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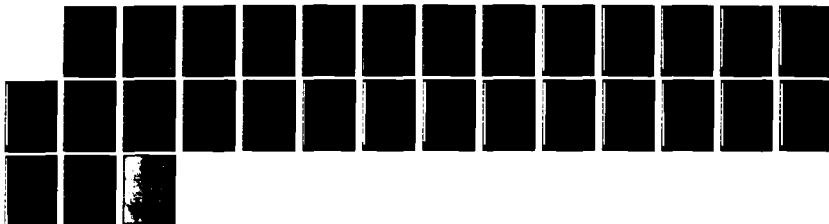
UNIMOLECULAR REACTIONS OF NITRITES AND NITRATES(U)
UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES
C MITTIG ET AL. 01 APR 83 N00014-80-C-0539

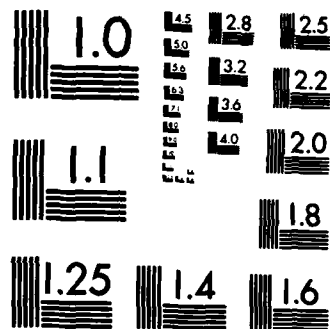
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM						
1. REPORT NUMBER	2. GOVT ACCESSION NO. A127825	3. RECIPIENT'S CATALOG NUMBER						
4. TITLE (and Subtitle) UNIMOLECULAR REACTIONS OF NITRITES AND NITRATES		5. TYPE OF REPORT & PERIOD COVERED Annual Report 4/1/82 - 3/31/83						
7. AUTHOR(s) Curt Wittig, Hanna Reisler		6. PERFORMING ORG. REPORT NUMBER						
8. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California Los Angeles, CA 90089		9. CONTRACT OR GRANT NUMBER(s) N00014-80-0539						
11. CONTROLLING OFFICE NAME AND ADDRESS Dr. Richard Miller, Office of Naval Research Code 432, 800 N. Quincy Street Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS						
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE April 1, 1983						
		13. NUMBER OF PAGES 27						
		15. SECURITY CLASS (of this report) Unclassified						
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE						
16. DISTRIBUTION STATEMENT (of this Report) Unlimited								
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)								
18. SUPPLEMENTARY NOTES								
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <table border="0"> <tr> <td>Alkyl nitrites</td> <td>methyl nitrite</td> </tr> <tr> <td>laser chemistry</td> <td>ethyl nitrite</td> </tr> <tr> <td>unimolecular reaction</td> <td>isopropyl nitrite</td> </tr> </table>			Alkyl nitrites	methyl nitrite	laser chemistry	ethyl nitrite	unimolecular reaction	isopropyl nitrite
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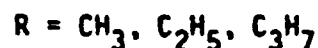
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ABSTRACT

Photodissociation of CH_3ONO , $\text{C}_2\text{H}_5\text{ONO}$, and $\text{C}_3\text{H}_7\text{ONO}$ have been studied using multiphoton ionization (MPI) to detect the NO fragment. Each of these molecules was dissociated by one photon (382-383 nm) and the fragment $\text{NO}(\text{X}^2\Pi)$ was excited and ionized in a subsequent (2+1) photon process. All events occurred within the same laser pulse duration (~ 7 ns), thus ensuring collision-free conditions. The MPI spectrum of NO was analyzed for rotational state distributions. When compared to a room temperature spectrum of NO at 300 K, the extent of NO rotational excitation observed in CH_3ONO was very large, ($E_{\text{rot}} > 2100 \text{ cm}^{-1}$) and the distribution of NO was found to be non-thermal. $\text{C}_2\text{H}_5\text{ONO}$ and $\text{C}_3\text{H}_7\text{ONO}$ on the other hand, produced NO fragments which displayed a Boltzmann behavior and could be characterized by $T_{\text{rot}} = 350 \text{ K}$ and 250 K respectively.



PHOTODISSOCIATION OF ALKYL NITRITES (RONO)

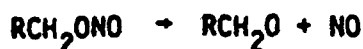


A. Introduction

Considerable attention has been paid to both pyrolysis and photolysis of alkyl nitrites. Most of the efforts have been directed toward the determination of the primary step in the unimolecular decomposition of these nitrites. A number of investigations have confirmed that the primary step in both decomposition routes is the production of nitric oxide and the alkoxyl radical.



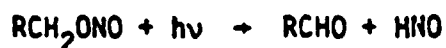
The following is a survey of relevant literature of the dissociation of alkyl nitrites. The earliest work reported was by Steacie and Shaw [59], who investigated the kinetics of CH_3ONO decomposition. This was followed by a similar study on $\text{C}_2\text{H}_5\text{ONO}$ [60]. The conclusion drawn by these authors were that both reactions were simple unimolecular changes, involving splitting of the RO-NO bond. Activation energies for both reactions were found to be ~ 37 kcal. The main product detected was NO along with the corresponding alcohol and aldehyde. To account for formation of these products a free radical mechanism was proposed by Rice and Rodowskas [61]:



However, by studying the decomposition of $\text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$ in presence of NO and $\text{C}_2\text{H}_5\text{ONO}$, Levy [62] proved that no decomposition of $\text{C}_2\text{H}_5\text{ONO}$ occurred in the presence of $\text{C}_2\text{H}_5\text{O}$ and so proposed a different route to account for the formation of alcohol and aldehyde in Steacie's experiments.



Absorption spectra of methyl and ethyl nitrite were obtained by Thompson and Purkis [63,64]. Banded absorption was seen for both compounds in the region 3000-4000 Å. They proposed the following mechanism:



The existence of rotational isomerization in alkyl nitrites was first suggested by Tarte [65]. He found the IR and UV spectra of these molecules to consist of two systems of diffuse bands whose relative intensities varied as the relative abundances of the two rotational isomers. The relative intensities of these doublets were found to be temperature dependent.

A quantitative estimate of the barrier to free rotation was given by Gray and Pratt [66]. These authors used the thermodynamic functions of CH_3ONO to measure the height of the barrier (7800 cal mole⁻¹). Primary nitrites were found to contain appreciable amounts of cis and trans, the cis form predominating at room temperature;

secondary largely as trans; and tertiary were found to exist exclusively as trans. For CH_3ONO in the gas phase the ratio was ~ 1 at room temperature. The mean value of ΔH for the isomerization cis \rightarrow trans was $130 \text{ cal mole}^{-1}$.

Photolysis of CH_3ONO in the region $2400\text{-}3600 \text{ \AA}$ was studied in an argon matrix at 20°K by Brown and Pimentel [67]. Primary products of photolysis under these conditions were found to be HCHO and HNO. HNO was identified by its IR spectrum and confirmed by bandshifts occurring upon deuteration. The question once again was the mechanism of dissociation. There was a controversy over which of the following was the primary process:



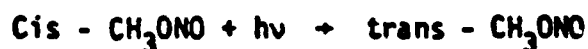
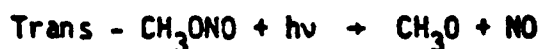
or



Detection of HCHO and HNO did not eliminate the latter reaction because equation (2) could be followed by an abstraction reaction:

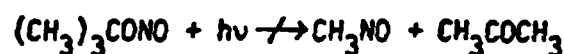


Based upon changes in intensities during the photolysis, the authors suggested that the cis form is lost more rapidly than the trans.

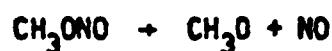


However, interpretation of further photolysis experiments by other workers showed decomposition to $\text{RO} + \text{NO}$ to be the primary process. Hanst and Calvert [68] confirmed that CH_3ONO dissociates

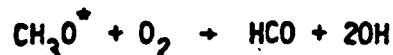
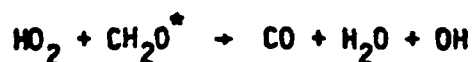
to $\text{CH}_3\text{O} + \text{NO}$ and not $\text{CH}_3 + \text{NO}_2$ or $\text{CH}_3 + \text{NO} + \text{O}$. To choose between these alternative dissociating pathways, they spectroscopically (IR) analyzed the products obtained when CH_3ONO was photolyzed in the presence and absence of O_2 and in the presence of excess NO . A similar conclusion was drawn by Kabasakalian and Townley [69] from photolysis of octyl nitrite. McMillan [70] studied the photolysis of t-butyl nitrite at 3660 \AA . Results indicated the primary process to be dissociation to $\text{t-BuO} + \text{NO}$ with a probable quantum yield of unity. A further study of McMillan, Calvert and Thomas [71] determined that CH_3NO which is formed as product occurs due to combination of $\text{CH}_3 + \text{NO}$ and not as a primary step:



An important experiment was that of McGarvey and McGrath [72] where a series of alkyl nitrites were studied using flash photolysis. During photolysis of CH_3ONO in the vacuum ultraviolet ($3600\text{-}1600 \text{ \AA}$) a new absorption spectrum with three diffuse bands at 2064, 2036, and 1994 \AA was observed. The spectrum was assigned to $\text{CH}_3\text{O}\cdot$ which was indicative of the initial breakdown as being:



With higher nitrites no OR was detected. It was also observed that in presence of O_2 only those nitrites with $-\text{CH}_2\text{ONO}$ reacted with O_2 to produce OH which was detected 50 μs after the flash. Both with and without O_2 , extremely rapid rise ($<50 \mu\text{s}$) of NO absorption was also observed. To account for production of OH the following mechanism was proposed:



It was also observed by Napier and Norrish [73] that the isothermal flash photolysis of CH_3ONO at 2000-2500 Å led to production of NO in its ground and vibrationally excited states. The spectrum of nitroxyl (HNO) was also observed and was greatly enhanced by addition of NO. With an excess energy of ~77 kcal, the appearance of (0,1) bands of γ ($A^2\Sigma^+ - X^2\Pi$), δ ($C^2\Pi - X^2\Pi$), ϵ ($D^2\Sigma^+ - X^2\Pi$) systems of NO with maximum intensity at short delays was found to be consistent with the reaction:

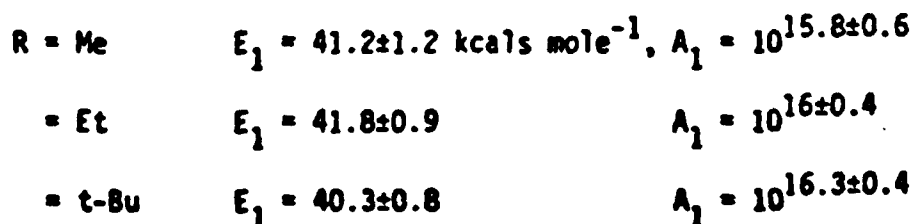


Dependence of HNO intensity on NO pressure indicated that it is formed by the abstraction reaction,



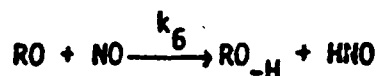
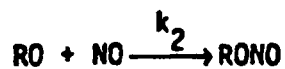
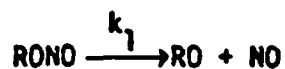
and not by direct molecular elimination.

A series of kinetic studies have been reported by Batt and Milne [74-76]. Arrhenius parameters were obtained for thermal decompositions of CH_3ONO , $\text{C}_2\text{H}_5\text{ONO}$, and $t\text{-C}_4\text{H}_9\text{ONO}$.



A further study by the same authors [77] was on the mechanism of HNO formation. They verified the mechanism as being the one

originally proposed by Levy,



and not by direct elimination: $\text{RONO} \xrightarrow{k_5} \text{RO-H} + \text{HNO}$. Arrhenius parameters were obtained from the experimentally measured rate constant k_{exp} for HNO production. These values were found to compare well with Arrhenius parameters predicted for the global rate constant $k_g = (k_1 k_6) / (k_2 + k_6)$. This verified that HNO was indeed produced by Levy's mechanism.

Emission from CH_3O , $\text{C}_2\text{H}_5\text{O}$, and $i\text{-C}_3\text{H}_7\text{O}$ radicals were observed in the photolysis of these nitrites between wavelengths of 2000 and 1100 Å, by Ohbayashi, Akimoto and Tanaka [78]. Emission was assigned to the ($A^2A_1 - X^2E$) transition of CH_3O^* . Bands of NO were also observed and based on these observations, the photodissociation process responsible for these spectra was assumed to be



Johnson et al. [79] observed fluorescence from electronically excited NO produced in the photolysis of $\text{C}_2\text{H}_5\text{ONO}$ at 123 and 147 nm. Emission was observed from ($v'=1-3$) of $A^2\Sigma^+$ state. There were no evidence of fluorescence from any $v' > 3$.

Photolysis of methyl nitrite has also been studied in the infrared. The first report of IR MPD of methyl nitrite was that of Hartford [80]. The focused output of CO_2 TEA laser was used to irradiate CH_3ONO . Time resolved IR emission was observed between

3.54 and 3.99 μm and was attributed to vibrationally excited CH_2O . This was confirmed by using the deuterated compound and observing D_2CO . It was concluded that CH_2O was formed in the exothermic disproportionation of the initially formed CH_3O . Another finding was that both cis and trans isomers yielded the same products and in the same proportion which suggests that the initial photodissociation step is unaffected by geometric conformation.

The most recent study on CH_3ONO has been that of Lahmani et al. [81,82]. Using synchrotron radiation as the source of excitation ($\lambda = 1100\text{-}1600 \text{ \AA}$), the fluorescence of photofragments from dissociation of CH_3ONO was measured. Electronically excited NO was observed, $\text{NO } A^2\Sigma^+ (v'=0,1,2)$ and also $C^2\Pi (v'=0)$ and $D^2\Sigma (v'=0)$. Quantum yields for NO production in these states were measured and energy disposal between CH_3O and NO fragments was explained in terms of statistical behavior with some restrictions on choice of CH_3O modes. In this paper it was pointed out that there is an exact agreement between thermochemical dissociation and the experimental ones which was indicative of predissociation rather than a direct photodissociation.

In summary then, it can be said that both kinetic and spectroscopic techniques have been applied by many researchers to prove that the primary decomposition step of alkyl nitrites is the production of NO and the corresponding alkoxy radical. Irradiation of these nitrites has been carried out at short wavelengths ($\lambda = 2000\text{-}1100 \text{ \AA}$) and this has been found to produce both electronically excited NO and the corresponding excited alkoxy radical.

In our previous work [42], we had undertaken the study of NO_2 by multiphoton ionization. One photon (382 nm) was required to dissociate NO_2 , two additional photons of the same wavelength to excite NO from its ground electronic state $X^2\Pi$ to an excited state $C^2\Pi$ ($v'=0$) and one more photon to ionize NO. In that experiment it was demonstrated that MPI is an extremely powerful probe of the internal states of the NO molecule. We thought it possible to gain some additional insight into the mechanism of dissociation and consequent energy distribution among the fragments, using the technique of MPI. So we have extended our earlier study to a series of nitrites where the alkyl group shows increasing complexity.

B. Results and Discussion

The O_{12} , NO spectra for the three different alkyl nitrites are shown in Figure 13 and the fittings are summarized below:

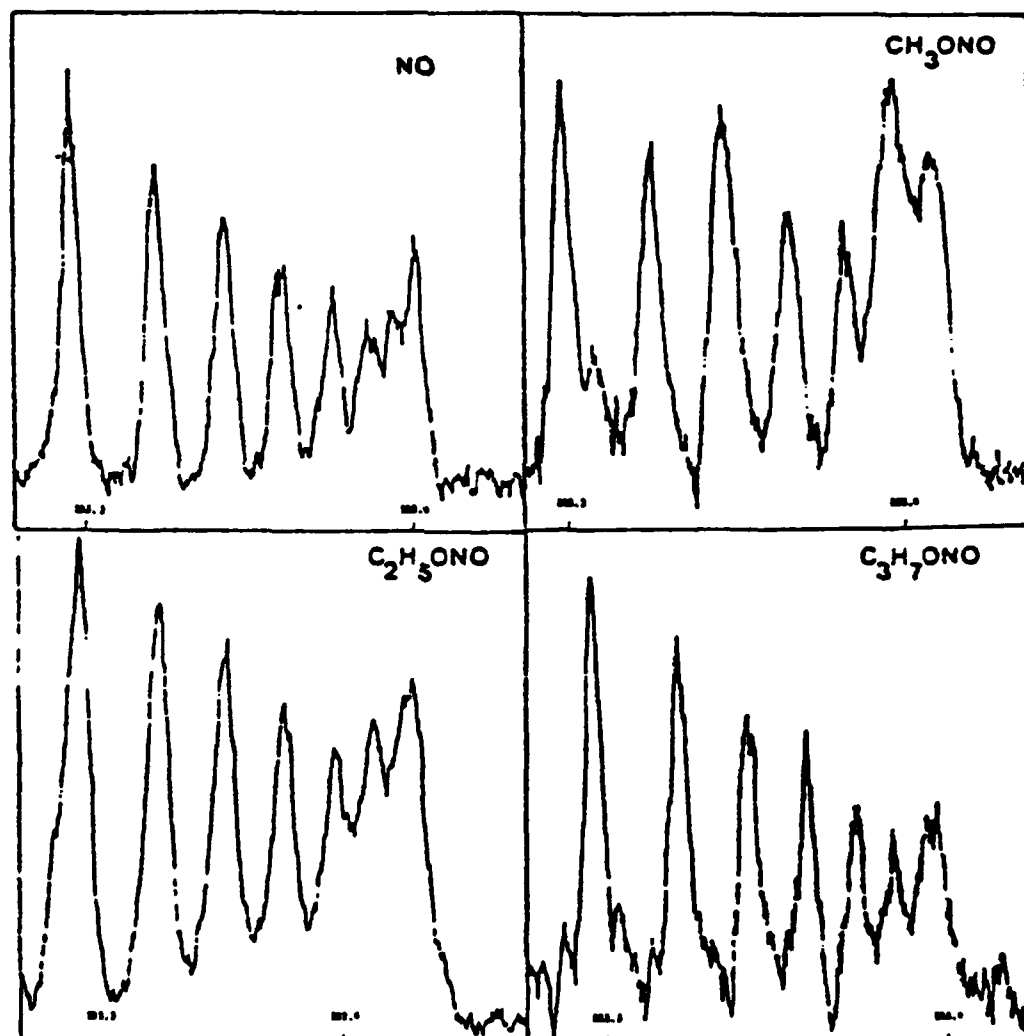
CH_3ONO : Distribution non-thermal	$T_{\text{rot}} > 3000^\circ\text{K} \pm 300^\circ\text{K}$
$\text{C}_2\text{H}_5\text{ONO}$: Distribution thermal	$T_{\text{rot}} = 350^\circ\text{K} \pm 35^\circ\text{K}$
$\text{C}_3\text{H}_7\text{ONO}$: Distribution thermal	$T_{\text{rot}} = 250^\circ\text{K} \pm 25^\circ\text{K}$

These results indicate that methyl nitrite is extremely hot rotationally. It is possible that the spectrum is contaminated with some lines from very high J levels of an S_{21} branch of a $\delta(0-1)$ transition. The ethyl and propyl nitrites on the other hand are quite cold rotationally and both molecules display Boltzmann behavior.

The dissociation energies of these nitrites are in the range of 1.81 eV ($\approx 14598 \text{ cm}^{-1}$). In the region of the P_{21} bandhead where

Figure 13. The $\delta(0-0)$ O_{12} spectra of NO and
of NO(ONO) where $R=CH_3$, C_2H_5 , and C_3H_7 .

ION INTENSITY



WAVELENGTH (nm)

the photon energy is 26178 cm^{-1} , this leaves an excess energy of 11895 cm^{-1} . This energy level diagram is shown in Figure 14.

With this dissociation energy, up to $v=6$ of vibrational excitation in NO is possible. However, in the region of the O_{12} branch where photon energies vary between 26088 and 26080 cm^{-1} , the excess energy available to products varies between 11805 and 11797 cm^{-1} .

There are a few alternative suggestions that can be offered to account for this experimentally observed behavior. The UV spectra of these molecules (Figures 15-17) indicate that at 383 nm , methyl nitrite displays only a slight shoulder in its absorption, while this feature becomes more pronounced in ethyl nitrite and in propyl nitrite it is an obviously structured absorption. So it is quite possible that even though we might be exciting the same kind of transition in all three cases namely the $n \rightarrow \pi^*$ band [83], the nature of the potential surfaces of the corresponding excited states are quite different. However, we have no reason to believe a priori that this is indeed the case. One possibility is that a predissociation mechanism exists and is more significant in propyl and ethyl nitrite. Had the dissociation been direct then it would have to occur, within one vibrational period. In such an event, increasing the number of degrees of freedom sequentially in these nitrites would not be expected to show such a drastic fall in the corresponding rotational temperature. Kinematic effects would of course play a role in increasing the fraction of translational energy of the NO fragment as the mass of the alkyl group increases. This would cause a corresponding decrease in the internal energy of

Figure 14. The energy level diagram of RONO showing the excess energy available to products after excitation of RONO in the P_{21} branch.

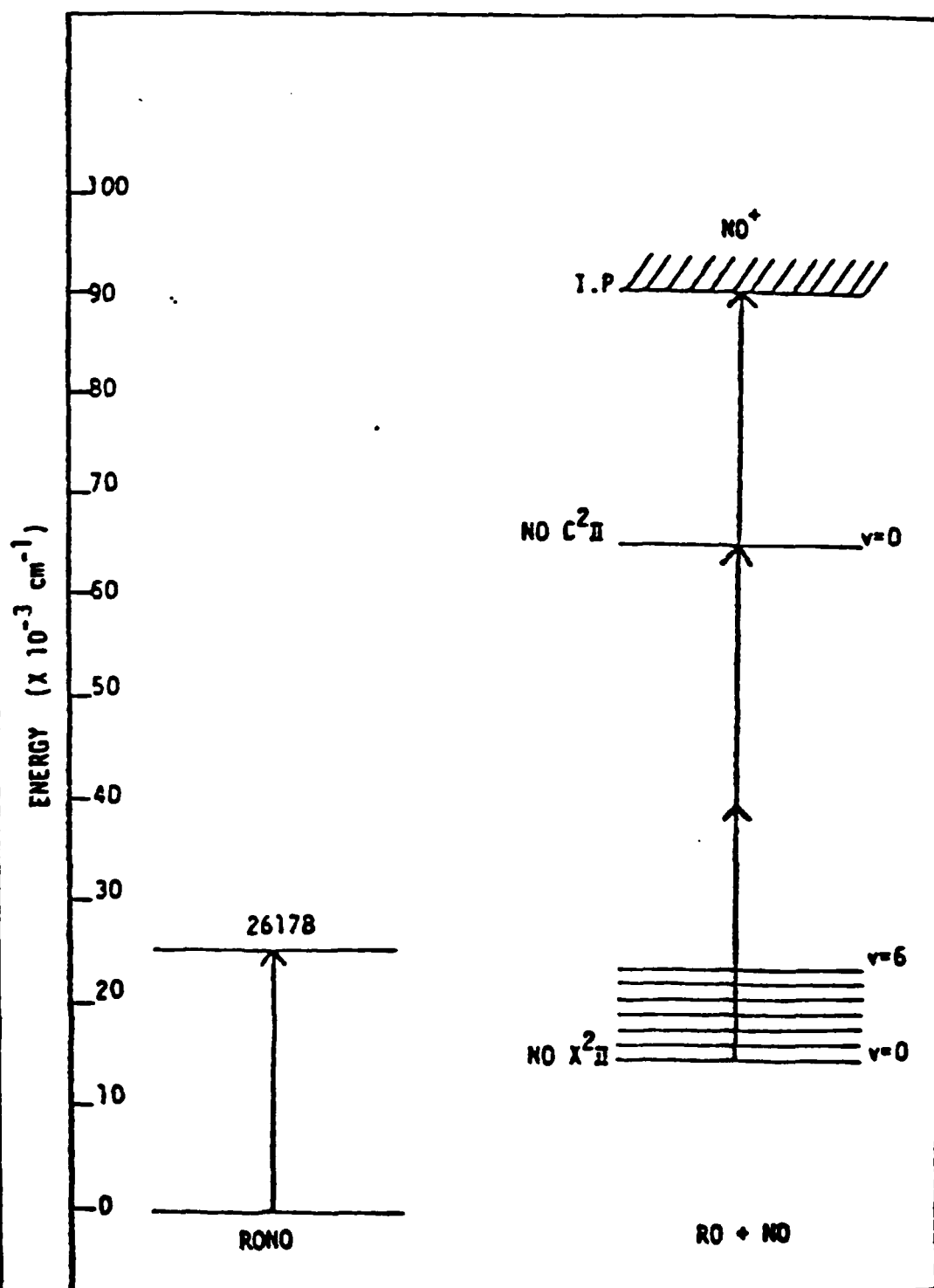


Figure 15. The gas-phase UV absorption spectrum of methyl nitrite. The wavelength corresponding to the O_{12} head (383.4 nm) is indicated.

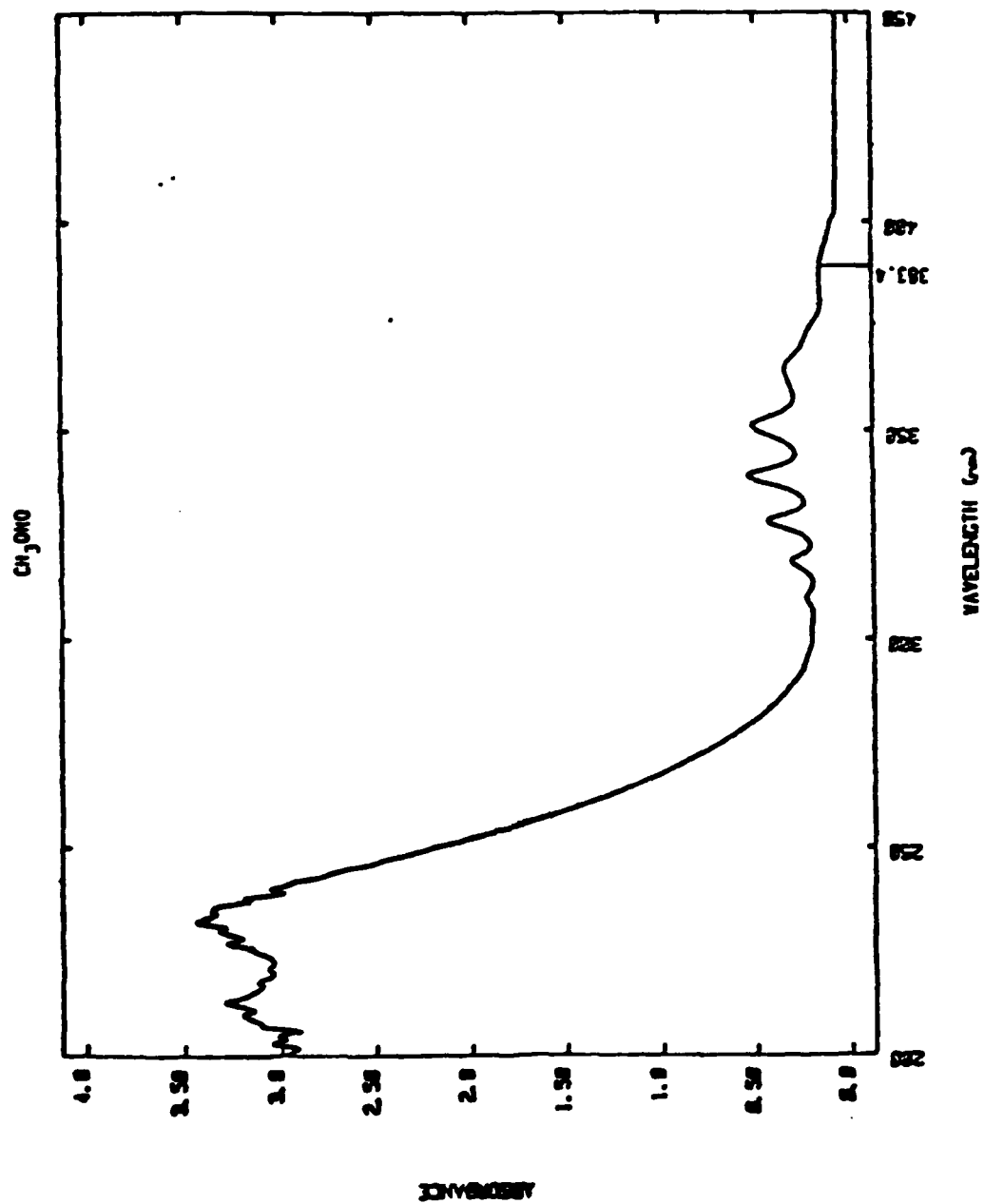


Figure 16. The gas-phase UV absorption spectrum of ethyl nitrite. The wavelength corresponding to the O_{12} head (383.4 nm) is indicated.

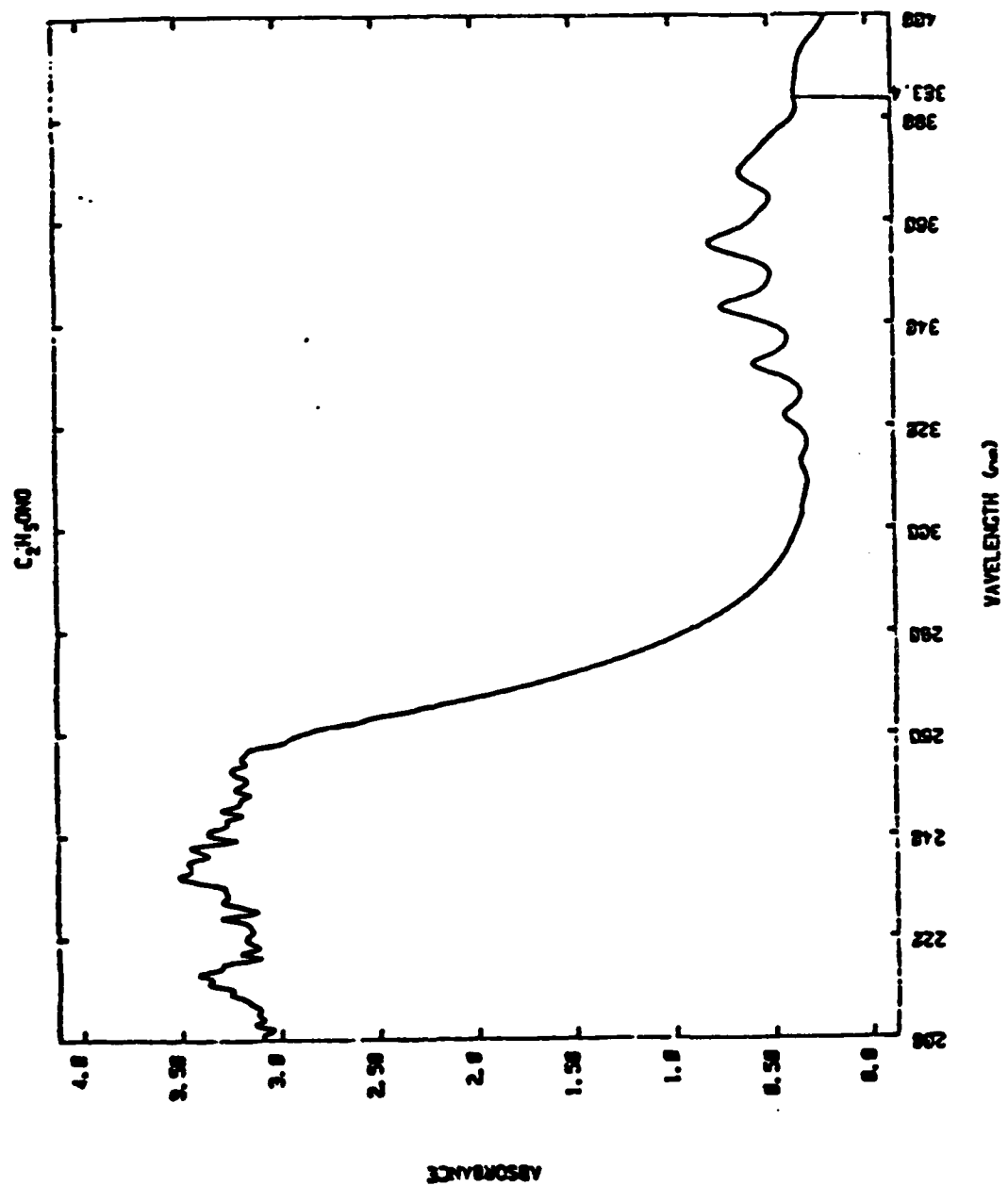
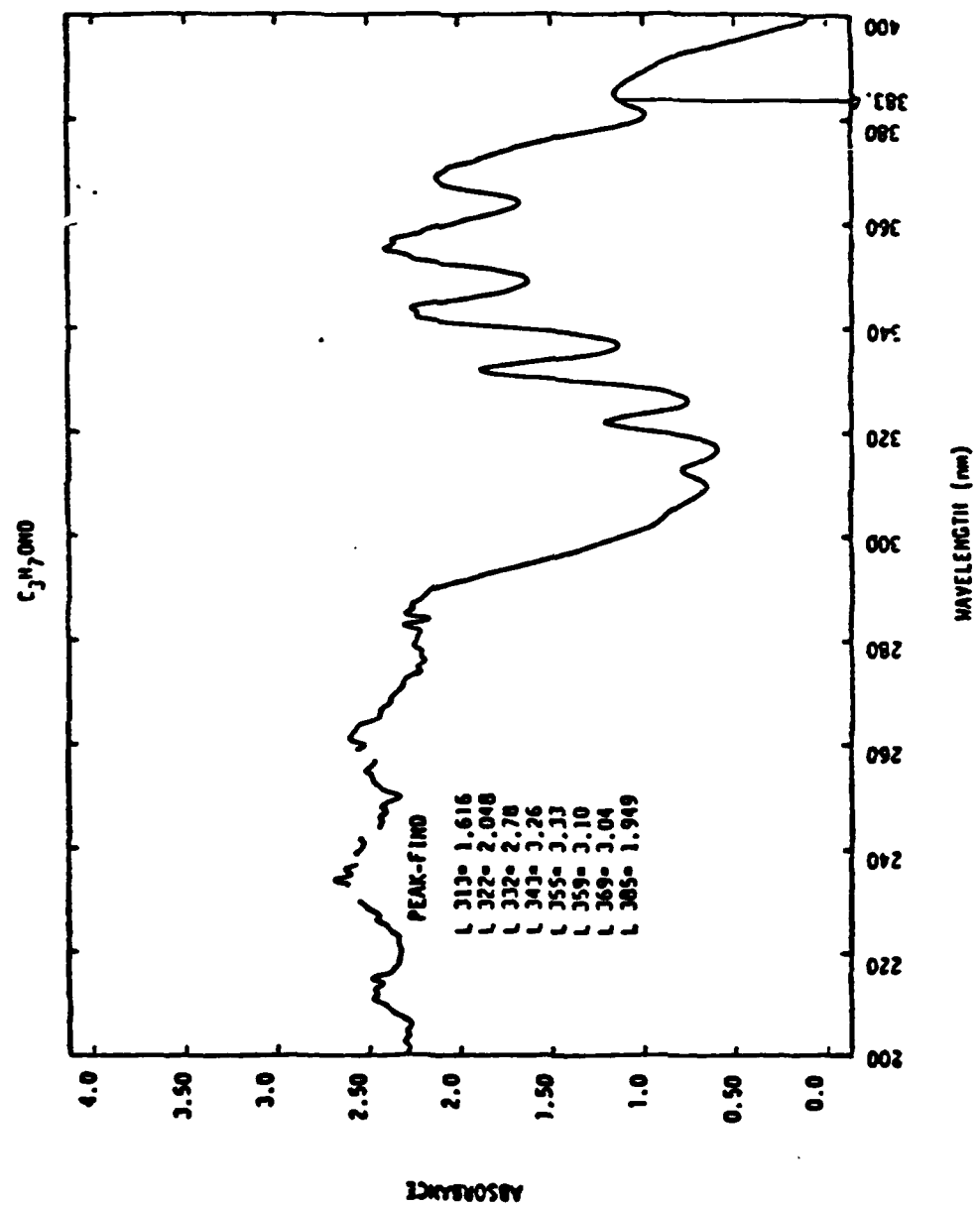


Figure 17. The gas-phase UV absorption spectrum of propyl nitrite. The wavelength corresponding to the O_{12} head (383.4 nm) is indicated.



NO. However, dynamical effects would not be expected to make any contribution unless there was sufficient time (greater than 10^{-13} s) for the energy to randomize. In the event of a predissociation however it is possible that some statistical redistribution of the excess energy occurs because the molecule now has a longer excited state lifetime than if it underwent direct dissociation. Such a mechanism would be consistent with the decreasing trend of T_{rot} from ethyl nitrite to propyl nitrite because the number of degrees of freedom in this case increases from 30 to 39, thereby decreasing the energy per degree of freedom in these molecules.

Alternatively it is possible that a direct decay mechanism exists but there are two or more different excited states that could be competing in the dissociation. If methyl nitrite dissociated from a highly bent state and ethyl and propyl nitrite from excited states that were linear, then one would expect a rotationally hot NO fragment to be produced from CH_3ONO but rotationally very cool NO fragments dissociating from $\text{C}_2\text{H}_5\text{ONO}$ and $\text{C}_3\text{H}_7\text{ONO}$. However all three nitrites were excited in the same range of wavelengths, so if the transitions in all three instances were the same then there isn't sufficient evidence to prove that geometries of the respective electronically excited states in these nitrites differ very significantly from each other.

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