$\hat{\mathbf{E}}\text{-}\mu\text{-}\mathbf{v}$ CORRELATION IN ONE-COLOUR PHOTOLYSIS/IONIZATION OF TERT-BUTYL NITRITE

P. MARCUS,[†] I. PLATZNER,[†] I. BAR[‡] and S. ROSENWAKS[‡]

[†] *Nuclear Research Center-Negev, Division of Chemistry, Beer-Sheva 84190, Israel*

[‡] *Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel*

(Received 23 June 1989; in final form 21 August 1989)

An anisotropic spatial velocity distribution was observed for NO⁺ produced following one-color photolysis/ionization of tert-butyl nitrite (TBN) by a pulsed polarized laser at 266, 355 and 532 nm in a time-of-flight mass spectrometer. The dependence of the NO⁺ fragment mass peak profile on the wavelength and on the polarization was monitored. The most striking feature is the varying fragment peak splitting obtained under the same experimental conditions by changing the laser polarization direction. This phenomenon is a result of the vector correlation between the laser polarization, $\hat{\mathbf{E}}$, at a given wavelength, the electronic transition dipole moment of TBN, μ , and the direction of the NO fragment velocity, $\mathbf{v}$. The dynamics of the photodissociation process and, in particular, its directional properties are discussed in view of these results.

KEY WORDS: $\hat{\mathbf{E}}\text{-}\mu\text{-}\mathbf{v}$ correlation, one-colour photolysis/ionization, t-butyl nitrite.

INTRODUCTION

A growing number of papers have discussed vector correlations in the elucidation of the dynamics of photodissociation.^{1,2} The first workshop on the dynamic aspects of stereochemistry³ points to an increasing interest in this field. The measurement of vector correlations provides essential information on dynamics of chemical reactions and other collisional phenomena.

Photofragment spectroscopy with mass spectrometric detection has the advantage of not being restricted to small photofragments with accurately known spectroscopic properties as laser induced fluorescence (LIF) requires. The spectra and angular distribution of the photofragments obtained by a time-of-flight mass spectrometer (TOFMS) allow the extraction of the translational energy distribution and anisotropy parameters in a straightforward way.^{4–10} The applications of TOFMS may be instrumental in verifying and complementing the results obtained by the LIF method.^{6–8}

In a TOFMS any initial ion velocity and spatial distribution of the ions in the mass spectrometer source will be reflected in the ion peak profile recorded, unless a compensation method like “time delay”¹¹ or “reflectron technique”¹² is used. In

other words, an anisotropy in the initial velocity and spatial distribution of the ions will appear in the TOF spectrum as a distorted peak profile.

A polarized laser beam will interact preferentially with molecules having the electronic transition dipole moment μ aligned parallel to its electric vector $\hat{E}$, as the transition probability is proportional to $|\mu \cdot \hat{E}|^2$. In the molecular frame, the direction of the fragment recoil velocity v nearly always bears a fixed angular relationship to μ . Therefore, if μ is aligned in the laboratory frame by the photolyzing light, v will also be aligned in the laboratory frame, provided that the dissociation takes place rapidly enough so that the alignment of μ is not lost before the moment of fragmentation.²

Nitrous acid (HONO) and its organic esters (RONO) have been the subject of photochemical investigation for a long time^{13,14}. Several detailed studies of methyl nitrite (MN),^{6,8,15–18} ethyl nitrite (EN),^{19,20} and *t*-butyl nitrite (TBN),^{21,22} were performed by different groups. The alkyl nitrite molecules, RONO, have a dissociation threshold energy of ~ 1.7 eV²³ implying that single-photon absorption can induce fragmentation to RO and NO radicals for wavelengths shorter than 730 nm. As in nitrous acid,^{24,25} the near-UV absorption of nitrites consists of a structured band system in the 300–400 nm range [S_1 ($n\pi^*$) $\leftarrow S_0$] and a broad unstructured band centered around 227 nm [S_2 ($\pi\pi^*$) $\leftarrow S_0$]. The photodissociation of TBN has been studied by probing the NO photofragment by single-photon LIF combined with polarization (for the S_1 and S_2 surfaces) and sub-Doppler spectroscopy (for the S_2 surface).²¹ The results of these studies point to different mechanisms for the photodissociation from the two excited states.

Following the LIF study of TBN, we report here on experiments aimed at getting a more complete picture of TBN photodissociation. TOF spectra were measured at dissociation wavelengths of 266, 355 and 532 nm in order to probe the two absorption bands. To study photofragmentation at these wavelengths we used one-color laser for photolysis/ionization and TOF mass-resolved ion detection. TOF mass-spectral peak profile provides direct information on the photofragment angular distribution. The results presented below show that a parallel transition dominates the absorption at 266 and 532 nm and that a perpendicular transition is consistent with absorption at 355 nm.

EXPERIMENTAL

The experimental setup consists of a combination of a laser and a TOFMS (Figure 1). The reaction cell was evacuated by a high speed differential pumping system to a background pressure of 10^{-7} Torr. A gas sample of TBN, or neat NO, was introduced to the cell through a 0.05 mm diameter “gold leaf leak” with molecular flow nearly parallel to the laser beam and perpendicular to the flight of the produced photofragments. The pressure in the reaction cell was maintained during the experiments in the 10^{-6} – 10^{-4} Torr range. The parent molecule was dissociated and the photofragments ionized by the same doubled, tripled or quadrupled Nd:YAG laser pulse (Quanta-Ray, DCR-2); its linear polarization was rotatable using a $\lambda/2$ waveplate. As a test, neat NO was also ionized at the same conditions. The laser

beam was focused into the ionizing region of the TOFMS (through a fused silica window) by a UV-grade lens of 20 cm focal length. The laser energy, as measured before the focusing lens, was 5–85, 0.7–19 and 0.15–6.5 mJ for 532, 355 and 266 nm, respectively. The laser flux at the focal point was calculated to be in the range of 10^9 – 10^{11} Watt/cm². The ions produced by the laser beam were directly sampled by a modified²² Bendix MA-2 TOFMS at 10 Hz repetition rate. The extraction and acceleration voltages were held at ground potentials during the photolysis and for an adjustable time delay, t_d , thereafter. This delay was maintained at a value of 0.1 μ s and during this time the ionized photofragments recoiled with the velocity imparted by the dissociation. After the delay t_d , the ions were extracted out of the ionization region by the application of a fast rise drawout pulse. The ionized photofragments were accelerated into the horizontally mounted drift-tube (100 cm long) toward the detector, where their arrival time was monitored. The arrival time was a sensitive function of the initial ion velocity. Since the ionization was obtained by a focused laser beam in a very small volume, the dependence of the arrival time on the initial fragments' position was negligible. Thus, the ions separated out in time according to their different velocities and their mass spectral peak shape provided information concerning the recoil velocity of photofragments at a particular wavelength to which

Figure 1 Schematic diagram of the photofragment TOFMS apparatus; DPS—Differential pumping system, HV—High vacuum pump, FV—Fore vacuum pump.

the laser was tuned. The ion signal was recorded as a function of arrival time with a fast Biomation 6500 transient digitizer and averaged (for 100–500 laser pulses) with an interfaced MINC-11 computer, yielding a mass spectrum.

The TBN (97%, Aldrich) was purified under vacuum distillation and stored in the dark. The NO (99.0%) was from Matheson.

RESULTS

The photodissociation and photoionization of the resulting photofragments occur within the same laser pulse (6–8 ns). The TOF spectra obtained at the dissociation wavelengths of 266, 355 and 532 nm are presented in Figures 2a–2c. The principal ion peaks in these spectra are: $m/e = 30$ (NO^+), $m/e = 43$ (C_3H_7^+ or CH_3CO^+), $m/e = 15$ (CH_3^+), $m/e = 14$ (CH_2^+), $m/e = 13$ (CH^+) and $m/e = 12$ (C^+). The parent ion has not been observed even at the lowest laser flux. The fragment ions are obtained for all laser energies mentioned above and they are characteristic of the laser wavelength (see Figure 2).

The arrival time distribution of NO^+ , produced by photolysis/ionization of TBN at 266, 355 and 532 nm with light polarized either horizontal or vertical to the drift-tube axis is shown in Figures 3a–3c, respectively. Experiments carried out at 266 and 532 nm with horizontal polarization show a characteristic double peak, while those with vertical polarization show an unsplit peak. At 355 nm the splitting is dependent on the laser flux. At energies of 0.7–3 mJ an opposite behavior (compared to 266 and 532 nm) is observed, i.e. a peak with two maxima is monitored for the vertical polarization, while for the horizontal polarization only one maximum is observed. For energies in the range of 4–19 mJ some splitting is observed also for the horizontal polarization, although the depth of the splitting for the vertical polarization is always larger than for the horizontal polarization under the same experimental conditions. In addition, the NO^+ signal near the center of the distribution for horizontally polarized light approaches the baseline more closely for 266 than for 532 (horizontal polarization) or 355 nm (vertical polarization). Also, at 355 nm (for vertical polarization) the depth of the splitting is not significantly dependent on the laser flux, whereas at 532 nm the depth increases with the flux. For comparison, neat NO gas is ionized and results in unsplit peak at all three wavelengths (Figures 3a–3c). This peak appears exactly at the center of the double peak of the NO photofragmented from TBN.

DISCUSSION

The fragmentation pattern is characteristic of the laser wavelength used for photodissociation and is maintained for all laser fluxes mentioned above. Relying on these findings (especially on the fact that the parent ion is not observed, even at the lowest laser fluxes) and according to the classification carried out in our previous work,²² we assume that the TBN molecule dissociates into two fragments: $\text{NO}\cdot$ and $(\text{CH}_3)_3\text{CO}\cdot$.

Figure 2 TOF spectrum of TBN (horizontal polarization) recorded at 10 ns resolution for (a) 266 nm, 3.5 mJ, 2.2×10^{-5} Torr (b) 355 nm, 5 mJ, 7.5×10^{-6} Torr and (c) 532 nm, 35 mJ, 7.5×10^{-6} Torr. Note that the full splitting at 266 nm is not observable under the present resolution.

The NO is a primary product of the photodissociation and apparently is ionized via a multiphoton ionization process. The other ions are obtained following additional fragmentation of the $(\text{CH}_3)_3\text{CO}\cdot$ radical.²² Detailed analysis of the mass spectra will be published in the future.

The peak profiles at the excitation wavelengths of 266 and 532 nm are similar (Figures 3a, 3c). As stated above, the ions recoil with a velocity determined by the dissociation dynamics. Their arrival time, after the acceleration by the drawout pulse to the detector, is a measure of their initial velocity. For dissociation with horizontal polarization, the profiles indicate that the NO molecules tend to recoil forward and backward along the polarization vector $\hat{E}$ and thus have different velocities relative to the field direction of the TOF leading to their arrival at the detector at different times. For vertical polarization both sets of the NO photofragments have the same

Figure 3 NO⁺ peak profile resulting from photoionization of neat NO and from photolysis/ionization of TBN for H (horizontal) and V (vertical) polarization recorded at 2 ns resolution for (a) 266 nm, 4 mJ, 2×10^{-5} Torr, (b) 355 nm, 2 mJ, 7.5×10^{-6} Torr (the neat NO intensity is reduced by a factor of 2) and (c) 532 nm, 15 mJ, 2×10^{-5} Torr.

velocity relative to the field direction and therefore reach the detector at the same time. The observed distribution is thus consistent with the transition moment, μ , tending to point parallel to the velocity, v .

On the other hand, for the dissociation at 355 nm (0.7–3 mJ) with vertically polarized light (Figure 3b), we conclude that the departure of the NO fragments is predominantly perpendicular to $\hat{E}$, leading to two maxima, while for the horizontal polarization there is no preferential distribution of the fragments along the field direction of the TOF and thus they reach the detector at the same time, leading to an unsplit maximum. This leads us to further conclude that at this wavelength μ is perpendicular to v . At higher energies (≥ 4 mJ) some splitting was obtained also for the horizontal polarization, which may indicate that at high laser fluxes there is a contribution from both parallel and perpendicular transition moments. This point will be specifically discussed later.

Furthermore, comparison of the peak profiles obtained in our experiments to the calculated arrival-time distribution for an ionized photofragment⁹ indicates that the NO fragment is produced in a predominantly parallel transition moment at 266 nm (as well as at 532 nm, see below), while at 355 nm (at low energies) the NO fragment is produced in a perpendicular transition. Also, the calculations of Ref. 9 predict that for perpendicular transition the depth of the splitting is less than that for a parallel transition (note that in Ref. 9 the drift-tube is vertical).

Consequently, the anisotropic distribution in Figures 3a–3c largely reflects the photodissociation channels of TBN at different wavelengths. Photodissociation of TBN at 266 nm takes place through the second absorption band, $S_2 \leftarrow S_0$, via charge transfer from the $(CH_3)_3CO$ donor to the NO acceptor and therefore it has been presumed that the transition moment μ is parallel to the CONO plane.²⁴ The arrival time distribution (Figure 3a) exhibits a characteristic behavior in which the fragment recoils parallel to $\hat{E}$ and implies that μ is aligned along the dissociative RO–NO bond and that v tends to point parallel to μ . Since the ground state of TBN has been assumed to have an A' symmetry²⁴ and the break up of the molecule occurs quickly with respect to rotation,²¹ the correlation of the transition dipole moment μ parallel to the molecular frame reveals the A' symmetry of the S_2 state.

The arrival time distribution produced by photodissociation at 532 nm resembles that produced at 266 nm. Considering the above description, this indicates that the NO photofragment recoils along $\hat{E}$, as would be expected for μ aligned parallel to the molecular frame. Note that the absorption coefficient of TBN at 532 is very small¹³ and therefore a two-photon process might be the major pathway for the dissociation at this wavelength. The fact that the splitting patterns at 266 and 532 nm are similar for the same polarization implies that the “total” transition moment has the same direction for both wavelengths. For a two-photon transition this implies that the transitions to and from the intermediate (virtual) state are both parallel. From symmetry considerations a feasible intermediate state could be the ground state. The increase in the depth of the splitting with laser flux at 532 nm is consistent with a two-photon dissociation mechanism. Presumably, some contribution from single-photon dissociation via the S_1 surface (a perpendicular transition) results in decreasing the splitting depth, especially at low fluxes.

In contrast to the results obtained at 266 and 532 nm, the results obtained at 355 nm at low laser fluxes indicate that the transition moment tends to be perpendicular to the fragment recoil direction. Upon excitation at 355 nm the S_1 state is reached via the promotion of one electron of the lone pair of oxygen to the antibonding orbital.²⁴ As pointed above, μ is aligned perpendicular to the direction of the dissociative O–N bond. This is consistent with the presumed classification of the $S_1 \leftarrow S_0$ as an $n\pi^*$ perpendicular transition.²⁴ Since the S_0 ground state has an A' symmetry, the correlation of the transition dipole moment perpendicular to the dissociative bond points to an A'' symmetry of the S_1 state. Upon excitation at 355 nm at high laser fluxes, the arrival time distribution indicates that NO photofragments recoil along $\hat{E}$ and also perpendicular to $\hat{E}$. This fact may imply that both single-photon dissociation via the S_1 surface (perpendicular transition) and two-photon dissociation may occur. Relying on the analogy to MN the absorption around 177.5 nm (two-photons at 355 nm) may be due to a $\pi\pi^*$ transition.²⁶ The two-photon photoexcitation may lead to dissociation process via the repulsive S_2 surface (parallel transition). Therefore, contributions from both parallel and perpendicular transition moments may be considered for the interpretation of the arrival time at high laser fluxes.

The TOF qualitative results exhibited for the TBN photodissociation are in line with results obtained by the methods of LIF for TBN and of LIF and MS for other alkyl nitrites.^{6,8,15–21} The scalar and vectorial properties of TBN photodissociation have been studied in detail by means of LIF combined with polarization and sub-Doppler spectroscopy.²¹ The findings of these studies demonstrate that the [$S_1(n\pi^*) \leftarrow S_0$] transition moment is perpendicular to the molecular plane, while the [$S_2(\pi\pi^*) \leftarrow S_0$] transition moment is in the molecular plane, approximately along the O–N bond. Relying on the similarity among the derivatives of alkyl nitrites¹⁴ we also can compare our results to those obtaining for MN^{6,8} and EN¹⁹ photodissociation. By detecting with a MS the flight times and angular distributions of the fragments, the direction of the transition moments for photodissociation of EN at the $\pi^* \leftarrow n$ electronic transition¹⁹ and of MN at $\pi^* \leftarrow n$ ^{6,8} and $\pi^* \leftarrow \pi$ ^{6,18} have been established. These studies indicate that the photodissociation at the first absorption band takes place with a transition moment which lies perpendicular to the bond that breaks, while at the second absorption band with a transition moment parallel to the bond. Splitting of the NO peak was also observed in the study of Inoue *et al.*⁸ at 355 nm. They proposed that the translational distribution for the photofragment indicates that there are two distinct paths by which $CH_3O\cdot$ and $NO\cdot$ radicals are produced from the photodissociation of MN; one is a single-photon and the other a two-photon dissociation. Their conclusion relies on the fact that one of the peaks disappears when the laser intensity is reduced. As previously mentioned, in the present study the peak profile is dependent on the wavelength of the photolysis light, the polarization and the absorption band in which the photolysis occurs, but it is maintained throughout the wide range of laser fluxes used in our experiments. This leads us to the conclusion that this behavior is a result of the vector correlation between the laser polarization direction, $\hat{E}$, the electronic transition of the TBN molecule, μ , and the direction of the NO photofragment velocity, v .

CONCLUSIONS

It was demonstrated that by using one-colour laser for photolysis/ionization of a polyatomic molecule and TOF mass-resolved ion detection it is possible to obtain information on the directional properties of photofragments resulting from photodissociation via different molecular states. We studied the photofragmentation of TBN at 266, 355 and 532 nm. Our results show that for dissociation via the S_1 surface the NO fragment recoils predominantly perpendicular to $\hat{E}$, as would be expected for μ aligned perpendicular to the dissociative bond, while for photodissociation via the S_2 surface the NO recoils predominantly along $\hat{E}$, as would be expected for μ along the dissociative bond.

Acknowledgment

We would like to thank P. J. Dagdigian, P. L. Houston and R. Lavi for many helpful discussions and Mr. M. Shmueli for technical assistance.

References

1. J. P. Simons, *J. Phys. Chem.* **91**, 5378 (1987).
2. P. L. Houston, *J. Phys. Chem.* **91**, 5388 (1987).
3. R. B. Bernstein, D. R. Herschbach and R. D. Levine, *J. Phys. Chem.* **91**, 5365 (1987).
4. a. G. E. Busch and K. R. Wilson, *J. Chem. Phys.* **56**, 3626 (1972).
b. G. E. Busch and K. R. Wilson, *J. Chem. Phys.* **56**, 3638 (1972)
c. G. E. Busch and K. R. Wilson, *J. Chem. Phys.* **56**, 3655 (1972).
5. R. Bersohn *IEEE J. Quantum Electronics* **QE16**, 1208 (1980).
6. a. B. A. Keller, P. Felder and J. R. Huber, *Chem. Phys. Lett.* **124**, 135 (1986).
b. B. A. Keller, P. Felder and J. R. Huber, *J. Phys. Chem.* **91**, 1114 (1987).
7. a. G. E. Hall, N. Sivakumar, R. Ogorzalek, G. Chawla, H. P. Haerri, P. L. Houston, I. Burak and J. W. Hepburn, *Faaday Disc. Chem. Soc.* **82**, 13 (1986).
b. R. O. Loo, G. E. Hall, H. P. Haerri and P. L. Houston, *J. Phys. Chem.* **92**, 5 (1988).
8. G. Inoue, M. Kawasaki, H. Sato, T. Kikuchi, S. Kobayashi and T. Arikawa, *J. Chem. Phys.* **87**, 5722 (1987).
9. S. M. Penn, C. C. Hayden, K. J. Carlson Muyskens and F. F. Crim, *J. Chem. Phys.* **89**, 2909 (1988).
10. M. Mons and I. Dimicoli, *Chem Phys.* **130**, 307 (1989) and references cited therein.
11. W. C. Wiley and I. H. McLaren, *Rev. Sci. Instr.* **26**, 1150 (1955).
12. E. W. Schlag and H. Neusser, *Acc. Chem. Resch.* **16**, 355 (1983).
13. J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966.
14. H. Reisler, M. Noble and C. Wittig, *Molecular Photodissociation Dynamics*, edited by J. Baggott and M. N. R. Ashfold, Royal Society of Chemistry, London, 1987.
15. a. F. Lahmani, C. Lardeux and D. Solgadi, *Chem. Phys. Lett.* **102**, 523 (1983).
b. O. Benoist d'Azy, F. Lahmani, C. Lardeux and D. Solgadi, *Chem. Phys.* **94**, 247 (1985).
c. O. Benoist d'Azy, F. Lahmani, C. Lardeux and D. Solgadi, *Chem. Phys. Lett.* **129**, 24 (1986).
16. U. Bruhlmann, M. Dubs and J. R. Huber, *J. Chem. Phys.* **86**, 1249 (1987).
17. C. G. Atkins and G. Hancock, *Laser Chem.* **9**, 195 (1988).
18. J. W. Winniczek, R. L. Dubs, J. R. Appling, V. Mckoy and M G. White, *J. Chem. Phys.* **90**, 949 (1989).
19. A. F. Tuck, *J. Chem. Soc. Faraday Trans. II* **73**, 689 (1977).
20. T. Ebata, H. Yanagshita, K. Obi and I. Tanaka, *Chem Phys.* **69**, 27 (1982).
21. a. D. Schwartz-Lavi, I. Bar and S. Rosenwaks, *Chem. Phys. Lett.* **128**, 123 (1986).
b. R. Lavi, D. Schwartz-Lavi, I. Bar and S. Rosenwaks, *J. Phys. Chem.* **91**, 5398 (1987).
c. D. Schwartz-Lavi and S. Rosenwaks, *J. Chem. Phys.* **88**, 6922 (1988).
d. J. August, M. Brouard, M. P. Docker, C. J. Milne, J. P. Simons R. Lavi, S. Rosenwaks and D. Schwartz-Lavi, *J. Phys. Chem.* **92**, 5485 (1988).

22. P. Marcus, I. Platzner, I. Bar and Rosenwaks, *Int. J. Mass Spectr. Ion Proc.* **82**, 319 (1988).
23. L. Batt and R. T. Milne, *Int. J. Chem. Kinet.* **8**, 59 (1976).
24. C. Larrieu, A. Dargelos and M. Chaillet, *Chem. Phys. Lett.* **9**, 465 (1982).
25. G. W. King and D. Moule, *Can. J. Chem.* **40**, 2057 (1962).
26. F. Lahmani, C. Lardeux, M. Lavollee and D. Solgadi, *J. Chem. Phys.* **73**, 1187 (1980).