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CN RADICAL PRODUCED IN THE INFRARED MULTIPHOTON DISSOCIATION OF ACRYLONITRILE

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Internal states of CN produced in the IR multiphoton dissociation of acrylonitrile have been studied by laser induced fluorescence and by luminescence. The temporal behavior of the fluorescence and the pressure dependence of the rotational temperature suggest the participation of collisions under the apparent collision free condition.

Multiphoton dissociation of polyatomic molecules by high power infrared pulsed lasers (IMPD) has recently been explored by numerous investigators.1) The principal goals to pursue IMPD lie in the application to state selective chemical reactions including isotope separation and in the elucidation of reaction mechanisms. An extensive number of studies have been reported which mainly concern with the final products of IMPD. However, of fundamental importance toward the goals is to know what kinds of species are primarily produced in IMPD and which internal (electronic, vibrational and rotational) states these species are in.

Observation of fluorescence of reaction products using a pulsed dye laser in time and wavelength resolved manner allows one to determine the internal energy distribution quantitatively and to follow the time evolution in nsec time scale. King and Stephenson and Guillory and his coworkers successfully applied the laser induced fluorescence technique to investigate the fragments produced by IMPD of halogenated methanes2) and CH_3R (R=OH,CN).3) Acrylonitrile has strong absorption around 950 cm^{-1} where CO_2 laser is very intense and is expected to be a subject of IMPD. Formation of C_2 radical from this compound has been reported.4) In this work electronic, vibrational and rotational states of CN produced by IMPD of acrylonitrile are determined by the use of laser induced fluorescence and their temporal behaviors are studied.

The block diagram of the experimental apparatus for the observation of laser induced fluorescence is shown in Fig. 1. A TEA CO_2 laser, constructed in our laboratory after the design of Mino-o, produced a multimode output power of about 1 J at R(14) line (972 cm^{-1}) of 10.6μ band, which was mainly used in this work. The temporal shape of the laser pulse measured using a photon drag detector (HTV) showed 70 nsec FWHM and the intensity fell nearly to zero in 100 nsec. A dye laser beam pumped by a nitrogen laser is made to overlap collinearly with the CO_2 laser beam focused by a Ge f=12.5 cm lens. The diameter of the dye laser beam is about 3 mm, ensuring spacial overlapping of the two beams. The fluorescence signal is detected by a HTV R562 photomultiplier used in conjunction with a Nikon 0.25 m monochromator and Brookdeal 9415/9425 boxcar integrater. By varying the dye laser wavelength the excitation spectra can be obtained. Time evolution of the ground state fragment is monitored by changing the time interval between the photolyzing pulse and the probe pulse. In this case the time resolution is limited either by a jitter between the

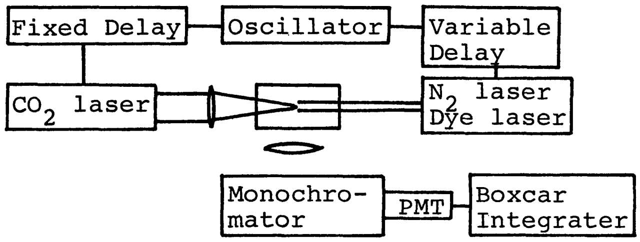

Fig. 1. Experimental apparatus

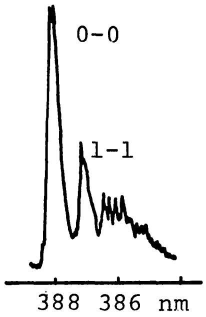

Fig. 2. Luminescence spectrum observed by the irradiation of CO_2 laser to 3 Torr of acrylonitrile

two pulses (<20 nsec) or the risetime of the pyroelectric detector (<30 nsec) to detect the onset of the IR pulse. The transit time of the PMT and the path lengths of both laser beams were taken into account. The temporal behavior of CN formed in the electronically excited state was monitored by taking the photographs of the oscilloscope traces. In this case the time resolution was determined by the response of PMT (~50 nsec).

As was discovered first by Letokhov et al.5), irradiation of intense IR pulse produces electronically excited radicals whose luminescence can often be visually seen. By focusing the CO_2 laser beam into acrylonitrile, CN(B→X), CH(A→X) and C_2 (d→a) emissions were observed, among which the CN $\Delta v=0$ transitions around 388 nm shown in Fig. 2 are by far the strongest. From a comparison with the well known spectra of CN,6) the two peaks are assigned as the P branch heads of $v'=0 \rightarrow v''=0$ and $v'=1 \rightarrow v''=1$ transitions. The intensity of the 1,1 band is about the half of the 0,0 band. Since the vibrational frequency of CN(B) is known to be 2164 cm^{-1}, vibrational temperature is calculated to be as high as 4460 K assuming the same Franck Condon factors for both transitions. Although the resolving power is too low to determine the rotational temperature from the band envelope, the fact that P branch heads show up prominently indicates CN(B) to be rotationally hot. Rotational temperature is estimated to exceed 1000 K from a computer simulation which shows P branch head becomes conspicuous over that temperature.

The rotational and vibrational energy distribution of the ground state CN radical may be determined from the excitation spectrum. Fig. 3 shows the spectra

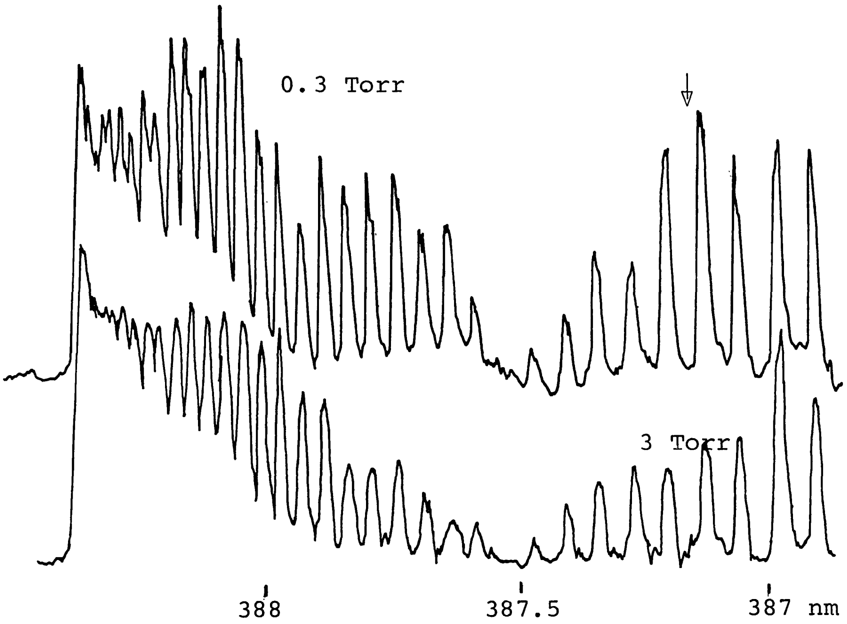

Fig. 3. A part of the excitation spectra of CN(X) radical which were formed by IMPD of acrylonitrile. The lower trace was recorded 2.4 μsec after the IR pulse for 3 Torr sample, and the upper one was recorded 1.4 μsec after the IR pulse for 0.3 Torr sample. The arrow indicates the position of the P branch head of the 1,1 transition.

taken for 0.3 and 3 Torr of acrylonitrile. Since laser induced fluorescence is at least two orders of magnitude stronger than the luminescence from CN(B) produced by the CO_2 laser alone, the contribution of the latter to the excitation spectra can be neglected. The spectra consist exclusively of the P and R branches of the 0,0 transition of CN(B←X), the bandhead of P branch lying at 388.3 nm. Again P branch makes a head, indicating that the rotational temperature is high. A comparison with simulated spectra as well as the analysis of the intensity distribution shows that the rotational energy distribution can be well described by a single rotational temperature of 600 and 800 K for each spectrum. The bandhead of 1,1 transition known to be located at 387.1 nm (indicated by an arrow in Fig. 3) is not observed at all. Suppose the upper limit of the intensity of the 1,1 transition is 1/100 of that of the 0,0 transition, the vibrational temperature of CN(X) is estimated to be less than 640 K, which is very different from that of CN(B).

Questions which arise are whether or not CN(B) is the precursor of all CN(X), and whether CN(X) and CN(B) are produced exclusively by a collisionless unimolecular reaction or a collisional process is also involved. Time evolution of the emission may give answers to the above questions. The rise and decay of the luminescence and the fluorescence excitation signals at 0.1 Torr are shown in Fig. 4. Formation of the radical in both states starts immediately with the onset of the CO_2 laser pulse. The concentration of CN(X) reaches maximum in about 400 nsec, which means the production of CN(X) stops at that time. Then it decays with apparent lifetime (1/e) of 6 μsec. The decay is probably due to that the species fly away out of the sight of the monochromator slit (2 mm) or the probe laser beam (3 mm). Indeed, the decay time is in the same order of magnitude as expected from the gas kinetic velocity. This temporal behavior does not change very much with varying the sample pressure between 0.1 and 3 Torr. On the other hand, the temporal behavior of CN(B) is very different. Since the radiative lifetime of CN(B) is known to be 66 nsec,7) the result shown in Fig. 4 means that the production of CN(B) still continues for at least several μsec after the end of the CO_2 laser pulse. In addition, the temporal behavior depends upon the sample pressure and input fluence in a very complicated manner.

Lesiecki and Guillory have reported a finite time delay in the formation of CN (X) and CN(B) from IMPD of acetonitrile.3) In their study the production of CN(X) starts about 100 nsec after the onset of the CO_2 laser pulse and reaches maximum in 3∼400 nsec, which is approximately the same time as the end of the photolyzing pulse. They attributed the temporal behavior to the result of sequential IMPD, that is, an intermediate formed by IMPD undergoes secondary IMPD and produces CN. However, in this study the production of CN(X) starts with the onset of the photolyzing pulse and what is more important, the production of both CN(X) and CN(B) keeps to continue

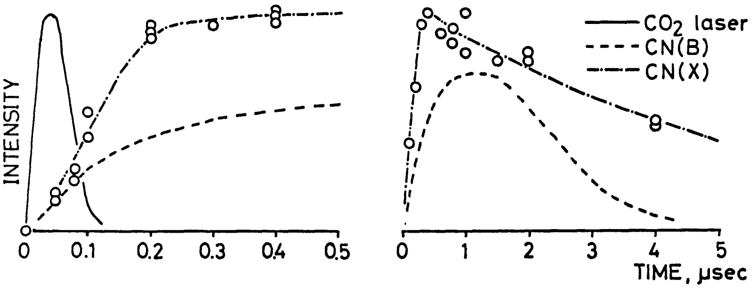

Fig. 4. Temporal behavior of ; ——— CO_2 laser pulse, —·—· laser induced fluorescence, - - - - luminescence, at 0.1 Torr of acrylonitrile. Note that intensities are not directly comparable.

after the end of the CO_2 laser pulse, as is seen in Fig.4. The difference may be probably due to the fact that the IR pulse width used here is shorter than that used in ref. 3).

From the difference in the temporal behavior of CN(X) and CN(B) it can be concluded that CN(B) is not the main supplier of CN(X). This is in accordance with the observation that the laser induced fluorescence is much more intence than the luminescence. Collisional effect is evident for the formation of CN(B), since the production continues as long as several μsec and the temporal behavior depends on the sample pressure. On the other hand, whether or not collisions participate in the formation of CN(X) is not so clear. Only a single collision is expected to occur every one μsec at 0.1 Torr and no appreciable pressure effect was observed as to the rise of CN(X) as mentioned above. These support the collisionless formation. However, if all CN(X) are assumed to be produced in a collisionless manner, the fact that the rise continues several hundreds nsec after the end of IR pulse must be interpreted in the following way. The time interval necessary for sufficient energy to be concentrated in a critical coordinate is long because the input energy is just above the threshold. An alternative explanation is that CN(X) which appears after the IR pulse is over is produced by collisions between energized parent molecules. We would like to choose the latter because of the observed pressure dependence of the rotational temperature shown in Fig. 3. The rotational temperature becomes higher with increasing sample pressure, which suggests the participation of collisions. A similar observation has been reported in ref. 3). Although collisional energy scrambling of CN with other molecules must have occured before the observation of the spectra, such collisions should reduce the rotational temperature and therefore can not explain the observed pressure effect. Consequently, in spite of the fact that the experimental condition employed is close to so called collision free in the time domain of the rise of CN(X), participation of collisions must be taken into account.

Recently two groups of authors very briefly reported quite different rotational temperature of CN(X) produced by IMPD of acrylonitrile.8) One gave higher (1000 K) and the other proposed lower (450 K) temperature than that reported in this work. A careful comparison of the experimental conditions and results may shed light on the understanding of the mechanisms of IMPD.

References

1) N.Bloembergen and E.Yablonovitch, Physcs Today 31, 23 (1978), V.S.Letokhov, ibid, 30, 23 (1977).
2) J.C.Stephenson and D.S.King, J.Chem.Phys. 69, 1485 (1978), J.C.Stephenson, D.S. King, M.F.Goodman and J.Stone, ibid, 70, 4496 (1979).
3) M.Lesiecki and W.A.Guillory, Chem.Phys.Lett. 49, 92 (1977), J.Chem.Phys. 69, 4572 (1978), S.E.Bialkowski and W.A.Guillory, J.Chem.Phys. 68, 3339 (1978).
4) J.D.Campbell, M.H.Yu, M.Mangir and C.Wittig, J.Chem.Phys. 69, 3854 (1978).
5) R.V.Ambartzumian, N.V.Chekalin, V.S.Letokhov and E.A.Ryabov, Chem.Phys.Lett. 36, 301 (1975).
6) G.Herzberg, Spectra of Diatomic Molecules(Van Nostrand Reinhold, New York, 1955).
7) W.M.Jackson, J.Chem.Phys. 61, 4177 (1974).
8) M.R.Levy, M.Magir, H.Reisler, M.H.Yu and C.Wittig, Faraday Disc.Chem.Soc. 67, 243 (1979), C.Miller and R.N.Zare, ibid, 67, 245 (1979).

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