CHEMISTRY LETTERS, pp. 995-996, 1993.

Rovibrational Distributions of CH($A^2\Delta$) Produced in e-C_2H_2 Collisions

Manabu TOKESHI, Keiji NAKASHIMA, and Teiichiro OGAWA*
Department of Molecular Science and Technology, Kyushu University, Kasuga, Fukuoka 816

Emission spectra of the CH($A^2\Delta$-$X^2\Pi$) transition produced in the electron impact dissociation of acethylene have been measured. The rovibrational distributions of CH($A^2\Delta$) depend on the electron impact energy ; the rotational temperature of CH($A^2\Delta$, v'=0) varied from 3200 K at 17 eV to 2500 K at 100 eV, and the ratio of the vibrational populations (P(v'=1)/P(v'=0)) varied from 0.45 at 17 eV to 0.80 at 100 eV.

Rovibrational distributions of a dissociating species provide key information for understanding the dissociation dynamics. Beenakker et al.$^{1,2)}$ measured the intensity distribution in the vibrational and rotational structure of the CH($A^2\Delta$-$X^2\Pi$) emission spectrum formed by dissociative excitation of C_2H_2 by electron impact and reported that the CH($A^2\Delta$-$X^2\Pi$) emission spectrum was independent of the energy of the incident electrons in the 15-1000 eV range and that the rotational distribution for each vibrational level could be represented by assuming one Boltzmann distribution. This spectrum consists mainly of three overlapping bands corresponding to the 0-0, 1-1 and 2-2 vibrational transitions in the 415-440 nm region. In this work, we have investigated precisely the vibrational and rotational distributions of the CH($A^2\Delta$) state and their electron energy dependence, and analyzed them by computer simulation in order to obtain information about the dissociation processes.

The exprimental apparatus for the measurement of the CH($A^2\Delta$-$X^2\Pi$) emission produced in e-C_2H_2 collisions has been described elsewhere.$^{3,4)}$ The pressure of the sample in the collision region was kept constant at 1 mTorr (1 Torr=133.322 Pa) or less where the emission intensity was found to be linear with pressure. The optical resolution was 0.12 nm FWHM.

The emission spectrum of the CH($A^2\Delta$-$X^2\Pi$) transition was measured for electron energies of 17-100 eV. The population of each vibrational state, P(v'), and their rotational temperature, Tr(v'), of CH($A^2\Delta$) were determined from the best fit simulation of the observed spectrum as summarized in Table.1. The rotational distribution was apparently statistical and could be expressed approximately with a single temperature. The accuracy for the determination of the Tr(v') is ±500 K and that for the P(v') is 10-20%. These vibrational and rotational distributions of the CH($A^2\Delta$) apparently depended on the electron impact energy ; the population of vibrationally excited states increased with the electron energy whereas the rotational temperature decreased. The rotational temperatures in the 17-100 eV range were similar with that of Beenakker et al.$^{1,2)}$ although they did not find the electron energy dependence. Meanwhile, the vibrational populations observed here deviated from their values at higher electron energies.

Beenakker et al.$^{2,5)}$ and Tsuji et al.$^{6)}$ found two threshold energies at 13.0±1.5 and 28±2 eV, and at 13.5±1.0 and ≈30 eV, respectively, in the excitation function of the CH($A^2\Delta$-$X^2\Pi$). Thus there are two major dissociation components of CH($A^2\Delta$) produced in e-C_2H_2 collisions. Thus the rotational distribution may be expressed with two rotational temperatures. The overlapping with three vibrational bands, however, obscured the difference in the two temperatures, and the rotational distribution could be expressed approximately with a single apparent temperature. The observed distributions at 17 eV should be assigned to the first component with a threshold energy at ≈13 eV : its rotational excitation is high but its vibrational excitation is weak. The second component sets in at about 28-30 eV, and its contribution increases with increasing electron energy. The changes in the rovibrational distributions in the 30-40 eV region should be caused by the second component, and we conclude that it is rotationally cooler but vibrationally hotter. The present result indicated that the detailed discussion of the dissociation processes in acethylene molecules have to take into consideration the vibrational and rotational energy.

We thank Dr. Masaharu Tsuji (Institute of Advanced Material Study) for providing the spectral simulation program used in this work.

Table1. Rotational temperature and relative vibrational populations of CH($A^2\Delta$) produced in e-C_2H_2 collisions

Electron energy/eV	17	25	30	35	40	50	60	70	100	15-1000[a)]
Tr(v'=0) (K)	3200	3200	2800	2500	2500	2500	2500	2500	2500	2700
Tr(v'=1) (K)	2000	2000	1800	1800	1800	1800	1800	1800	1800	1600
Tr(v'=2) (K)	1000	1000	1000	1000	1000	1000	800	800	800	500
P(v'=1)/P(v'=0)	0.45	0.45	0.55	0.70	0.75	0.75	0.80	0.80	0.80	0.38± 0.13
P(v'=2)/P(v'=0)	0.07	0.08	0.09	0.12	0.13	0.13	0.14	0.14	0.14	0.11± 0.03

a) Beenakker et al.[1,2)]

References

1) C.I.M.Beenakker, P.J.F.Verbeek, G.R.Möhlmann, and F.J.de Heer, *J.Quant.Spectrosc.Radiat.Transfer,* **15**, 333(1975).
2) C.I.M.Beenakker, Thesis,University of Leiden (1974).
3) T.Ogawa, H.Tomura, K.Nakashima, and H.Kawazumi, *Chem.Phys.*, **113**, 65(1987).
4) M.Tokeshi, S.Miyachi, K.Nakashima, and T.Ogawa, *Eng.Sci.Repts.Kyushu Univ.,* to be submitted.
5) C.I.M.Beenakker and F.J.de Heer, *Chem.Phys.,* **6**,291(1974).
6) M.Tsuji, T.Ogawa, Y.Nishimura, and N.Ishibashi, *Bull.Chem.Soc.Jpn.*, **49**, 2913(1976).

(Received March 10, 1993)