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FORMATION OF CN (B²Σ) IN THE ELECTRON IMPACT DISSOCIATION OF CYANIDES

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Summary

Dissociative excitation of HCN, CH₃CN, C₂N₂, ClCN and BrCN by electron impact was studied by observation of the CN violet $(B^2\Sigma - X^2\Sigma)$ bands with medium resolution. Distribution of spectral intensity was essentially independent of the electron energy (80 - 300 eV). Vibrational populations and effective rotational temperatures (1000 - 2000 K) of CN $(B^2\Sigma)$ were estimated by a band-envelope analysis. For HCN, CH₃CN and C₂N₂ the vibrational populations for $0 \leqslant v' \leqslant 6$ were approximately exponential with an effective vibrational temperature of about 7000 K, whereas for ClCN and BrCN significant enhancements in the populations were observed particularly around $v' = 2$ and 3. For HCN, ClCN and BrCN the populations for $v' = 11 - 15$ are estimated to be 1 - 7% of those for $v' = 0$, while for CH₃CN and C₂N₂ no tail bands with $v' = 11 - 15$ were clearly observed. The populations of CN $(B^2\Sigma)$ are contrasted with those produced by impact of metastable argon atoms and by photodissociation reported. The CN red $(A^2\Pi - X^2\Sigma)$ bands observed from CH₃CN, ClCN and BrCN were much weaker than the corresponding bands observed from metastable impact.

Introduction

The violet $(B^2\Sigma - X^2\Sigma)$ and red $(A^2\Pi - X^2\Sigma)$ emission bands of CN radicals have been studied in reactions of active nitrogen with organic molecules [1 - 4], in collision of metastable rare-gas atoms with cyanides [5 - 8], and in photodissociation of cyanides by vacuum ultra-violet radiation [9, 10] Distributions of the vibrational and rotational energies into individual levels have been analyzed in detail, and possible formation mechanisms of the CN radicals have been proposed.

There seems to be no systematic study in this respect for the CN radicals produced by electron impact, except that the excitation cross-sections of CN from cyanogen by electron impact were recently measured by Korol and

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Kishko [11]. In most studies of electron-impact excitation and/or fragmentation of gas molecules, emission spectra of excited species were analyzed in order to derive excitation functions [12 - 17], and the only examples of population analyses are the studies of OH ($A^2\Sigma$) radicals formed from H_2O and H_2O_2 by Horie *et al.* [18, 19] and of C_2 ($A^3\Pi_g$) from C_2H_2 and C_2H_4 by Polyakova and Fizgeer [20].

The purpose of the present study is to determine the initial distribution of vibrational and rotational energies of CN ($B^2\Sigma$) formed from five simple cyanides by impact of 80 - 300 eV electrons and to critically compare the distribution with known distributions for the same state produced in other processes. A comparison of the dissociative excitation of the linear molecules, HCN, ClCN, BrCN and C_2N_2, with those of non-linear molecules such as H_2O and H_2O_2 is another point of interest.

Experimental

A schematic drawing of the apparatus is shown in Fig. 1. The apparatus consists of an electron source, a collision chamber and a spectrometer. The electron source and the collision chamber are evacuated separately by oil diffusion pumps to about 6×10^{-6} Torr, as measured by an ionization gauge.

A tungsten filament 0.15 mm diameter was heated by 2 V d.c. Electrons accelerated by three electrodes were introduced into the collision chamber through a slit (2×5 mm^2) covered with a stainless steel mesh (3 lines/mm). The electrodes e and f were grounded, and a negative potential of 80 - 300 V was applied to the filament. The energy spread of the electrons was estimated to be a few eV. The distance between the filament and the target g was about 4 cm. The maximum beam current measured at g was about 500 μA for 300 V. Most of the following experiments were made at 100 - 300 μA.

Samples of BrCN and CH_3CN were obtained commercially; those of HCN and ClCN were prepared by the reaction of sodium cyanide with sulfuric acid and with chlorine [21], respectively. Cyanogen was obtained by thermal
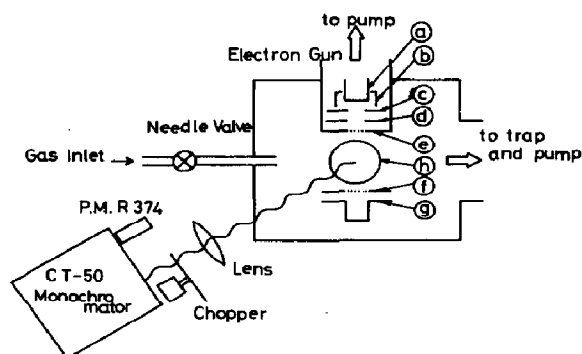

Fig. 1. Schematic design of the apparatus. a, Tungsten filament; b, repeller electrode; c, d and f, electrodes; e, slot with a grid; g, electron target; g, quartz window.

decomposition of silver cyanide at 380 °C [21]. The samples were purified by vacuum distillation and no impurity effect was observed in any of the emission spectra. The gases were fed into the collision chamber through a 0.4 mm i.d. stainless steel nozzle at a constant pressure controlled by the temperature of the sample holder and a needle valve. The gas molecules were allowed to cross the electron beam about 4 cm from the nozzle tip. The sample pressures during the emission experiments were measured by an ionization gauge to be 3×10^{-4} Torr for CH_3CN and $(0.5-1) \times 10^{-4}$ Torr for the other gases. A liquid nitrogen trap was installed in the collision chamber.
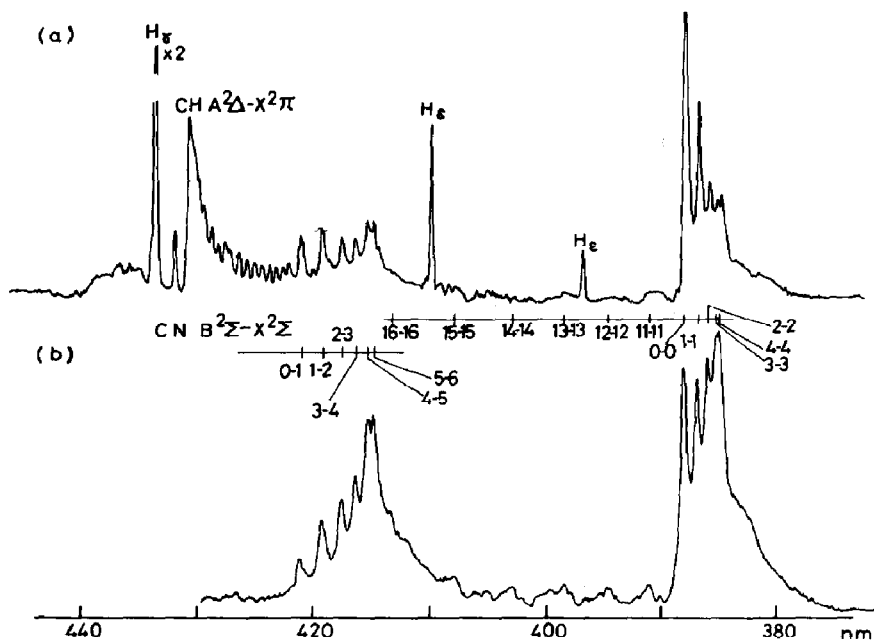
The light signal from 350 to 480 nm modulated at 225 Hz by a mechanical chopper was detected by a 0.5 m Czerny-Turner scanning monochromator equipped with a 1200 Gr/mm grating blazed at 1.2 μm and an HTV R374 photomultiplier. The light signal from 480 to 700 nm was detected by modulating the electron beam to eliminate stray light from the filament. The electrode c in Fig. 1 was used to chop the electron beam by applying a 1.5 kHz square wave with a pulse height of 60 V. The second and third orders of the grating were used with the aid of color filters (Toshiba V-Y47 and V-C1C) for the observations of 480 - 700 and 350 - 480 nm, respectively. The photocurrents were fed into a lock-in amplifier connected to a recorder. With a slit width of 150 μm the spectral resolution was about 0.3 nm. The relative intensity response of the detection system was calibrated by a halogen lamp (JC-24-150 of Ushio Electronic Corporation). The color temperature of the lamp was determined at Electrotechnical Laboratory. Wavelength calibration was obtained by reference to the emission lines of a mercury lamp.

Observed spectra

CN ($B^2\Sigma$–$X^2\Sigma$) violet bands

Typical emission spectra from CH_3CN and $BrCN$ in the range 370 - 440 nm are shown in Fig. 2. The $\Delta v = 0$ and $\Delta v = -1$ bands of the CN violet system ($B^2\Sigma$–$X^2\Sigma$) were observed from all the cyanides studied and were assigned following the table by Wallace [22]. In addition, the CH ($A^2\Delta$–$X^2\Pi$) band system and intense lines of the hydrogen Balmer series (H_γ–H_ϵ) were observed from CH_3CN, as shown in Fig. 2. The CH band system and the Balmer lines were also observed from HCN but their intensities were much weaker. Weak tail bands of the $\Delta v = 0$ sequence of the CN violet system ($v' = 11 - 15$) with intensities of the order of 1% of those for $v' = 0$ were observed from HCN, ClCN and BrCN. No corresponding tail bands were clearly observed from CH_3CN and C_2N_2.

The intensities of the violet bands were found to decrease monotonically with the vibrational quantum number v, and hence, the bands showed no indication of a sizable population disorder, in contrast to the strong disorder observed in the vibrational populations of CN ($B^2\Sigma$) produced by the reaction of active nitrogen with hydrocarbons [1 - 4] and by impact of metastable argon atoms with halogen cyanides [5, 6, 8]. At 300 V relative inten-

Fig. 2. CN $B^2\Sigma-X^2\Sigma$ violet emission spectra from (a) e+CH$_3$CN and (b) e+BrCN. Incident energy and current of electrons: 200 eV and 50 μA. Sample pressures: 3 $\times$ 10^{-4} Torr for CH$_3$CN and 1 $\times$ 10^{-4} Torr for BrCN.

Fig. 3. Dependence of the intensities in arbitrary units of the CN violet (0,0) band on electron current: O, C$_2$N$_2$, 160 eV, 4.5 $\times$ 10^{-5} Torr; □, BrCN, 300 eV, 6.5 $\times$ 10^{-5} Torr.

Fig. 4. Dependence of the intensities in arbitrary units of the CN violet (0,0) band on sample pressures: □, C$_2$N$_2$, 160 eV, 360 μA: O, ClCN, 160 eV, 100 μA; ●, ClCN, 130 eV, 200 μA.

sities of the (0,0) violet bands for CH_3CN, C_2N_2, HCN, ClCN and BrCN were estimated to be 1 : 2.4 : 5.4 : 4 : 5.

Dependence of the emission intensities on the electron current and on the sample pressure are shown in Figs. 3 and 4, respectively. In all cases the spectral intensities measured were proportional to the beam current up to about 300 μA and to the sample pressure up to about 1×10^{-4} Torr. Therefore, electron-impact dissociative excitation of the cyanides studied were found to be consistent with one-electron processes in the present ranges of electron density and sample pressure.

CN ($A^2\Pi - X^2\Sigma$) red bands

Typical emission spectra from ClCN and CH_3CN from 500 to 690 nm are shown in Fig. 5. The bands were assigned as sequences of the $A^2\Pi - X^2\Sigma$ system of CN (Δv = 5, 6, 7 and 8 for ClCN and Δv = 4 and 5 for CH_3CN). The red bands from BrCN appeared to have similar profiles to those from ClCN. No measurements of the red bands from C_2N_2 and HCN were made in the present study. The red bands from CH_3CN had detectable intensities only for $v' \leqslant 10$ as shown in Fig. 5. On the other hand, from ClCN and BrCN the red bands for $v' \leqslant 9$ were either undetected or weaker than those for $v' \leqslant$ 10. The intensity ratios of the red bands to the violet bands from CH_3CN and ClCN in the present electron impact spectra were at most 1/5 of the corresponding ratios observed in the spectra from metastable argon impact [8].
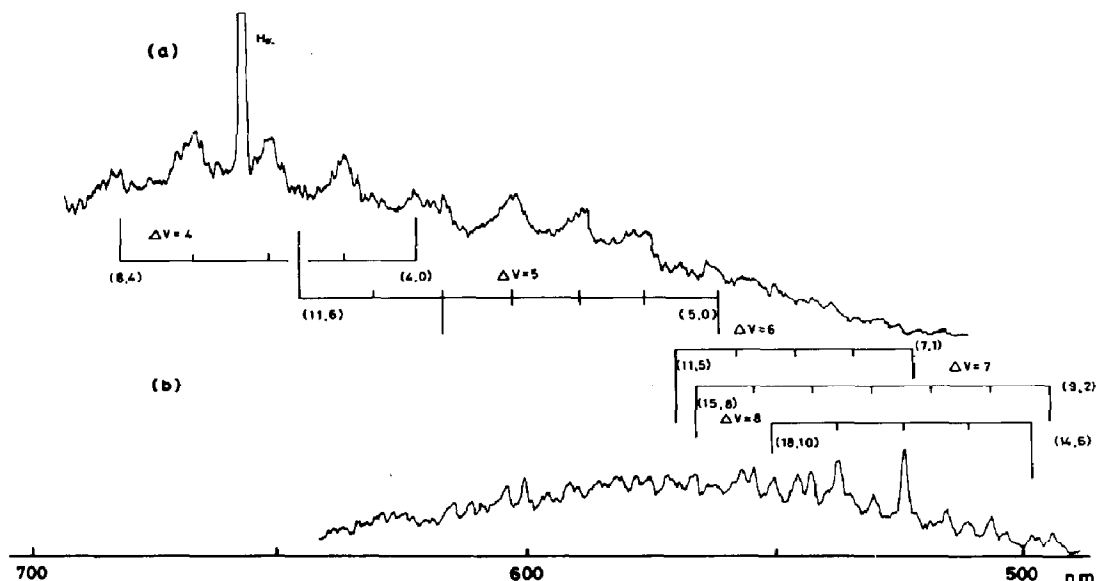

Fig. 5. CN $A^2\Pi - X^2\Sigma$ red emission spectra from (a) CH_3CN, 3×10^{-4} Torr, 100 eV and 65 μA, and (b) ClCN, 1×10^{-4} Torr, 130 eV and 115 μA.

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Band envelope analysis of vibrational populations

The vibrational population distribution of CN ($B^2\Sigma$) were determined quantitatively by analysis of the $\Delta v = 0$ band envelopes [7]. An effective Boltzmann rotational temperature T_{rot} was assumed. A HITAC-8800/8700 computer system in the Computer Center of the University of Tokyo was used for numerical calculations.

Transition wavelengths and intensities were calculated for rotational quantum numbers K up to 90 by use of the band origins given by Jenkins *et al.* [23], the rotational constants determined by Jevons [24] and the Franck–Condon factors calculated by Spindler [25]. Band envelopes were computed by convolution of the calculated intensities of the P and R branches with a slit function, which was estimated from the observed shape of the Hg-404.7 nm line. Effective rotational temperatures were assumed to be equal for all the vibrational levels.
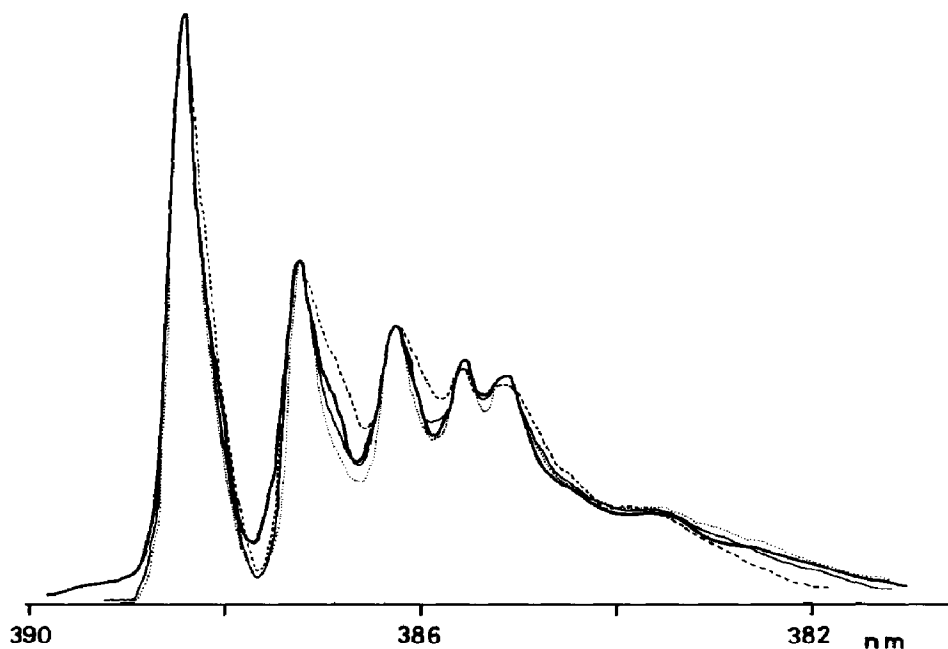

Fig. 6. Comparison of calculated band envelopes of the CN violet $\Delta v = 0$ bands with the observed envelope (thick solid line) in the electron impact dissociation of HCN. The effective rotational temperatures are assumed to be constant for all the vibrational levels: ......, $T_{rot} = 2000$ K; _____, $T_{rot} = 1500$ K; -----, $T_{rot} = 1000$ K. Vibrational populations were adjusted to obtain best fits.

Typical band envelopes for HCN calculated at 0.1 nm intervals are compared in Fig. 6 with the observed spectrum. The best agreement is obtained for $T_{rot} \simeq 1500$ K. For $T_{rot} > 2000$ K the width of the envelope is too narrow, while for $T_{rot} < 1000$ K the width is too broad and the tail fades

TABLE 1

Vibrational energy (E_v in eV) and relative populations (N_v) of CN $B^2\Sigma$ produced by electron impact on cyanides[a]

v	E_v[b]	N_v					σ[c]
		HCN	CH$_3$CN	C$_2$N$_2$	ClCN	BrCN	
0	0.1335	1.00	1.00	1.00	1.00	1.00	——
1	0.3968	0.53	0.68	0.61	0.94	0.92	0.05
2	0.6551	0.46	0.39	0.47	0.92	1.00	0.05
3	0.9081	0.35	0.27	0.32	0.85	1.00	0.05
4	1.1556	0.20	0.19	0.22	0.60	0.70	0.04
5	1.3971	0.13	0.12	0.14	0.45	0.55	0.04
6	1.6324	0.09	0.08	0.10	0.30	0.37	0.04
7	1.8611	(0.06)	(0.05)	(0.07)	(0.21)	(0.25)	—
8	2.0827	(0.03)	(0.03)	(0.05)	(0.14)	(0.18)	—
9	2.3969	(0.02)	(0.02)	(0.03)	(0.10)	(0.13)	—
10	2.5034	(0.01)	(0.01)	(0.02)	(0.06)	(0.09)	—
11	2.7021	0.01	0.01	0.01	0.06	0.07	0.03
12	2.8933	0.006	—	$\leq$ 0.006	0.05	0.06	0.03
13	3.0773	0.008	—	—	0.06	0.07	0.03
14	3.2542	0.006	—	—	0.04	0.06	0.02
15	3.4247	$\leq$ 0.004	—	—	$\leq$ 0.02	0.04	0.02

[a] Estimated for 300 eV electrons. Populations are essentially independent of electron energy (80 - 300 eV). Populations estimated by smooth interpolation are enclosed in parentheses.
[b] Ref. 27. [c] Estimated uncertainties in N_v. The populations for HCN are estimated to be somewhat more accurate.

out more rapidly (at about 383 nm) than does the observed spectrum. Similar analyses for CH$_3$CN, C$_2$N$_2$, ClCN and BrCN gave best-fit effective rotational temperatures of 1200, 1500, 2000 and 1500 K, respectively, with estimated uncertainties of about 500 K due to the overlapping of the observed bands and to the approximations made in the analysis.

The relative vibrational populations of the CN ($B^2\Sigma$) state determined in this analysis are listed in Table 1 and illustrated in Fig. 7. Populations for the v = 7 - 10 levels could not be estimated precisely because the bands were severely overlapped with those for lower v. For HCN, ClCN and BrCN the observed populations for v = 11 - 15 are about 1 - 7% of those for v = 0. The estimated vibrational populations and effective rotational temperatures were found to be essentially independent of the energy of the incident electrons in the range from 80 to 300 eV. The vibrational populations for the B states formed from CH$_3$CN, HCN and C$_2$N$_2$, shown in Fig. 7, decrease uniformly with v, whereas strong enhancements are observed in those formed from ClCN and BrCN, particularly near v = 2 and 3.
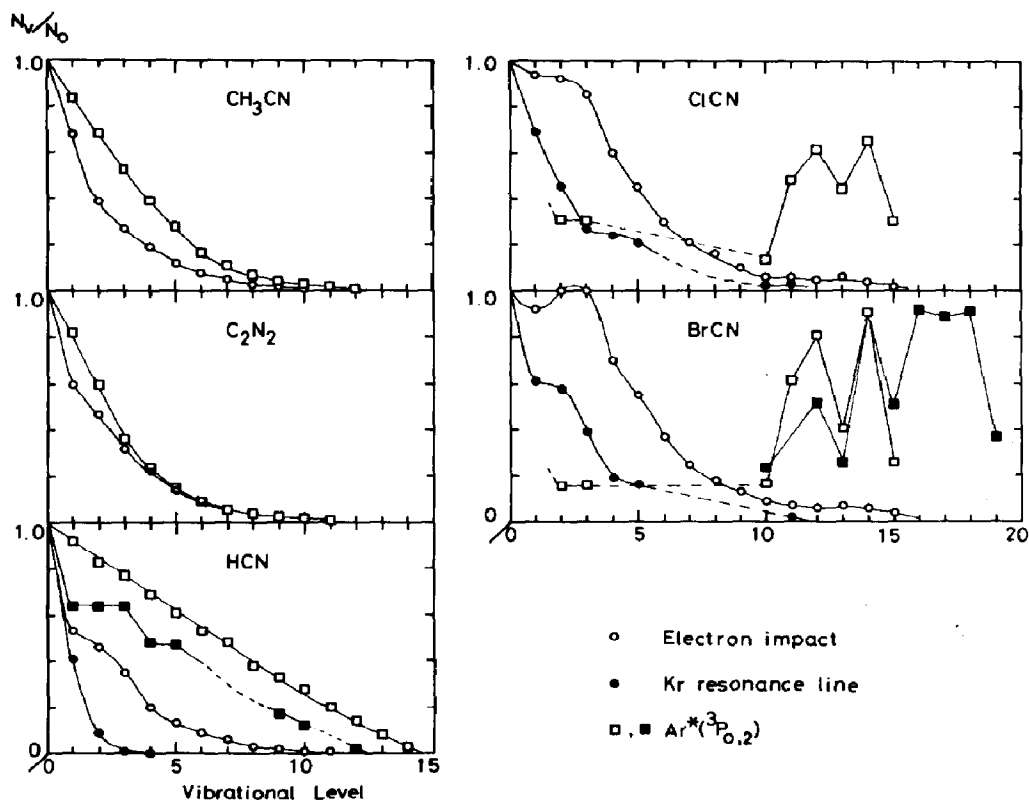
Fig. 7. Relative vibrational populations, N_v/N_0, of the CN ($B^2\Sigma$) radicals produced by impact of 300 eV electrons on cyanides (O). The effective rotational temperatures are assumed to be 1500, 1200, 1500, 2000 and 1500 K for CH_3CN, C_2N_2, HCN, ClCN and BrCN, respectively. For comparison, the corresponding populations observed in the impact of metastable argon ($^3P_{0,2}$) atoms (■ for ref. 6 and □ for ref. 8) and the krypton resonance line (● for ref. 9) are illustrated.

Results and discussion

Vibrational populations for $B^2\Sigma$)

The CN ($B^2\Sigma$) states formed from cyanides by dissociative excitation initiated by impact of electrons, photons and metastable atoms have distinctly different vibrational populations. Their features are illustrated in Fig. 7.

In comparison with the photodissociation of cyanides by the krypton resonance lines (10.0 and 10.6 eV) [9], higher vibrational levels of the B states are excited by electron impact. This difference seems to be mainly due to the difference in the impact energy, since the populations produced by photodissociation had appreciable dependence on the wavelength of the radiation, and higher vibrational levels were excited when the incident photon energy was greater.

The populations observed from electron impact excitation differ from those observed from the impact of metastable argon atoms (11.5 and 11.7 eV) [5 - 8] primarily in the following aspects: (a) for HCN, CH_3CN and C_2N_2, the vibrational populations produced by electron impact are analogous to one another and decrease nearly exponentially, corresponding to an effective vibrational temperature of about 7000 K. This indicates that differences in the bond dissociation energies for these cyanides do not seem to affect the vibrational populations of the B state. From metastable impact, their populations differ from one another. For HCN the population decreases nearly linearly, while for CH_3CN and C_2N_2 higher vibrational levels are more densely populated than in the electron-impact case, their effective vibrational Boltzmann temperatures being about 9000 and 11000 K, respectively; (b) for ClCN and BrCN, the populations from electron impact show enhancements but no other appreciable irregularities (Fig. 7), whereas anomalies are clearly observed in a number of the vibrational levels obtained from metastable impact [6, 8]. In the latter case a significant mixing by rotational perturbations enhances the B states resonating with the A and other states [6]. The absence of irregularities in the present measurements implies that a major fraction of the B states are formed directly by the dissociative excitation. (According to Bennett and Dalby [26], cascading processes from higher excited states to the B states can be ignored in the present discussion). In agreement with this observation, relative intensities of the red to the violet bands are smaller from electron impact than from metastable impact.

Vibrational vs. rotational excitation for $B^2\Sigma$

The average energies transmitted to the vibrational degrees of freedom of the $B^2\Sigma$ state were estimated as a sum of the vibrational energy [27] times the estimated population, as listed in Table 2. The populations for $v' = 7 - 10$ were interpolated smoothly as listed in parentheses in Table 1. The rotational energies were estimated from the effective rotational temperature as kT_{rot}. Even though electrons can supply sufficient energy to the internal energies of the fragments, the average vibrational excitation is found to be smaller than from the metastable impact of HCN, C_2N_2 and CH_3CN. The three methods seem to give similar rotational energies to the CN radicals, except in the photodissociation of ClCN by the krypton resonance lines reported by Mele and Okabe [9]* and in all cases vibrational excitation exceeds rotational excitation. From electron impact vibrational excitation is 5 to 7 times as large as rotational excitation. A similar trend was observed for C_2 ($A^3\Pi_g$) formed from acetylene by electron impact [20].

The present observation exhibits a striking contrast with the corresponding electron impact and photodissociation of bent triatomic molecules such as H_2O [28] and NO_2 [29], where energies transmitted to the vibration of diatomic fragments are only a small fraction of those transmitted

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*See footnote b of Table 2.

TABLE 2

Vibrational and rotational energies (eV) transmitted to CN $B^2\Sigma$ in the dissociative excitation of cyanides[a]

		Vibration	Rotation			Vibration	Rotation
CH_3CN	e	0.62	0.11	C_2N_2	e	0.66	0.13
	m	0.9	—	ClCN	e	0.91	0.17
HCN	e	0.66	0.13		p	0.8	0.61[b]
	m	1.2	0.2	BrCN	e	0.93	0.13
	p	0.26	0.13		p	0.74	0.25

[a] e = impact of 80 - 300 eV electrons [present study]; m = impact of metastable argon ($^3P_{0,2}$) atoms with 11.72 and 11.54 eV [7]; p = photodissociation by krypton resonance lines with 10.64 and 10.03 eV [9]. [b] In the photodissociation of ClCN by the xenon resonance lines (8.4 and 9.5 eV), 0.13 eV is transmitted to rotation [9].

to their rotation. For example, the rotational energies transmitted to OH ($A^2\Sigma$) from H_2O by impact of electrons and photons are an order of magnitude larger than those transmitted to CN ($B^2\Sigma$) formed from the cyanides listed in Table 2. This strong rotational excitation of the OH radical was accounted for as a result of a large change in the bond angle in H_2O upon excitation and a long-range interaction between the separating fragments through which the diatomic fragment is given a significant angular momentum. On the contrary, dissociative excitations of triatomic cyanides (linear in the ground state) take place in such a way that the resulting CN radicals are given much smaller angular momenta. Consequently, it seems unlikely that any excited states with bent structures play an important part in the formation of the CN ($B^2\Sigma$) state.

Formation of $A^2\Pi$

The CN ($A^2\Pi-X^2\Sigma$) band system observed from electron impact on CH_3CN consists mainly of transitions from $v' \geqslant 10$ and has a profile similar to those observed from argon metastable impact on CH_3CN [30]. Hence, formation of the CN ($A^2\Pi$) state from CH_3CN by electron impact as well as by metastable impact is expected to be a direct process. On the other hand, the same system observed from ClCN by electron impact has transitions with $v' \geqslant 10$ more intense than those with $v' < 10$. In this connection, the red bands observed in photodissociation [9] are either extremely weak and composed mainly of transitions from $v' \geqslant 10$ or do not appear at all. According to Mele and Okabe [9] the $B^2\Sigma$ state formed by dissociation crosses over to the $A^2\Pi$ state since their potential curves cross at low vibrational levels of the $B^2\Sigma$ state. The present observation may suggest an analogous mechanism of formation of the $A^2\Pi$ state in electron impact on ClCN. Nevertheless, direct formation is probably a dominant process since the observed intensities of the red band do not exhibit perceptible anomalies, which otherwise should appear in a number of vibrational levels of each sequence.

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