Fluorescence Emissions of Cycloalkanes and Mono-olefin by Controlled Electron Impact

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Emission spectra of cyclohexane, methylcyclohexane, *trans*-decalin and tetramethylethylene were measured under the controlled electron-impact (5—100 eV) excitation. A broad band was observed in the ultraviolet region in addition to lines and bands from such fragments as H, CH, and C_2. This broad band was assigned to the fluorescence emission from the excited parent molecule, since its peak and lineshape resemble the fluorescence measured for liquid and since the threshold energy agrees with the absorption onset. The emission cross sections for these emissions were determined at an electron energy of 50 eV.

The intense absorption band of the saturated and mono-olefinic hydrocarbons lies in the far ultraviolet region.[1,2] A very weak broad fluorescence appears upon excitation by VUV photon,[3–8] UV two-photon,[9,10] X-ray[11] or β-ray.[12] Lipsky *et al.*[3–5] systematically investigated this fluorescence for a variety of normal and cyclic alkanes, and their alkyl derivatives; the fluorescence quantum yield increases almost linearly with number of carbon atoms for normal alkanes and depends on the molecular structure for cyclic and branched alkanes. The fluorescence lifetimes of these compounds are of the order of 10^{-9} s as measured by the excitation of the hydrogen flashlamp,[7] the synchrotron radiation,[8] the nitrogen laser[10] and the pulsed X-ray.[11]

The electron is a powerful excitation source, and it can induce not only an electric-dipole allowed but also an optically-forbidden transition.[13] Aromatic molecules show their characteristic emission which is apparently similar to optical fluorescence;[14–17] however, optically-forbidden levels are preferentially excited in the case of benzene.[18] Some of the amino compounds also show an excited molecular emission.[19] However, most organic molecules do not give their own fluorescence emission, mainly because nonradiative processes are fast.

We have recently obtained the fluorescence emission of such hydrocarbons as cyclohexane, methylcyclohexane, *trans*-decalin and tetramethylethylene upon the controlled electron-impact excitation, and discussed the dynamics of molecular excitation.

Experimental

The apparatus consists of a stainless steel collision chamber and a highly sensitive photodetection system. The collision chamber was evacuated with a 4″ oil-diffusion pump with a liquid nitrogen trap. The base pressure was of the order 10^{-5} Pa and the operating pressure was 2.7×10^{-2} Pa (uncorrected ionization gauge reading). Electrons from a tungsten filament were accelerated and collimated with electrostatic lenses, and were monitored with a Faraday cup. The sample was jetted into the collision region through a multichannel nozzle and was crossed to collide with the electron beam.

The optical emission produced in the collision region was observed through a quartz window and a quartz lens at an angle of 60° with respect to the electron beam. The spectrum in the entire region was recorded with a SPEX 1670 monochromator equipped with a 1200 grooves/mm grating blazed at 300 nm and with an HTV R585 photomultiplier. The spectrum in the 190—300 nm region was recorded with the same monochromator equipped with a 1200 grooves/mm grating blazed at 500 nm and used in the second order and with an HTV R166UH solar blind photomultiplier; this system offers a higher sensitivity in the above region. Photons were counted with an ORTEC 9315 photoncounter, and data were stored and analyzed with an NEC PC8800 microcomputer.

The instrumental response of the optical system was calibrated as a function of wavelength with a standard deuterium lamp. Corrected spectra were obtained in units of relative number of photons per wavenumber.

The excitation function and the threshold energy were measured with the latter optical system. The electron energy was calibrated with the threshold of N_2^+ (391.4 nm) at 18.75 eV and its energy resolution was ±0.8 eV.

Cyclohexane (Dojindo, luminasol grade), methylcyclohexane (Nakarai, spectroscopic grade), *trans*-decalin (Nakarai, guaranteed grade), tetramethylethylene (Tokyo Kasei, guaranteed grade), ethylene (Seitetsukagaku, research grade) and carbon monoxide (Takachiho, research grade) were used as supplied. The purity of cyclohexane was >99.98% from gas chromatographic analysis.

Results and Discussion

The emission spectrum of cyclohexane by controlled electron impact at an electron energy of 80 eV shows the Balmer lines of the excited hydrogen atom and bands of the CH (the A-X and B-X transitions) and C_2 (the d-a transition) radicals, as shown in Fig. 1. No molecular emission of cyclohexane was clear in this figure because of low sensitivity.

By using the more sensitive photodetection system for the 190—300 nm region as mentioned in the Experimental, a broad band could be observed for cyclohexane at an electron energy of 50 eV, as shown in Fig. 2. This spectrum was not corrected for the instrumental response. No vibrational structure was clear and the spectral feature did not vary with the bandpass width of 1—10 nm. In addition, atomic lines of C (247.9 nm), C^+

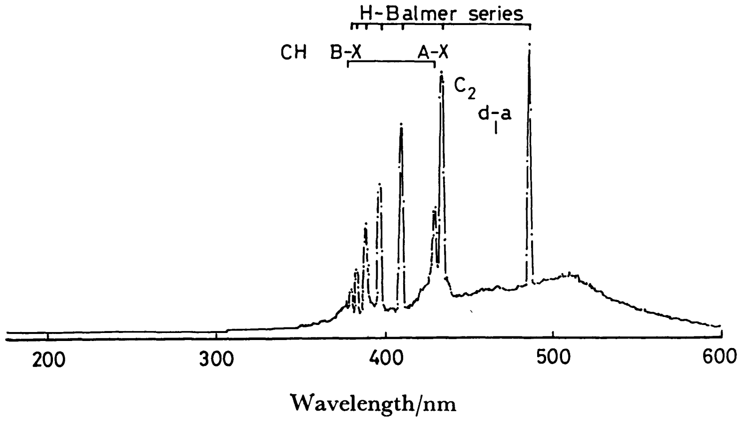

Fig. 1. A typical eminssion spectrum of cyclohexane by controlled electron impact. Electron energy 80 eV, Optical resolution 2 nm. Broad continuum (300—600 nm) is stray light from the hot filament.

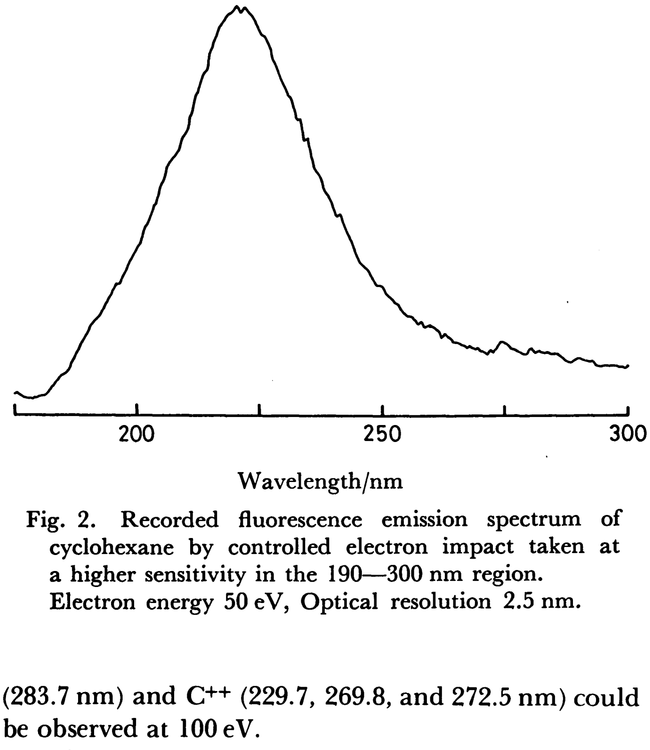

Fig. 2. Recorded fluorescence emission spectrum of cyclohexane by controlled electron impact taken at a higher sensitivity in the 190—300 nm region. Electron energy 50 eV, Optical resolution 2.5 nm.

(283.7 nm) and C^{++} (229.7, 269.8, and 272.5 nm) could be observed at 100 eV.

This broad band resembles the equilibrated fluorescence[3,5] excited optically for neat liquid. Thus, the observed band of cyclohexane is assigned to the fluorescence transition from the lowest excited singlet state (S_1) to the ground state (S_0). The intensity of the fluorescence emission was proportional to both the electron beam current (0—80 μA) and the gas pressure ($(0.7—4.0)\times10^{-2}$ Pa); so the excited cyclohexane should be produced in a one-electron primary collision process.

The lifetime of the excited cyclohexane is 1.2—1.3 ns.[7] Therefore, no collisional relaxation of the S_1 state occurs in the pressure used. The peak and the band shape of the observed emission did not change for incident electron energies of 30—100 eV and agree with those of the equilibrated fluorescence. Thus, the major emitting state should be the S_1 state for all incident energies. The electron-impact excitation is a nonresonant process and is equivalent to the one by white light, whose maximum energy is that of the incident electron;[20] electrons can excite many vibronic levels simultaneously. Cyclohexane has a number of vibrational modes, and fluorescence from highly excited vibronic levels would lack any structural features. The fluorescence emission of aromatic hydrocarbons except benzene excited by electrons resembles the equilibrated fluorescence.[17] The trapped electron spectra for saturated hydrocarbons indicated excitation to the lowest triplet state as a result of electron exchange processes;[21] however, the transition from a triplet state should not give an intense emission as observed here.

The excitation function for the fluorescence emission of cyclohexane is shown in Fig. 3. The excitation function increased from threshold rapidly to 12 eV, and then decreased gradually to higher energies. The threshold energy was 6.9±1.0 eV, and agrees with the onset of the absorption spectrum (7.1 eV)[1] within experimental uncertainties. This finding supports that the observed emission is due to the S_1—S_0 transition. The highly excited states produced directly by electrons should decay nonradiatively or result in photodissociation.

Methylcyclohexane, *trans*-decalin and tetramethylethylene also show the broad fluorescence emission. Figure 4 shows their spectra taken at an electron energy of 50 eV; these spectra were smoothed and corrected for the wavelength response of the instrument. Each spectrum well resembles the fluorescence band measured for liquid,[3—6] as shown in Table 1; the vapor spectrum by photoexcitation was shown to be almost identical to the one for liquid. Therefore, they were assigned to the fluorescence emission from the excited parent molecules. No fluorescence, however, could be observed from ethylene with the present instrument. Its fluorescence quantum yield is extreme-

TABLE 1. WAVELENGTH OF THE MAXIMUM (λ_{max}) AND THE FULL WIDTH AT HALF MAXIMUM ($\Delta\lambda$) OF THE FLUORESCENCE EMISSIONS OF CYCLOALKANES AND MONO-OLEFIN

Compound	λ_{max}/nm		$\Delta\lambda$/nm	
	This work	Lipsky *et al.*	This work	Lipsky *et al.*
Cyclohexane	202	201[a)]	32	34[a)]
Methylcyclohexane	214	213[a)]	41	39[a)]
trans-Decalin	215	217[a)]	43	44[a)]
Tetramethylethylene	254	263[b)]	36	40[b)]

a) Ref. 5. b) Ref. 6.

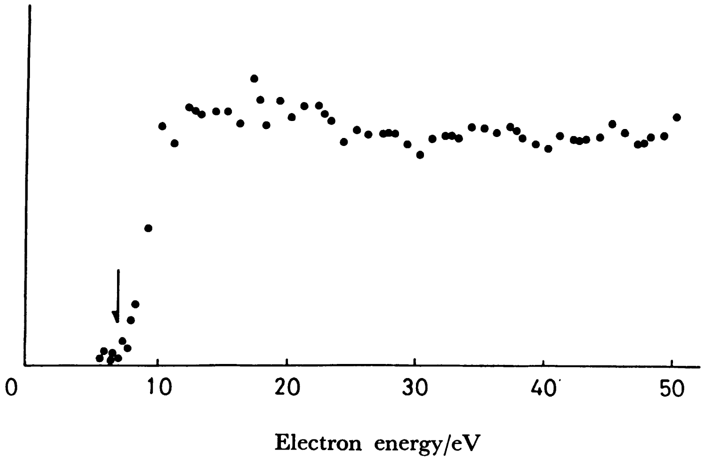

Fig. 3. Excitation function for the fluorescence emission of cyclohexane.

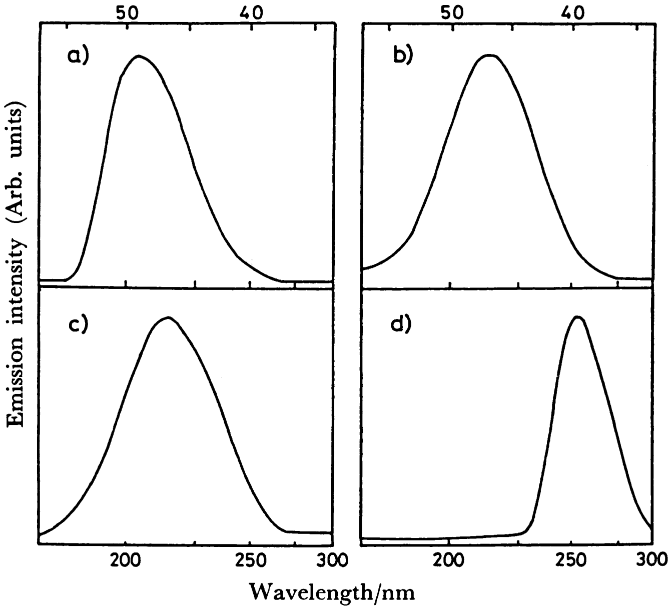

Fig. 4. Corrected emission spectra of (a) cyclohexane, (b) methylcyclohexane, (c) *trans*-decalin (d) tetramethylethlene. Electron energy 50 eV, Optical resolution 10 nm. All spectra are normalized at the intensity maxima.

ly small (ϕ_f<4×10^{-7}) for neat liquid.[6)]

The emission cross sections (σ_{em}) of these bands were measured with reference to the CO$^+$ emission (the B-(v'=0)—X(v''=0) transition, 219.0 nm,[22)] by comparing the area of the corrected emission spectrum; the sensitivity of the ionization gauge (S)[23)] was corrected. The results obtained at an electron energy of 50 eV are summarized in Table 2 together with the optical oscillator strength (f) of the corresponding absorption band[1,28)] and the fluorescence quantum yield (ϕ_f).[5,6)] The error would be about 50%; its major source is uncertainties in the pressure measurements. The emitting species do not escape from the viewing region during their lifetimes[6–8,24)] of 10^{-8}—10^{-9} s.

When the energy of the incident electrons substantially exceeds the excitation energy of the molecule, the Born approximation is applicable; the excitation cross section into the level i (σ_{exc}(i)) is expressed by the optical oscillator strength (f(i)) and the transition energy (E(i)). The probability of optical emission from this level is proportional to the fluorescence quantum yield (ϕ_f(i)). Thus, the emission cross section (σ_{em}(i)) is given as follows:[17,25)]

$$\sigma_{em}(\mathrm{i}) = \phi_f(\mathrm{i})\sigma_{exc}(\mathrm{i}) = b\phi_f(\mathrm{i})f(\mathrm{i})/E(\mathrm{i})$$

where b is a proportionality constant. This equation can be used for an order of magnitude estimation of the excitation process by the controlled electron impact.

The emission cross sections of the hydrocarbons are

TABLE 2. EMISSION CROSS SECTIONS (σ_{em}) FOR THE S_1-S_0 TRANSITION OF HYDROCARBONS AT AN INCIDENT ELECTRON ENERGY OF 50 eV

Compound	$\sigma_{em}\times10^{17}/\text{cm}^2$	f	$\phi_f\times10^3$ [d]	S[e]
Cyclohexane	1.3	0.3[b]	8.8	6.4
Methylcyclohexane	1.7	—	11.2	6.7
trans-Decalin	13	—	23.0	9.6
Tetramethylethylene	2.6	0.01—0.02[c]	0.35	5.8
CO^+ $(B(v'=0)-X(v''=0))$	0.98[a]	—	—	1.02

a) Ref. 22. b) Estimated value from thc absorption spectrum in Ref. 1. c) Ref. 28. d) Refs. 5 and 6. e) Ref. 23.

much larger than that of benzene ($\sigma_{em}=4.8\times10^{-19}$ cm^2)[16] although the fluorescence quantum yields are contrary ($\phi_f=0.22$ for the zero point level of benzene),[26] because the excitation to the S_1 state of benzene is synmetry forbidden and less efficient ($f=0.0013$).[27]

The optical oscillator strength increases gradually with the number of C–C and C–H bonds for alkanes.[1] Therefore, the emission cross section shows a close correlation to the product of the optical oscillator strength and the fluorescence quantum yield for cycloalkanes. For tetramethylethylene, however, the fluorescence maximum is blue-shifted compared to that for neat liquid and for vapor (1.66×10^4 Pa with 8.47×10^4 Pa of N_2),[6] and the emission cross section is larger than expected from the optical oscillator strength and the fluorescence quantum yield. The observed emission originates from the S_1-S_0 transition for cycloalkanes. In contrast, the valence state (π^*) and the 3 s Rydberg state lie in the equivalent energy region for mono-olefins.[28] Hirayama *et al.* suggested that the emitting state is probably the Rydberg state and an internal conversion from the Rydberg state to the valence state is very efficient.[6] Since a collisional nonradiative decay may be suppressed under low-pressure conditions, the emission cross section of tetramethylethylene is large and its fluorescence band is shifted to blue.

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