-N_2O_3 can absorb laser photon with 266 nm irradiation and can be interconverted into sym-N_2O_3 and *trans–cis* N_2O_3 in an Ar matrix because of no transition located around 266 nm for sym-N_2O_3.

It is noted that thermal equilibrium exists among three isomers. As electronically excited state is formed after absorption of photon, the thermal relaxation in matrix cage also occurs [18,19]. There may be a local heating of the lattice immediately surrounding N_2O_3. Such a local heating will occasionally allow the matrix environment to relax sufficiently to permit thermal equilibrium among three isomers.

According to our experimental measurement and theoretical prediction, the photo-induced isomerization processes for N_2O_3 isomers can be summarized by an isomerization cycle as shown in Fig. 3. From this isomerization cycle, it is reasonable to conclude that upon irradiation at 355 nm the *trans–cis* N_2O_3 can be produced via two photochemical channels started from asym-N_2O_3 and sym-N_2O_3, respectively. The sym-N_2O_3 can be produced by photoisomerization of asym-N_2O_3 with 632.8 nm irradiation; it can further be converted into *trans–cis* N_2O_3 with the irradiation at 355 nm. The least stable *trans–cis* N_2O_3 can exist under 355 nm photon irradiation due to its weak absorbance at this region.

4. Conclusion

Laser irradiation of NO and NO_2 mixture at different wavelength in an argon matrix results in a series of photochemical reactions leading to produce three different conformers of N_2O_3, i.e. asym-, sym-, and *trans–cis* N_2O_3. The changes of the absorption bands in the IR spectra of these isomers observed before and after laser irradiation show that the asymmetric conformer of N_2O_3 can be converted into the symmetric form under 632.8 nm irradiation, or converted into *trans–cis* N_2O_3 under 355 or 266 nm irradiation. By 355 nm irradiation the sym-N_2O_3 can also be converted to *trans–cis* form, and back again to sym-N_2O_3 upon photoisomerization with 632.8 nm irradiation. With the CIS method, the vertical energies of excited states of three isomers are investigated. Based on the calculated electronic spectra of three N_2O_3 isomers it is reasonable to explain that the photochemical reactions between three isomers are carried out by selective laser induced reaction at different wavelength.

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