2A5b Elucidation of the O-N bond cleavage pathway of CH_3ONO by product state correlation

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Methyl nitrite (CH_3ONO) has a strong and dissociative absorption band centered at 210 nm, which is assigned to the $S_2 \leftarrow S_0$ transition. It is known that, following to the $S_2 \leftarrow S_0$ transition, the O-N bond cleavage predominantly occurs producing NO and CH_3O. [1] In addition to these known products, we detected also the CH_3 and O photofragments in our previous experiments, showing the existence of the competing dissociation pathways. In the present study, we have attempted to reveal the production mechanism of NO, which is the product of the main pathway of the CH_3ONO photodissociation. The whole energy partitioning in the main pathway is obtained by measuring both the final state distribution and the state-resolved scattering distribution of NO, the latter of which gives us the internal (vibrational and rotational) energy distribution of the counter product of CH_3O, methoxy radical.

We have carried out the pump-probe experiment of CH_3ONO at the photolysis wavelength of 213 nm. Photofragments of NO ($X^2\Pi,v$), produced from CH_3ONO the molecular beam, were detected by using [1+1] REMPI spectroscopy. We have measured the REMPI spectrum of NO via the $A^2\Sigma^+,v' \leftarrow X^2\Pi,v''$ band and the state-resolved scattering distributions using ion-imaging.

The observed REMPI spectrum of each vibrational state clearly showed the NO fragment populated in the extremely highly rotational excited states. We performed the simulations of the rotational structure of the REMPI spectrum to estimate the internal energy of NO. We fixed the laser wavelength at a rotational line and applied ion-imaging to the NO in the single rovibrational state. The translational energy release obtained from the scattering distribution was found to be constant irrespective of each vibrational state, at about 140 $kJmol^{-1}$. The highly rotational excitation of NO are caused by   difference of the equilibrium CH_3O-N-O structure in the S_0 state and S_2 state. The O-N bond cleavage reaction completes from the bent CH_3O-N-O structure before intramolecular vibrational energy redistribution to the CH_3O moiety. The whole energy partitioning determined in the present measurements is summarized in Table1.

Table1   The whole energy partitioning in the CH_3ONO+hv(213nm) reaction (E_{avl} = 389.4 $kJmol^{-1}$)

NO	E_{vib}(NO)	J_{center}	ΔJ	E_{rot}(NO)	$\langle E_{int}(NO)\rangle$	$\langle E_{trans}(CM)\rangle$	E_{int}(CH_3O)
$v = 0$	0	44.5	15	43.2	43.2	280	66.8
$v = 1$	22.4	55.5	21	65.4	87.8	280	18.2
$v = 2$	44.5	52.5	27	62.4	106.9	280	3.1

Reference [1] J.R.Huber *et al*, *Chem. Phys. Lett.* **124**, 135-139 (1986).