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H. Okabe, M. Kawasaki, and Y. Tanaka

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The photodissociation of CH₂I₂: Production of electronically excited I₂

H. Okabe

Molecular Spectroscopy Division, National Bureau of Standards, Washington, D. C. 20234

M. Kawasaki^{a)} and Y. Tanaka^{b)}

Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo, 152, Japan (Received 23 July 1980; accepted 2 September 1980)

The primary photodissociation process of CH_2I_2 leading to the formation of electronically excited $I_2({}^3\Pi_{2e})$ has been studied. The process occurs with yields less than 1% for light of wavelengths below 1320 ± 10 Å. The I₂ (${}^{3}\Pi_{2e}$) initially produced by the Kr (1165, 1236 Å) lines is vibrationally excited up to v' = 35. The addition of near atmospheric Ar or N₂ deactivated vibrational quanta to v' = 0, 1, and 2 but little electronic quenching was observed. The quantum yield of $I_2({}^3\!\Pi_{2g})$ production is 0.006 at 1236 Å. At 1306 Å little vibrational excitation of $I_2({}^3\Pi_{2e})$ was seen. In addition, very weak I_2 emission bands in the 2500-2900 and 4500-4900 Å regions were found in CH_2I_2 photodissociation by the Kr lamp. The absorption cross sections of CH₂I₂ in the 1100 to 1500 Å region have been measured and compared with the I₂ (${}^{3}H_{2r}$) fluorescence excitation spectrum. The results show that the I_2 emission bands arise mainly from the underlying absorption continua and not from structured features of CH_2I_2 , suggesting that the σ - σ * transitions in the C-I bond are responsible for yielding $I_2({}^3\Pi_{2g})$, while Rydberg tranitions are ineffective in forming $I_2({}^3\Pi_{2g})$. The dissociation process $CH_2I_2 \xrightarrow{h\nu} CH_2(X {}^3B_1) + I_2({}^3\Pi_{2g})$ involves an energy barrier of almost 1 eV, in agreement with other molecular detachment processes. The Kr photosensitized reaction of CH_2I_2 on the other hand gives rise to the $I_2(H)$ emission in addition to emissions observed in direct photolysis. This state is likely to be ${}^{1}\Sigma_{u}^{+}$ rather than ${}^{3}\Sigma_{u}^{+}$.

INTRODUCTION

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The molecular detachment process plays an important role in the photodissociation of some simple molecules. Such processes are found, for example, in the photolysis of NH_3 , H_2O , H_2CO , and CH_4 (the product being H_2 ¹ and in COCl₂² (the product is electronically excited Cl₂). In the photolysis of halomethanes, the major primary process is the production of halogen atoms, while the formation of molecular products appears to be a minor process.³

The emission bands at 3420 Å were first observed by Dyne and Style⁴ in the vacuum ultraviolet photolysis of $CH_{2}I_{2}$, the emission being ascribed to the production of an electronically excited I2. The same emission bands are excited in I₂ by absorption of light of wavelength near 1350 Å only in the presence of Ar or N_2 .⁵ The 3420 Å laser emission has recently been observed in an Ar-CF₃I mixture by an electron beam excitation.⁶ The 3420 Å emission system has been ascribed to the transition to the ground state⁷ or to the $B^{3}\Pi(0_{u}^{*})$ state⁸ of I₂. However, the recent iostope shift analysis of this emission spectrum by Tellinghuisen⁹ strongly indicates the transition to be ${}^{3}\Pi_{2e} \rightarrow {}^{3}\Pi_{2u}$, corresponding to the 3425 Å absorption bands of I2 at high temperatures observed by Skorko.¹⁰ Since this assignment appears to be generally accepted, the discussion of the present results is based on this assignment.

The quantum yield and threshold energy for I_2 (${}^{3}\Pi_{2x}$) production are of intrinsic interest as well as of importance for the feasibility of photodissociation laser. A comparison of the absorption spectrum of CH₂I₂ with the I₂ $({}^{3}\Pi_{2_{\mu}})$ fluorescence excitation spectrum may provide information on the type of transition responsible for I_2 $({}^{3}\Pi_{2*})$ production, leading to an understanding of the dynamics of the photodissociation process. The present studies are made along these lines.

EXPERIMENTAL

The experimental arrangements have been described before in Ref. 11. Briefly, a hydrogen discharge lamp was used for measuring absorption and fluorescence excitation spectra in combination with a 1 m near normal incidence vacuum monochromator with a 600 lines mm⁻¹ grating. The fluorescence intensity I_{t} was monitored at right angles to the incident beam of intensity I_0 . A broad band filter with 2200 to 4200 Å transmission was placed in front of a photomultiplier measuring I_t . The fluorescence spectrum resulting from the photolysis of CH₂I₂ by resonance lamps was obtained by means of a 0.3 m plane grating scanning monochromator with a 2400 lines mm⁻¹ grating. The detector was a 13 stage photomultiplier with S-13 spectral response. The photolvsis lamps used were Kr (1165, 1236 Å), Xe (1470Å), and O atom (1306 Å) resonance lamps. The pressure was measured by a calibrated transducer. Methylene iodide, obtained commercially, was vacuum distilled and stored in liquid nitrogen.

RESULTS

Fluorescence spectra

The fluorescence spectra observed by the photodissociation of 20 N m⁻² (0.15 Torr) flowing CH_2I_2 by the Kr (1165, 1236 Å) resonance lamp are shown in Fig. 1. The spectra were taken at a scanning speed of 50 Å min⁻¹

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a) Present address: Department of Chemistry, Faculty of Engineering, Mie University, Tsu, 514, Japan.

^{b)}Present address: Dainihon Ink Chemical Corp., Izumi-ohotsu, Osaka, 595, Japan.



FIG. 1. The fluorescence spectra of I_2 in the photolysis of 0.15 Torr CH_2I_2 by the Kr (1165, 1236 Å) resonance lamp; scanning speed 50 Å min⁻¹; time constant 2 s. (A) 3000-3600 Å region; resolution 4 Å, flow system. (B) 3000-3600 Å region; 700 Torr of Ar added, resolution 4 Å, static system; the peak near 3100 Å indicates OH ($^{2}\Sigma^{-2}\Pi$) emission from H_2O impurity. (C) 4500-5000 Å region; resolution 8 Å. (D) 2400-3000 Å region; resolution 8 Å.

with a time constant of 2 s. The main fluorescence spectrum lies in the 2900-3550 Å region with a peak at about 3420 Å as shown in Fig. 1 (A) (a slitwidth of 300 μ m was used corresponding to a nominal resolution of 4 Å).

The spectrum is identical in shape and position with that found originally by Elliott⁷ when I_2-N_2 mixtures were excited by light of an Al spark. This emission is later assigned by Tellinghuisen⁹ as the transition from ${}^{3}\Pi_{2e}$ to ${}^{3}\Pi_{2u}$. With the addition of increasing amounts of N_2 or Ar to CH_2I_2 , the peak intensity increases successively with the concomitant decrease in the intensity towards shorter wavelengths. Figure 1(B) shows the



FIG. 2. The emission spectrum of I_2 observed in the photodissociation of a 0.15 Torr CH_2I_2 and 700 Torr Ar mixture by the Kr lamp; resolution 2 Å, scanning speed 10 Å min⁻¹; 2 s time constant; the band assignments are those by Tellinghuisen.⁹



FIG. 3. (A) The emission bands in the 1800-2400 Å region observed in the irradiation of a 0.3 Torr CH₂I₂ and 0.5 Torr Kr mixture by the Kr lamp. (B) The emission bands for 0.3 Torr CH₂I₂ photolysis; resolution 3 Å; scanning speed 15 Å min⁻¹; 8 s time constant.

emission spectrum observed when a mixture of 93 kN m^{-2} (700 Torr) Ar with 20 N m^{-2} (0.15 Torr) CH₂I₂ was photodissociated by the Kr lamp in a static system. The 3420 Å peak intensity becomes more than twice that without Ar, while the total integrated intensity remains the same with or without added Ar. In addition, some vibrational structures become apparent. The peak at 3100 Å is due to the OH $(^{2}\Sigma - ^{2}\Pi)$ fluorescence arising from the photolysis of H₂O impurity. Besides the 3420Å bands two other weak band systems, each amounting to about 5% in intensity of the main band peak, are found in the 2500-3000 and 4500-5000 Å regions as shown in Figs. 1(C) and 1(D) (taken at a resolution of 8 \AA). The 2800 Å band system (peaks at 2725, 2770, 2830, and 2880 Å) has been seen by Elliott⁷ from I_2 excited by active nitrogen. The diffuse 4700 Å system has peaks at 4600, 4670, and 4765 Å. The spectroscopic assignments of the two systems, seen also in discharge of I_2 -Ar mixtures, ¹² have apparently not been made except for the 2725 Å band that corresponds to the F-X transition.¹²

Figure 2 shows the 3420 Å emission spectrum at a resolution of 2 Å with a scanning speed of 10 Å min⁻¹ and 2 s time constant. The vibrational assignments are made according to Tellinghuisen.⁹ No vibrational features are apparent in the absence of Ar or N₂. The analysis indicates that the upper state $({}^{3}\Pi_{2t})$ is populated up to v' = 2.

No emission was observed in the photodissociation of CH_2I_2 by the Xe (1470 Å) resonance lamp. At 1306 Å a weak emission was observed near 3420 Å with a spectral distribution similar to Fig. 1(B). Figure 3(A) shows the emission spectrum observed in the irradiation of a 40 N m⁻² (0.3 Torr) CH_2I_2 and 66 N m⁻² (0.5 Torr) Kr mixture by the Kr lamp and Fig. 3(B) is the spectrum arising from CH_2I_2 photolysis without Kr added. The excitation of the CH_2I_2 -Kr mixture also produces the emission shown in Fig. 1(A). The 1800–2400 Å emission bands are similar to those found by Haranath and

Rao¹³ in condensed discharge of pure I_2 vapor and are attributed by them to the H-X system.

Quantum yield

The quantum yield of 3420 Å I₂ fluorescence ϕ_f (CH₂I₂) in the 1236 Å photolysis of CH₂I₂ may be obtained in comparison with that of OH ($^{2}\Sigma^{-2}\Pi$) emission ϕ_f (H₂O) in the 1236 Å photolysis of H₂O:

$$\frac{\phi_f (\mathrm{CH}_2\mathrm{I}_2)}{\phi_f (\mathrm{H}_2\mathrm{O})} = \frac{I_f (\mathrm{CH}_2\mathrm{I}_2)}{I_f (\mathrm{H}_2\mathrm{O})} \frac{I_a (\mathrm{H}_2\mathrm{O})}{I_a (\mathrm{CH}_2\mathrm{I}_2)}$$

where I_f is the integrated fluorescence intensity and I_a is the absorption for 1 cm path length 2 cm away from the window at 1236 Å. At 20 N m⁻² (0.15 Torr) values obtained for the 1236 Å line are

$$\frac{I_f (CH_2I_2)}{I_f (H_2O)} = 0.18, \ \frac{I_a (H_2O)}{I_a (CH_2I_2)} = 0.33$$

when the contributions of 50% and 6% to I_f by the 1165 Å line for CH₂I₂ and H₂O, respectively, are subtracted. Adopting ϕ_f (H₂O) = 0.1 at 1236 Å, measured by Lee *et* $al.^{14} \phi_f$ (CH₂I₂) = 0.006 is obtained. Black, ¹⁵ on the other hand, obtained ϕ_f of approximately 0.002 at 1216 Å.

Fluorescence excitation spectrum and absorption cross section

The 3420 Å band intensities I_f in the photodissociation of CH₂I₂ were measured as a function of incident wavelength in the 1100–1350 Å region. The slitwidth of 200 μ m corresponding to a nominal resolution of 3 Å was used in this region. Figure 4 shows the intensity of the fluorescence normalized to that of incident light I_0 as a function of incident wavelength in the 1100–1350 Å region obtained for approximately 33 N m⁻² (0.25 Torr) CH₂I₂. The inset shows the fraction of light absorbed I_a/I_0 in the 1230–1310 Å region measured with the same resolution. The threshold for the production of the 3420 Å bands is at 1320±10 Å corresponding to 9.39



FIG. 4. Fluorescence excitation spectrum of the 3420 Å emission in the photodissociation of 0.25 Torr CH_2I_2 in the 1100-1350 Å region: resolution 3 Å; the inset shows the fraction of absorption for 0.25 Torr CH_2I_2 with the same resolution. The fluorescence yield is 0.6% at 1236 Å.



FIG. 5. The absorption cross sections of CH_2I_2 in the 1100– 1500 Å region; resolution ~ 0.8 Å, pressure ~ 30 m Torr; a Rydberg series converging to I. P. = 10.21 eV is indicated.

±0.07 eV. Black¹⁵ obtained 1420 ± 10 Å for the threshold with an apparently better sensitivity. Several peaks superimposed on the continua in the 1230-1310 Å region are apparent in absorption, while only the continuous transitions are important in the production of the 3420 Å emission. Figure 5 shows the absorption cross sections of CH₂I₂ in the 1100-1500 Å region measured with a slitwidth of 50 μ m corresponding to a nominal resolution of 0.8 Å. The absorption cross section σ is defined as $I_t = I_0 e^{-\sigma n I}$, where I_t and I_0 are transmitted and incident light intensities, respectively, n is the number of molecules per cm³, and l is the path length in cm. The absorption cross sections agree within 10% with those measured by Russell.¹⁶

DISCUSSION

Direct photodissociation of CH₂I₂ by the Kr lamp

Black¹⁵ has shown that the I₂ (3420 Å) fluorescence intensity reaches maximum within 10 ns after flash in the photodissociation of 6 mTorr CH₂I₂. The result indicates that I₂ (${}^{3}\Pi_{2_{f}}$) production is a primary event

$$CH_2I_2 \xrightarrow{h\nu} CH_2 + I_2 (^{3}\Pi_{2s})$$

and is not due to secondary reactions such as¹⁷

I
$$(6s^4P) + CH_2I_2 = CH_2I + I_2 (^3\Pi_{2g})$$

$$\Delta H_0 = -1.19 \text{ eV}^{17}$$

that require the reaction time of at least 50 μ s.

The reaction

$$CH_2I_2 \xrightarrow{\mu\nu} CH_2I + I (6s^4P)$$

requires a photon energy of 8.89 eV corresponding to the incident wavelength 1395 Å. No emission expected from electronically excited I atoms has been observed in the 1800-2100 Å region in the photolysis of CH_2I_2 by the Kr lamp.

Figure 6 shows the transition ${}^{3}\Pi_{2e} \rightarrow {}^{3}\Pi_{2u}$ proposed by Tellinghuisen⁹ for the 3420 Å emission. The potential energy curves follow those given by Mulliken.⁵ Using the vibrational constants obtained by Tellinghuisen,⁹ it may be shown that initially produced I₂ (${}^{3}\Pi_{2e}$) molecules in the photodissociation of CH₂I₂ by the Kr lamp are vibrationally excited up to v'=35. They are collisionally

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FIG. 6. The potential energy diagram of I₂. The potential curves follow those by Mulliken.⁵ The 3420 Å emission is assigned to the ${}^{3}\Pi_{2g} \rightarrow {}^{3}\Pi_{2u}$ transition according to Tellinghuisen.⁹

deactivated by the addition of 700 Torr Ar or N_2 to v'=0, 1, 2. The I-I distance in the ground state CH_2I_2 may be estimated to be 3.6 Å from an I-C-I angle of 114° and a C-I distance of 2.13 Å.18 Referring to Fig. 6, the internuclear distance of I_2 (${}^{3}\Pi_{2s}$) is 3.5 Å. Hence, if the I_2 (³ II_{2s}) molecule is photodissociated from CH_2I_2 without change in configuration, the I_2 , $({}^3\Pi_{2g})$ molecule would have no vibrational energy. The result that the I_2 (${}^3\Pi_{2s}$) molecule is formed with large vibrational energy from CH₂I₂ by the Kr lamp indicates that upon light absorption the I-C-I bending as well as C-I symmetric stretching vibration is excited, resulting in the formation of vibrationally excited I_2 (${}^3\Pi_{2g}$) as the two C-I bonds are simultaneously ruptured. The excitation of I-C-I bending vibration must be proportional to the incident photon energy, since at 1306 Å little vibrational excitation of I_2 $({}^{3}\Pi_{2e})$ was observed. The vibrational distribution of I_{2} $({}^{3}\Pi_{2s})$, when near atmospheric Ar is added, must be Boltzmann as the lifetime of I_2 (${}^{3}\Pi_{2r}$) is 17 ns and the deactivation efficiency by Ar is about 0.1.¹⁵ although spectral resolution is not sufficient to confirm this experimentally.

Kr sensitized photodissociation of CH₂I₂

As shown in Fig. 3, the Kr sensitized photodissociation of CH_2I_2 gives rise to the fluorescence in the 1800-2300 Å region in addition to those shown in Fig. 1. The similar emission bands have been observed by Haranath and Rao¹³ in condensed discharge of pure I_2 vapor and as-

signed by them to the H-X transition. The electronic energy of this state is 48 072 cm⁻¹ (5.96 eV) with designation ${}^{3}\Sigma_{\mu}^{*13}$ or 51 427 cm⁻¹ (6.376 eV) with ${}^{1}\Sigma_{\mu}^{*.19}$

The energy required for the reaction

$$CH_{2}I_{2} \rightarrow CH_{2} (\bar{X}^{3}B_{1}) + I_{2} (H)$$

is 9.37-9.79 eV.²⁰ Hence, the reaction is energetically possible with 10 eV energy of Kr $({}^{3}P_{1})$. In the Kr sensitized photolysis of NH₃, both NH $({}^{1}\Pi)$ and NH $({}^{3}\Pi)$ emissions are observed²¹:

$$NH_3 \rightarrow NH (^{1}\Pi) + H_2,$$

$$NH_3 \rightarrow NH (^{3}\Pi) + H_2,$$

while in direct photolysis only the NH (${}^{1}\Pi$) emission is found, 22 indicating that the spin conservation rules are not as strict in the Kr sensitized reaction as in the direct photolysis. Similar observations have been made for the Kr photosensitized reaction of ethylenimine, 23 i.e., both NH (${}^{1}\Pi$) and NH (${}^{3}\Pi$) have been found, Accordingly, it seems reasonable in the sensitized photolysis of CH₂I₂ to assume that the I₂ (*H*) state is ${}^{1}\Sigma_{u}^{*}$ rather than ${}^{3}\Sigma_{u}^{*}$ since the production of H (${}^{1}\Sigma_{u}^{*}$) is detected only in the sensitized reaction but not in the direct photolysis.

Fluorescence excitation spectrum

The thermochemical threshold for the process

$$CH_2I_2 \rightarrow CH_2 (\bar{X}^3B_1) + I_2 (^{3}\Pi_{2g})$$

is at 8.43 \pm 0.05 eV,²⁴ corresponding to 1470 \pm 10 Å, while the production of I_2 $({}^3\Pi_{2\text{c}})$ in CH_2I_2 photodissociation has been seen only below the incident wavelength 1320 ± 10 Å, i.e., an excess energy of 0.96 eV is required for the production of $I_2({}^{3}\Pi_{2r})$. A large energy barrier for the molecular detachment process has also been observed for photodissociation processes¹ in $NH_3 \stackrel{h\nu}{\rightarrow} NH (b^1 \Sigma^*)$ + H_2 , $H_2CO \stackrel{h\nu}{\rightarrow} H_2 + CO$, and $H_2O \stackrel{h\nu}{\rightarrow} H_2 + O(^1S)$. Presumably, the large excess energy is required in these reactions to bring two H atoms near the equilibrium internuclear distance to form H_2 . As shown in Fig. 4, several peaks apparent in the absorption spectrum (see the inset) are absent in the fluorescence efficiency curve in the 1240-1320 Å region. In analogy with the assignments in CH₂Br₂, ²⁵ these peaks must belong to Rydberg transitions from four 5p orbitals to upper s, p, d orbitals of I atoms. One such formula for ns - 5p transitions is, in cm⁻¹,

$$\nu_n = 82350 - \frac{R}{(n-4.25)^2}, \quad n = 6, 7, 8, \dots,$$

 $R = 109.737 \text{ cm}^{-1}.$

converging to the third ionization potential at 10.21 eV^{26} as shown in Fig. 5. The quantum defect of 4.25 is chosen in accordance with that used for CH₃I.²⁷

The underlying continua may be assigned to the transitions from the C-I bonding σ to the antibonding σ^* orbitals as analogous assignments have been made for the CH₂Br₂ absorption continua.²⁵ Such transitions are likely to excite the symmetric C-I stretching and I-C-I bending vibrations resulting in the production of vibrationally excited I₂ (${}^{3}\Pi_{2g}$). On the other hand, the Rydberg transitions, localized in the I atoms, may excite mainly the C-I stretching vibration ending in the formation of I atoms. The degree of vibration in I_2 (${}^3II_{2r}$) increases from the 1306 Å photolysis to the 1165, 1236 Å photolysis, indicating that the I-C-I bending vibration is more excited at the shorter wavelengths.

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