Formation of Excited Molecules and Atoms by Controlled Electron Impact on Hydrogen Chloride and Chlorinated Methanes

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The dissociation, ionization, and excitation of hydrogen chloride and chlorinated methanes under controlled electron-impact excitation were studied at low pressures. The photoemissions (200—600 nm) were observed and assigned to HCl^+, CH, CH^+, CCl, H, and Cl^+. Such species as H and HCl^+ from HCl, and H and CH from CH_2Cl_2 were concluded to be produced by some one-electron processes. The photoemission of the HCl^+ produced from CH_2Cl_2 increases quadratically with the electron-beam current; in this case HCl^+ is mainly produced by the molecular elimination of HCl and the successive ionization excitation by the second electron. The threshold energies of the photoemissions were found to be 16.8 eV for HCl^{+*} from HCl, 19.8 eV for H* from HCl, and 17.6 eV for CH*(A) from $CHCl_3$. The processes of the excitation of these species near the threshold were discussed.

Information on the primary ionization, dissociation, and excitation of atoms and molecules can be obtained by the measurement of the emission spectrum excited by controlled electron impact at low pressures, since the excited molecule will normally emit radiation before undergoing a collision. This information is pertinent to various aspects of physics and chemistry, such as gaseous electrical discharges, collision phenomena, mass spectroscopy, and radiation chemistry. The emission spectra of aromatic molecules and of H_2S, CS_2, and thiols obtained by this method have been reported, and the processes of excitation have been discussed.[1-3]

The electronic spectrum of HCl^+ ($A^2\Sigma^+ - X^2\Pi$) has been measured by Brice and Jenkins,[4] Norling,[5] and Sheasley and Mathews.[6] The photoelectron spectrum of HCl was obtained by Lempka *et al*[7] and Turner *et al.*[8] Haugh[9,10] studied the collision of HCl with He^+, Ar^+, and Kr^+, and found an unusual vibrational distribution and the quadratic intensity dependence of the vibrational bands on the target-gas pressures.

Spectroscopic studies of the dissociative excitation of chlorinated methanes have been carried out by means of an electron-impact method[11] and by means of an electric discharge method.[12] The photoemission of HCl^+ was observed even though chlorinated methanes have no H-Cl bond. However, the mechanisms of their fragmentation and excitation processes have been left unsolved.

In the present report, the emission spectra of hydrogen chloride, dichloromethane, and chloroform under controlled electron-impact excitation will be presented, and compared with the results of the previous investigations. The mechanism of the excitation and dissociation by electron-impact will be discussed in terms of the intensity of the emission and threshold behavior.

Experimental

The experimental arrangement used in this work has been described elsewhere;[1,13] however, the apparatus has been partly modified in order to improve it. Thermal electrons emitted by a heated tungsten filament are accelerated and are then introduced into a collision chamber through a hole (4 mm in diameter). The energy of the electrons is externally controlled from 10 to 450 eV. The sample gas is jetted through a nozzle (0.1 mm in diameter) and collides with the electron beam. The pressure during the operation, as measured with a Penning gauge, is of the order of 10^{-4} mmHg, though the density of the gas in the middle of the molecular jet may be higher.

The collision cell used in the measurement with the electron energy near the threshold contains a brass cylinder inside the glass cell to remove the effect of space charges and secondary electrons. In order to avoid a space-charge effect, electron-beam currents of less than 5 μA have been used when the electron energy is below 30 eV. The electron energy scale is calibrated by thresholds of the molecular lines of N_2 (3371 Å, 11.1 eV[14]) and N_2^+ (3914 Å, 18.4 eV[14]).

The photoemission is observed perpendicularly to both the electron beam and the molecular beam. A JASCO CT-50 monochromator equipped with an EMI 9558QB or an HTV R585 photomultiplier is used for the photoelectric detection. The monochromator has a 1200 line/mm grating blazed for 500 nm and has a reciprocal dispersion of 1.65 nm/mm. A Teledyne Philbric 1026-01 OP amplifier is used for the measurement of strong emissions, and an NF PC-545A photon counter, for the measurement of a weak signal near the threshold. The spectral sensitivity of the light detection system is determined by using a rohdamine B cell and by using an Ushio JC 24-150 halogen lamp.[15] The deviation of the two calibration curves is below 10% between 280 and 450 nm. The band intensities were determined by means of the peak height for the measurement of the intensity dependences on the electron-beam current and the gas pressure. However, the peak area was measured for the determination of the relative intensity of vibrational structures; the experimental uncertainty of the intensity measurements is, in this case, estimated to be about 20%.

The hydrogen chloride and deuterium chloride (99%) were obtained from the Takachiho Chemical Ind. and from Stohler. The dichloromethane and chloroform were obtained from Kishida, and the deuterated chloroform (99%) from Merk. Each sample was frozen and pumped repeatedly to remove any dissolved gases.

Results

Hydrogen Chloride and Deuterium Chloride. Typical emission spectra of HCl and DCl by controlled electron impact are shown in Fig. 1. A slit width of 50 μm was used for these measurements. The electron energy was 300 eV, and the electron-beam current was 1 mA. The dominant bands extending from 270 to 460 nm in these spectra are assigned to the $A^2\Sigma^+ - X^2\Pi$ transition of HCl^+. More than 6 vibrational levels of the upper

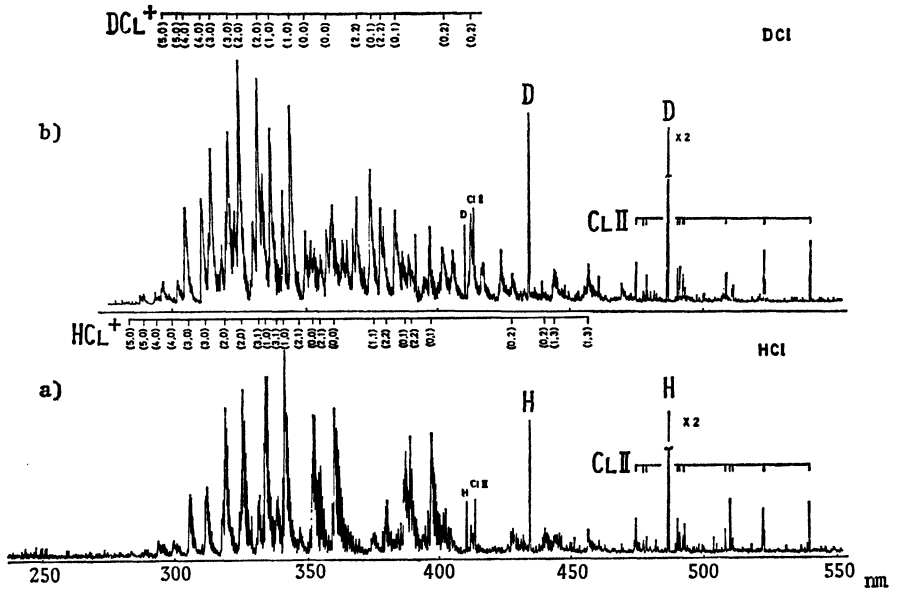


Fig. 1. Emission spectra of HCl (a) and DCl (b) by controlled electron impact. Electron energy 300 eV; electron-beam current 1 mA.

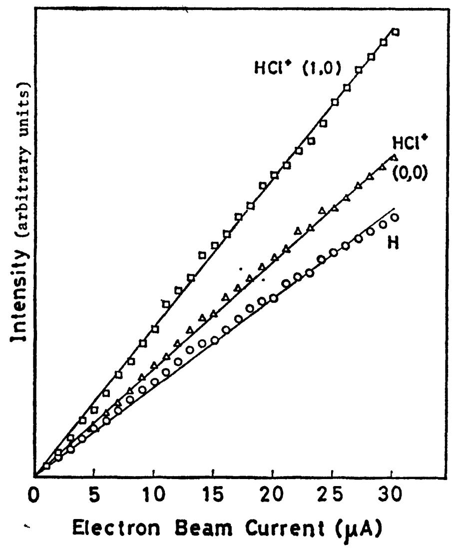


Fig. 2. Dependence of photoemission intensities of H (○) and HCl^+ (△ and □) on the electron-beam current. Electron energy was 300 eV.

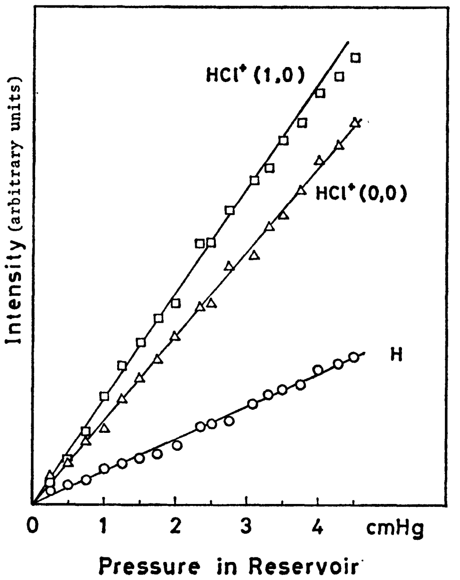


Fig. 3. Dependence of photoemission intensities of H (○) and HCl^+ (△ and □) on the gas pressure in the gas reservoir. Electron energy was 300 eV and the electron-beam current was 50 μA.

electronic state ($A^2\Sigma^+$) of HCl^+ are excited by electron impact. The strong bands of the $A-X$ system of HCl^+ are, in the order of calibrated intensities, (2, 0), (1, 0), (0, 0), and (0, 1). The intensity of the (v′, 0) band in a v″ progression is found to be the strongest; the intensity decreases at higher vibrational levels of v″. The DCl^+ spectrum shows an isotope shift in the vibrational structure. Such fragment species as H or D and Cl^+ are also observed, as is indicated in the figure.

The dependencies of the photoemission intensity of the H_β line and the HCl^+ bands from HCl on the incident electron-beam current and the target-gas pressure are shown in Figs. 2 and 3 respectively. The gas pressure was measured in the gas reservoir, where the pressure was estimated to be proportional to that in the collision chamber. Linear relations hold in all cases, and the intensity of the photoemissions of H and HCl^+ from HCl is given as follows:

$$I = k_1[\mathrm{e}][\mathrm{HCl}] \qquad (1)$$

where I and k_1 stand for the emission intensity and a proportionality constant.

The threshold energies (minimum appearance potential) of the photoemissions of HCl^+ and H were measured; they are shown in Table 1, together with the calculated values. For the ionization excitation of HCl, the threshold energy was calculated by adding up the ionization energy of HCl and the excitation

Table 1. Threshold energy for ionization and dissociation excitation for HCl and $CHCl_3$

Process		Threshold energy (eV)		
		Calcd	Obsd	
HCl $\xrightarrow{e}$	$HCl^{+*}(0, 0)$	16.3	16.8±1.0	(a)
	$H^*(n=4) + Cl(3p^{5\,2}P)$	17.2	19.8±1.0	(b)
	$H^*(n=4) + Cl(4s^{1\,4}P)$	26.1		(c)
	$H^*(n=4) + Cl(4s^{1\,2}P)$	26.4		(d)
$CHCl_3$ $\xrightarrow{e}$	$CH^*(A) + Cl_2(X) + Cl(3p^{5\,2}P)$	12.0		(e)
	$CH^*(A) + Cl_2(A) + Cl(3p^{5\,2}P)$	14.2		(f)
	$CH^*(A) + 3Cl(3p^{5\,2}P)$	14.4	17.6±1.0	(g)
	$CH^*(A) + Cl_2(C) + Cl(3p^{5\,2}P)$	19.1		(h)

$I(HCl) = 12.82\ eV^{16)}$, $D(H\text{-}Cl) = 4.48\ eV^{14)}$

$$\begin{aligned} E_{calcd\,(e)}(CH^*) &= D(CCl_3\text{-}H) + D(CCl_2\text{-}Cl) + D(CCl\text{-}Cl) + D(C\text{-}Cl) - D(C\text{-}H) - D(Cl\text{-}Cl) + h\nu \\ &= 3.90^{17)} + 2.36^{18)} + 3.45^{18)} + 5.33^{18)} - 3.47^{14)} - 2.48^{14)} + 2.87 \\ &= 12.0\ eV \end{aligned}$$

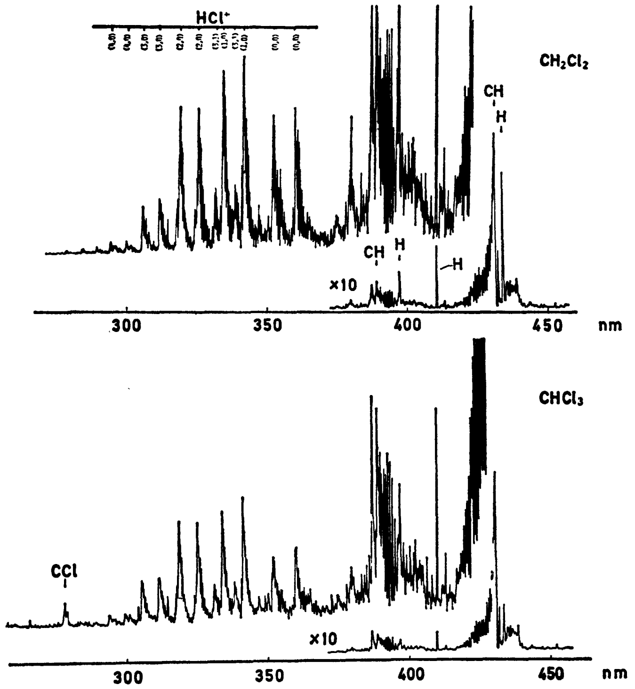


Fig. 4. Emission spectra of dichloromethane and chloroform by controlled electron impact. Electron energy 300 eV.

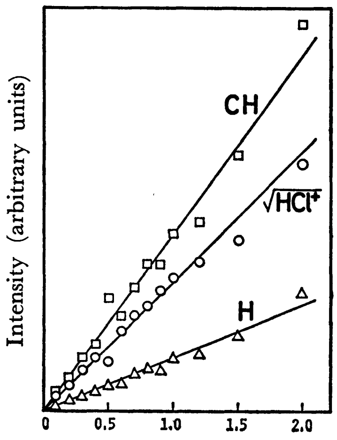


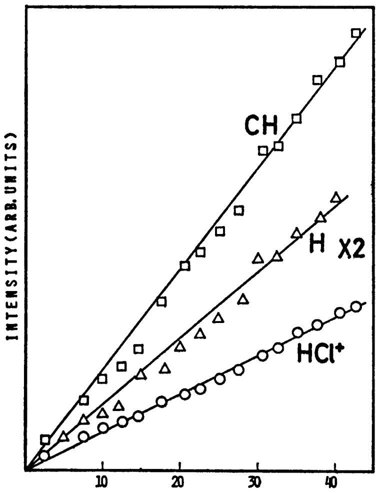
Fig. 5. Dependence of photoemission intensities of H (△), CH (□), and HCl^+ (○) on the electon-beam current. The square root of the intensity of HCl^+ is shown so that the quadratic dependence is clearly indicated. The electron energy was 300 eV.

energy of HCl^+. For the dissociation processes of HCl, the threshold energy was calculated by adding up the dissociation energy into fragments in their ground states and the relevant excitation energies of one or both of fragments, as given in Table 1. The calculated values can be expected to be smaller than the observed values by the amount of the kinetic, vibrational, and rotational energies of the species produced.

Dichloromethane and Chloroform. Typical emission spectra of dichloromethane and chloroform are shown in Fig. 4. The hydrogen Balmer series and HCl^+ doublet bands are obtained as in the case of HCl. The bands at 431 and 432 nm are assigned to the (0, 0) and (2, 2) bands of the $A^2\Delta - X^2\Pi$ transition of the CH radical, and the band at 387 nm, to its $B^2\Sigma^- - X^2\Pi$ transition. CCl shows a weak band at 278 nm, which is superimposed on the (6, 0) band of HCl^+. The emission at about 350 nm is assigned to CH^+ (see also Fig. 7). The 2800 Å and 2368 Å systems of CCl and the sharp line of the neutral carbon atom at 248 nm are also observed.

The spectrum of chloroform is identical to that of dichloromethane except for the relative amount of the fragments produced; for example, the ratio of the emission intensity of CH to that of H in $CHCl_3$ is much larger than that in CH_2Cl_2. Deuterated chloroform gives the bands of DCl^+.

The intensity of the photoemissions of H and CH produced from CH_2Cl_2 is proportional to both the electron-beam current and the gas pressure, as in the case of HCl, as is shown in Figs. 5 and 6. On the other hand, the square root of the emission intensity of HCl^+ is proportional to the electron-beam current (Fig. 5), while the pressure dependence of the intensity of HCl^+ is linear, as are H and CH (Fig. 6). The



Pressure (in gas reservoir; mmHg)

Fig. 6. Dependence of photoemission intensities of H (△), CH (□), and HCl^+ (○) on the gas pressure in the gas reservoir. The electron energy was 300 eV and the electron-beam current was 200 μA.

above findings give the following equations for the emission intensity of HCl^+ from CH_2Cl_2:

$$I = k_2[e]^2[CH_2Cl_2] \qquad (2)$$

and for that of H and CH:

$$I = k_2[e][CH_2Cl_2] \qquad (3)$$

The threshold energy of the photoemission of CH ($A^2\Delta-X^2\Pi$) was also measured; it is shown in Table 1, together with the calculated values.

Discussion

Hydrogen Chloride and Deuterium Chloride. The first vibrational quanta in the $A^2\Sigma^+$ and $X^2\Pi$ ionic states of HCl^+ and the ground state of the neutral molecule (HCl) are 1527, 2568, and 2886 cm^{-1} [14] respectively. The reduction of the vibrational quantum upon ionization in the $^2\Sigma^+$ state is much greater than that in the $^2\Pi$ state, as a result of the difference in the bonding nature of the orbital from which the electron is ejected for ionization. This is consistent with the difference in the bond length of the three species involved: 1.514 Å for HCl^+ ($^2\Sigma^+$), 1.315 Å for HCl^+ ($^2\Pi$) and 1.275 Å for the ground state of HCl.[14] This difference in the bond length is responsible for the greater population in the higher vibrational levels in the $^2\Sigma^+$ state, as is to be expected from the Franck-Condon factors for the transition between HCl (ground state) and HCl^+ ($A^2\Sigma^+$).

The emission intensity of a diatomic molecule in a transition from the v′ vibrational level of the upper state to the v″ vibrational level of the lower state is given by this expression:[14]

$$I_{v'v''} = KN_{v'}\nu^4Re^2q_{v'v''} \qquad (4)$$

where K is a constant, $N_{v'}$ is the number of molecules in the upper state, Re is an electronic transition moment, and $q_{v'v''}$ is a Franck-Condon factor. If Re is constant for a series of transitions, the emission intensity of a band depends on the product of ν^4 and the Franck-Condon factor. Haugh[19] pointed out that Re decreases strongly at a large interatomic distance for the $A^2\Sigma^+-X^2\Pi$ transition of HCl^+. In the present study, the intensities of the bands seem to give a displacement from the calculated Franck-Condon factors; the observed v′ progression with v″=0(v′, 0) is relatively more intense than the expected value. This displacement may be elucidated by Haugh's suggestion that the electronic transition moment decreases with an increase of v″.

The intensities of both H and HCl^+ are proportional to the electron-beam current and the gas pressure, as is shown in Equation (1). Thus, the ionization excitation and the dissociative excitation of HCl are concluded to proceed by one-electron unimolecular processes as follows:

$$HCl + e \rightarrow \begin{cases} HCl^{+*} \rightarrow HCl^+ + h\nu \\ H^*,\ Cl^{+*} \rightarrow H,\ Cl^+ + h\nu \end{cases}$$

where the asterisk stands for an excited state.

In the collision of HCl with He^+,[10] the ratio of the vibrational intensity of the (0, 0) band to the (1, 0) band at various target-gas pressures was not constant. The quadratic intensity dependence of the vibrational bands with the target-gas pressures has been obtained, and a reactive intermediate has been suggested. These are, however, not observed in the present case, and so no intermediate species need be considered in the present study. A difference in the method of the excitation sometimes results in a different distribution of the vibrational populations of the products, as may be seen also in the case of CN.[20]

The calculated and observed threshold values for the ionization excitation of hydrogen chloride agree well, as is shown in Table 1. This result shows that HCl^{+*} is also produced by a direct ionization-excitation of HCl near the threshold. For Balmer β of the hydrogen atom (4861 Å) from HCl, the observed onset potential is 19.8±1.0 eV. This onset is unambiguously due to the dissociation process (b), which is followed by the simultaneous formation of Cl in the ground state. In Reaction (b) the dissociation products carry off an excess energy of about 2.6 eV; the hydrogen atom shares 97% of the total excess energy. Ogawa *et al.*[21] measured the Doppler width of the light emission of H* formed by the 300 eV electron-impact on HCl and determined the kinetic energy to be 7.3 eV. Thus, the H atom produced by electron-impact seems to be hot.[21]

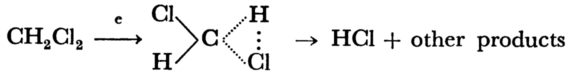
Dichloromethane and Chloroform. Though dichloromethane and chloroform have no direct H–Cl bond, the bands of the hydrogen chloride ion are clearly observed at high electron-beam currents. There are three plausible mechanisms for the formation of HCl^{+*}. The first one is a recombination of two atomic species:

$$H + Cl \rightarrow HCl^{+*}$$

where H and Cl, which may be ionic or excited, are produced in the primary processes. The second is an abstraction mechanism:

$$H(\text{or Cl}) + CH_2Cl_2 \rightarrow HCl^{+*}.$$

The third is a molecular elimination mechanism:



$$HCl \xrightarrow{e} HCl^{+*}.$$

The first and third mechanisms are compatible with the quadratic dependence of the emission intensity on the electron-beam current, while the second one is not. The third mechanism is supported by the linear relation between the photoemission intensity and the target-gas pressure, while the first and the second ones are not. The spectrum of a mixture of D_2O and CCl_4 was investigated; if either a recombination or an abstraction mechanism were correct, the emission from DCl^+ would be observed. No DCl^+ bands could be observed, however, even when the emissions of D and Cl^+ were very strong.

The spectrum of HCl^+ has well-resolved vibrational and rotational structures. The rotation-vibration bands of HCl^+ obtained from HCl were compared with those from CH_2Cl_2, as is shown in part in Fig. 7. The structures not only of the parts shown in Fig. 7, but also of the other parts of rotation-vibration bands were found to coincide completely. The relaxation processes of the electronically excited species can be ignored in the present study. Thus, this result reveals that the HCl^{+*} species obtained from CH_2Cl_2 may be formed *via* HCl in the ground state, since the intensity distribution of a band is related with the wave function of the initial and final states, as is given in Eq. (4). If these species were formed through other processes, the rotation-vibration bands would change clearly.

Dibeler and Bernstein[22] observed the CCl_2^+ ion from $CHCl_3$ and $CDCl_3$ by using a mass spectrometer. The impact voltages used in their study were 50 and 70 eV, smaller than the one used in the present study; however, no significant differences in emission spectra have been observed in this energy region, and their results can be carried over on the present study. They suggested that the CCl_2^+ ion was formed primarily by dissociation of neutral HCl or DCl molecules from $CHCl_3$ or $CDCl_3$, rather than by dissociation into the separated atoms, and that the amount of HCl thus produced was larger than that of HCl^+. These results support the molecular elimination mechanism suggested above.

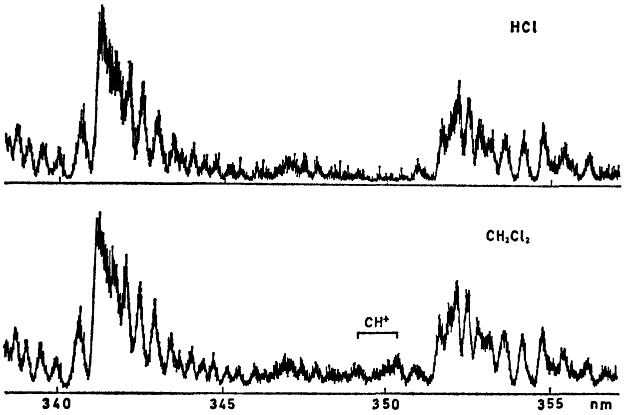


Fig. 7. Comparison of rotation-vibration bands of HCl^+ obtained from HCl with that from CH_2Cl_2. Slit width 50 μm.

Thus, the excited HCl^+ from chlorinated methanes is concluded to be produced mainly by the molecular elimination mechanism.

Since the intensity of the photoemissions of H and CH are expressed in Equation (3), it can be concluded that H and CH are produced in some one-electron unimolecular processes.

The relative intensity of the band of CH to the line of H from chloroform is larger than that in the case of dichloromethane. Since the formation of the CH radical requires the C–H bond rupture in CH_2Cl_2, and since the bond energy of a CH bond is larger than that of a C–Cl bond, the CH radical would be produced more easily from $CHCl_3$. The observation of the 2368 Å system of CCl and the C(I) atomic line in $CHCl_3$ can be explained in the same way.

For the dissociative excitation leading to CH* (4314 Å) from $CHCl_3$, the calculated and the observed threshold are also shown in Table 1. The energy consideration requires that the dissociation process involves Reactions (e)—(g) near the observed threshold. In Reaction (e), however, the excess energy is about 5.6 eV; this energy should be carried away mainly as the translational energy, since CH is not rotationally and vibrationally excited and since the rotational energy of Cl_2 would be small. This value seems to be too large for the total kinetic energy of CH*, Cl, and Cl_2. Even if Cl_2 were vibrationally excited up to the dissociation limit, CH*, Cl, and Cl_2 would still have about 3.2 eV as the kinetic energy. Reaction (e), therefore, makes only a small contribution to the formation of CH* near the threshold region.

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