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Research paper

Internal and translational energy partitioning of the NO product in the S_2 photodissociation of methyl nitrite

Masataka Sumida, Shu Masumoto, Mitsue Kato, Katsuyoshi Yamasaki, Hiroshi Kohguchi *

Department of Chemistry, School of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739-8526, Japan

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ABSTRACT

State-resolved scattering distributions of the NO product in the photodissociation of CH_3ONO were measured at 213 nm with resonantly-enhanced multiphoton ionization spectroscopy and ion-imaging. The spectra of the NO product displayed the vibrational population up to the $v = 3$ state having the rotational state-distribution with a Gaussian-like function. The scattering data of the NO ($v = 1$) product indicate that the rotational excitation of the NO fragment and the translational energy release are fairly well compensated. This result is explained as being an outcome of the strong repulsion in the CH_3O—NO bond in the S_2 state.

1. Introduction

Alkyl nitrite (R-ONO) is one of the most intensively investigated polyatomic molecules in photodissociation dynamics studies. Since the —ONO part mainly contributes to photoabsorption as a chromophore, nitrites with different alkyl groups ($R = CH_3$ [1,2], ethyl [3], *iso*-propyl [3], *tert*-Butyl [3–5], *n*-Butyl [2,6], *iso*-amyl [6]) display analogous ultraviolet absorption spectra; the first absorption band ($S_1 \leftarrow S_0$) in the 300–400 nm region exhibits a partially resolved vibronic structure, whereas the second absorption band ($S_2 \leftarrow S_0$) at wavelengths shorter than 250 nm is broad and structureless. The electronic characters of the $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$ states, which are described by the electronic configurations of the nonbonding (n) and $\pi(\pi^*)$-orbitals in the —ONO moiety, are responsible for the similarities in the absorption spectra, and so provide common features in the photochemistry of alkyl nitrites. Both S_1 and S_2 photodissociations are known to generate RO (alkoxy radical) + NO as the main products.

The different appearances of absorption spectra can be explained as being a consequence of the individual nuclear motions on the S_1 and S_2 potential energy surfaces (PESs). The S_1 reaction mechanism is interpreted as vibrational predissociation [7]. Theoretical studies have indicated that a shallow potential well near the Franck-Condon region associated with the $S_1 \leftarrow S_0$ transition suppresses the immediate CH_3O–NO bond breaking, so that the NO stretching motion oscillates several times before the cleavage is completed [8–10]. The reaction time evaluated by a classical trajectory calculation on the theoretical S_1 PES [9] is in agreement with the result of a femtosecond time-resolved study of 125 ± 25 fs [11]. On the other hand, dissociation on the S_2 PES is considered to be fast and direct because a steep down-hill PES structure without a potential hump is found in theoretical calculations [12]. These contrasting nuclear motions on the S_1 and S_2 PESs are compared by Suter et al. [12]. However, it is noted that experimental data for the S_2 photodissociation are not as abundant as those for the S_1 photochemistry.

Ultrafast spectroscopy was used by Farmanara et al. to determine an S_2 lifetime of 25 ± 15 fs at an excitation wavelength of 199 nm [13]. This real-time measurement experimentally corroborates the direct reaction mechanism indicated by previous theoretical studies. The kinetic energy release at photolysis wavelengths of 248 nm and 193 nm was measured by Huber and coworkers by employing photofragment translational spectroscopy [1,3,14,15]. The energy partitioning to translational energy, which was evaluated to be approximately half of the available energy (E_{avl}), was compared with simple impulsive models assuming that the instantaneous repulsion in the CH_3O—NO bond classical-mechanically causes the vibration and rotation of the CH_3O and NO products. The angular distribution of the photofragment obtained with time-of-flight (TOF) spectroscopy indicates anisotropic scattering biased parallel to the photolysis laser polarization direction; [1,14,16] the upper limit of the reaction time estimated from the anisotropic parameter is comparable to that expected for direct bond dissociation. The state-distribution measured by Winniczek [16] with resonantly-enhanced multiphoton ionization (REMPI) spectroscopy of the NO ($v = 0$) photofragment shows the

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* Corresponding author at: Kagamiyama 1-3-1, Higashi-Hiroshima, Hiroshima 739-8526, Japan.

E-mail address: kohguchi@hiroshima-u.ac.jp (H. Kohguchi).

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highly rotational excitation of the NO product. This peculiar rotational state-distribution of NO was also measured by laser-induced fluorescence (LIF) spectroscopy at a photolysis wavelength of 266 nm, which is located at the edge of the $S_2 \leftarrow S_0$ absorption [17]. Generation of NO in the highly rotational excited states can be understood to result from the instantaneous dissociation of the bent CH_3O—NO structure, which has a bond angle of ≈115° [18,19] in the S_0 state. Although ultraviolet laser photolysis of CH_3-ONO has been applied to the spectroscopic studies of CH_3O radical as the cooled radical beam source [20–23], the nascent state distribution of CH_3O under collision-free conditions has not been determined for the photodissociation dynamics [24].

In this letter, we present the results of REMPI spectroscopy and state-resolved ion-imaging of the NO product in a pump-probe scheme. The photolysis laser wavelength of 213 nm is located near the maximum of the $S_2 \leftarrow S_0$ absorption band. From the results, which contain a wide spread of the vibrational and rotational states, the translational energy release as a function of the final state of the NO fragment is obtained. The energy partitioning between the rotational and translational energies is discussed in connection with the impulsive repulsion in the CH_3O—NO bond, which is a simple model of the S_2 photodissociation.

2. Experimental

We carried out the pump-probe experiment with an ion-imaging apparatus, which was previously used for our photodissociation dynamics studies of polyatomic molecules [25,26]. A molecular beam of CH_3ONO was irradiated with pump (photolysis) and probe (ionization) laser pulses. The photolysis laser light (213 nm) was the fifth harmonic of the output of a YAG laser (Continuum, NY), which was generated by sum-frequency mixing of the second and the third harmonics with a β-barium borate (BBO) crystal. The NO photofragment was ionized by [1 + 1] REMPI spectroscopy via the $A^2\Sigma^+ - X^2\Pi$ transition in the 217–258 nm region. The probe laser pulse was the frequency-doubled output of a YAG-pumped dye laser system (Spectra Physics LAB-170, Cobrastretch). The pulse energy of both lasers were carefully controlled to suppress unwanted noise originating solely from the probe laser (one-color noise) as much as possible; typical pulse energies of the pump and probe laser beams were 30 μJ/pulse and 10 μJ/pulse, respectively. Approximately 20 ions were detected in a two-dimensional detector in a single pump-probe cycle. The probe laser wavelength was calibrated by using the optogalvanic spectrum of a Ne hollow cathode lamp, which was simultaneously recorded with the REMPI spectra.

A gaseous sample of CH_3ONO, which was diluted with He to a concentration of 0.5% in use, was synthesized by the reaction of methanol with sodium nitrite in a sulfuric acid medium. Sulfuric acid was dropped into a saturated $NaNO_2$ solution in a 1:1 mixture of H_2O and CH_3OH at ice temperature. The synthesized CH_3ONO was collected in a liquid nitrogen trap after passing through a trap cooled with methanol slush. A solid substance with a pale yellow color, CH_3ONO, was vaporized under controlled temperature conditions, and the purified CH_3ONO produced in this manner was sampled in a vacuum line for the experiment.

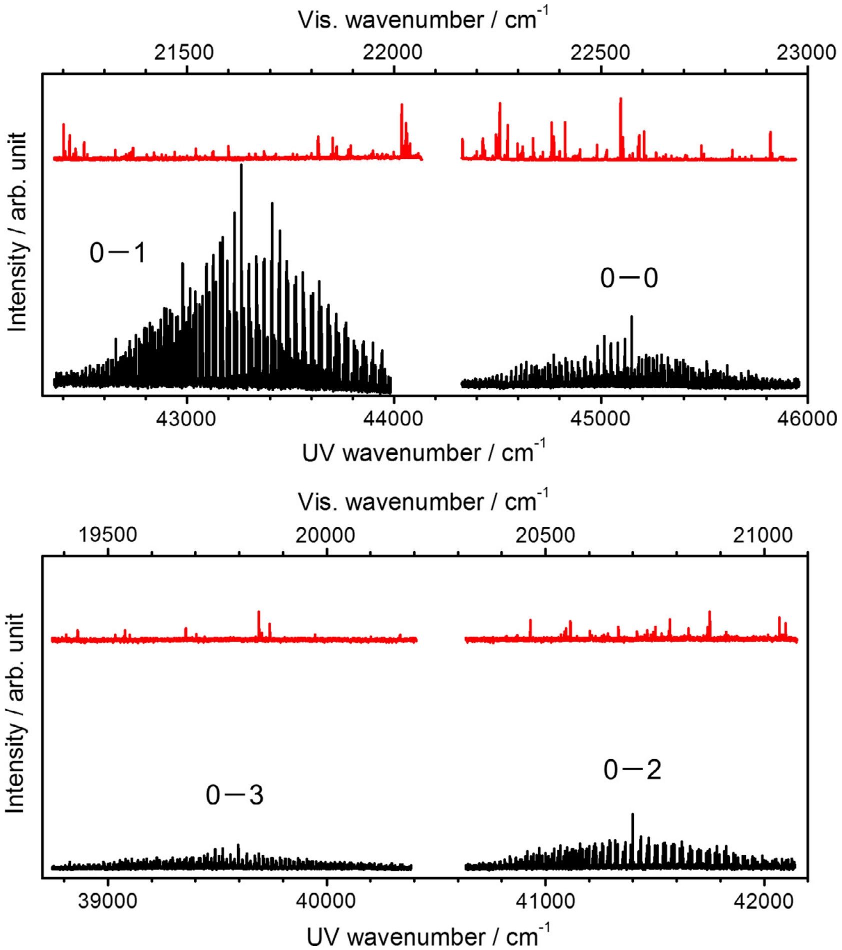

Fig. 1. A wide range of the REMPI spectrum of the NO product in the photodissociation of CH_3ONO at 213 nm. The intensity of each vibrational band is normalized by the Frank-Condon factor. The optogalvanic spectrum for wavelength calibration is plotted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)