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LASER-INDUCED FLUORESCENCE DETECTION OF CN, OH, AND N_2^+ PRODUCED BY CONTROLLED ELECTRON IMPACT

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Combination of electron-impact excitation and laser-induced fluorescence offers a useful technique for a detection of the dissociation fragments. The rotational temperatures of CN, OH, and N_2^+ produced by controlled electron impact on CH_3CN, H_2O, and N_2O were 550±20, 560±100, and 400±20 K, respectively.

Emission spectra of various radicals and ions have been investigated by electron-impact excitation and dissociation of molecules, since the emission spectroscopic method is very sensitive and the electron-impact method is very efficient.$^{1)}$ However, the method is applicable only to the excited species. Investigation on the ground state fragment species is important, since most of chemical reactions of practical importance proceed through electronically ground states; but the detection of the ground state fragments has not been carried out owing to the lack of a sensitive technique for the ground state species. Laser-induced fluorescence (LIF) technique has been shown to be a sensitive method to detect a small quantity of reaction product (radical or ion). Thus, the combination of the two techniques should be useful and interesting for a detailed analysis of the reaction dynamics.

In this letter we will report a LIF detection of fragment species (CN, OH, N_2^+) produced by controlled electron impact on CH_3CN, H_2O, and N_2O. Their rotational population distributions have been analyzed and rotational temperatures have been determined. To our best knowledge, a LIF detection of any fragment species produced in electron-molecule collisions has never been reported.

The experimental apparatus and the gating sequence have been described elsewhere.$^{2)}$ In brief, the sample gas jet was crossed to collide with a beam of electron in a stainless-steel collision chamber. The base pressure was of the order of 10^{-6} Torr and the operating pressure 10^{-3} Torr (uncorrected ionization gauge reading): thus, the collision of the fragment species can be ignored in a time scale of 10 μs. Actually the fragment species fly out from the observation region within a few microseconds.$^{3)}$ A dye laser beam (Molectron UV-24:DL14) was introduced into the collision region; the linewidth of the dye laser was about 0.02 nm. The electron beam and the laser beam were in a single plane and the fluorescence was observed perpendicularly to the two beams through a quartz window and an optical filter. The signal was obtained with an NF-BX531 boxcar intergrator. The accumulation of the photon signal and system control were carried out by an NEC PC8801 microcomputer.

The LIF excitation spectrum of CN produced by controlled electron impact on CH_3CN has well-resolved rotational structure, as a typical spectrum is shown in Fig. 1. The energy of the electron was 300 eV. The dye laser was scanned from 385.5 to 389.0 nm, and the LIF signal of the B(v'=0) - X(v"=1) transition of CN was observed at around 421.6 nm. The width of each rotational line is almost identical with the bandwidth of the dye laser. As is clearly shown in the Figure, CN is rotationally hot. The rotaional lines were simulated with an effective Boltzman temperature as a parameter. The observed intensity distribution was well reproduced with a rotational temperature of 550±20 K.

The rotational temperature of CN($B^2\Sigma^+$) produced by controlled electron impact on CH_3CN was found to be 1200 K.4) Thus, the ground-state fragment is rotationally cooler than the excited-state fragment; this finding indicates the difference in the electronic and molecular structure of the intermediate excited states of acetonitrile for the formation of the ground and excited CN fragments.

A typical LIF spectrum of OH produced by controlled electron impact on H_2O is shown in Fig. 2. The energy of the electron was 150 eV. The dye laser was scanned from 306.4 to 307.2 nm, and the LIF signal from the A($^2\Pi$,v'=0) state of OH was detected with a Toshiba UV-D36 colored filter. The signal-to-noise ratio of the observed spectrum was not very good as compared with the one of CN because of the weak dye-laser intensity in the ultraviolet region. The R_{21} lines are barely

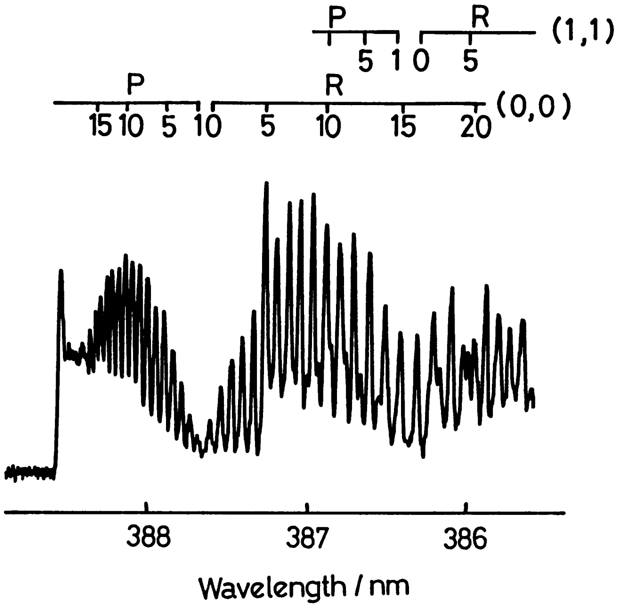

Fig. 1. LIF excitation spectrum of CN produced by controlled electron impact on CH_3CN.
Electron energy 300 eV,
Sample pressure 5.8 mTorr.

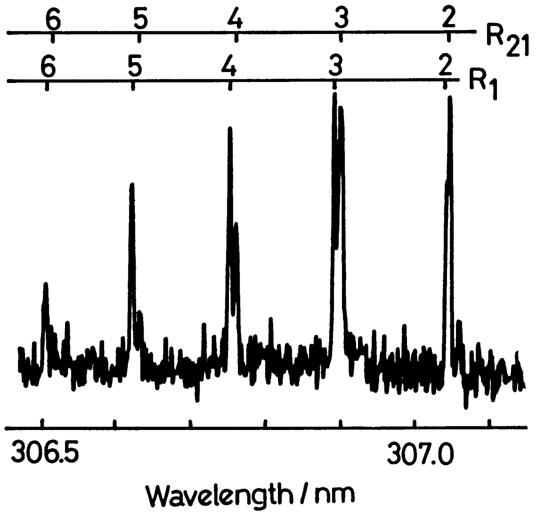

Fig. 2. LIF excitation spectrum of OH produced by controlled electron impact on H_2O.
Electron energy 150 eV,
Sample pressure 5 mTorr.

separated from the R_1 line. The semi-logarithmic plot of the intensity of the observed rotational lines, $\ln[I_{J'J''}(2J''+1)/S_{J''}^{J'}]$, over the rotational energy was linear, where J' and J" are the upper and lower quantum numbers of the transition and S is the Hönl-London factor. The result is shown in Fig. 3; thus, the rotational states are approximately in a thermal equilibrium. The rotational temperature of OH was 560±100 K.

The rotational population distributions of OH(X) and OH(A) were determined by optical excitation and by electron-impact excitation of water; they were rotationally hot and were not expressed with a single Boltzmann.5-7) This finding was related to the electronic configuration and the molecular structure of the excited water molecule.5)

A typical LIF excitation spectrum of N_2^+ produced by controlled electron impact on N_2O is shown in Fig. 4. The energy of the electron was 300 eV. The The LIF signal of the B(v'=0) - X(v"=1) transition of N_2^+ was detected at around 427.8 nm with an interference filter. The P and R branches of nitrogen molecular ion were well resolved. The semi-logarithmic plot of the rotational line intensities over the rotational energy was linear and showed that the rotational states were approximately in a thermal equilibrium, as is shown in Fig. 3. The rotational temperature of the ion was 400±20 K.

The rotational population distribution of N_2^+, which has recently measured at various electron energies from threshold to 750 eV, is approximately Boltzmann. The rotational temperature depends on incident electron energies and is about 325 K at 300 eV.3)

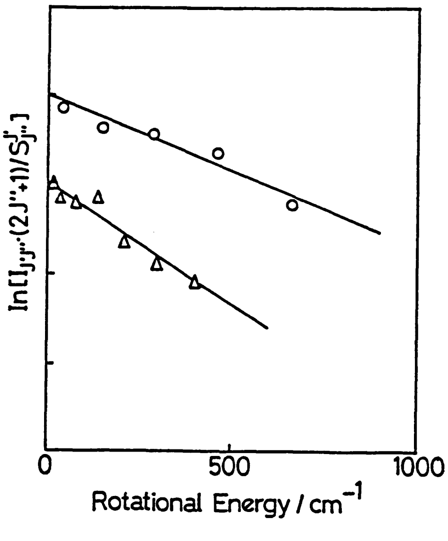

Fig. 3. Boltzmann plot of rotational line intensity over the rotational energy.

○ : OH

△ : N_2^+

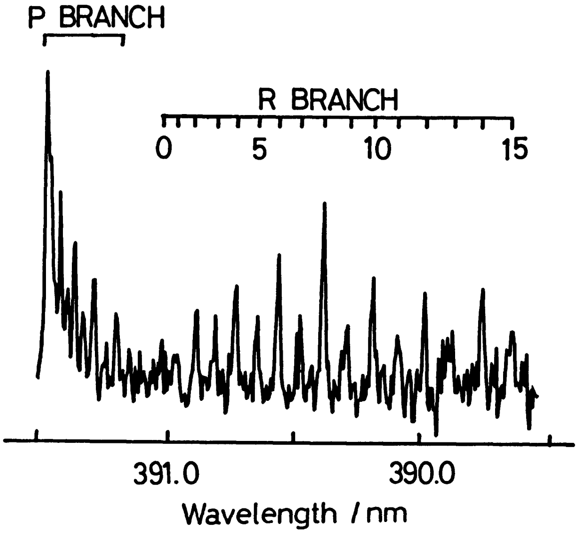

Fig. 4. LIF excitation spectrum of N_2^+ produced by controlled electron impact on N_2O. Electron energy 300 eV, Sample pressure 1.4 mTorr.

The rotaional temperature of the ground-state fragment may be perturbed by cascade contributions. This contributions were found to be small for $N_2^+(X)$ from N_2O produced by He^+ excitation.[8)] The production cross section of the ground-state fragment has to be measured for an estimation of the cascade process.

LIF excitation spectra have been obtained for several molecular ions produced by electron impact in a free jet expansion.[9,10)] Rotational population distributions of N_2^+ produced by electron impact was a Boltzmann for a thermal source[11)] but was not for a free jet source[10)]; the detailed analysis showed that N_2^+ was found to exhibit much higher rotational excitation than predicted by either the dipole or dopole plus n quadrupole model.[10)] Meanwhile, the electron energy dependence of the rotational temperature of N_2^+ indicates the increasing contribution of multipole transitions at lower incident electron energy.[3)] These findings indicate that the ionization-excitation process is more complex than has previously been expected. The rotational population distributions observed in the present experiment are approximately fit to a Boltzmann as in the case of an excited fragment.[12)] It is not yet clear how the electronic and structural configuration of the intermediate molecular states controls the final rotational population distribution.

This letter shows the usefullness of the combination of the electron-impact excitation and the laser-induced fluorescence. The details of discussion on the dissociation dynamics will be described elsewhere.

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