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CHEMILUMINESCENT REACTIONS OF C^{2+} IONS WITH H_2 MOLECULES

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Chemiluminescence spectra produced by reactions of C^{2+} ions with H_2 molecules were observed with a spectral resolution of 20 Å at collision energies between 5.4 and 22 eV in the center-of-mass system. Emission from the singlet system $CH^+(B\ ^1\Delta)$ was observed as well as the bands due to the triplet system $CH^+(b\ ^3\Sigma^-)$.

In recent years collision processes of doubly charged ions have drawn attention in relation to astrophysics, upper atomosphere processes, plasma physics and chemistry, gaseous electronics, ets. The reaction of C^{2+} ions with H_2 molecules is of special interest because it is closely connected with elementary processes to yield the simplest hydrocarbon radicals. No experiment, however, has been published on the reaction of C^{2+}, except the research by Viggiano et al.[1] They measured the rate constants of the overall reactions taking place in a selected ion flow tube at 300 K, but did not determine the molecular species and states of the individual products. This article describes the results on the chemiluminescent reactions of C^{2+} ions with H_2 molecules using a beam-cell method. As far as we know, this is the first report on chemiluminescent reactions of doubly charged ions in the gas phase.

Details of the experimental apparatus used in this work have been already published,[2] but a brief description is given here. C^{2+} ions are formed from CO gas at discharge voltages of 60-100 V and discharge currents of 200-400 mA in an arc discharge ion source. The pressure of the source gas was held at about 0.6 Torr. Ions produced in the ion source are extracted and accelerated to a specified energy, and then introduced into a magnetic 90° mass analyzer to select C^{2+} ions. Use of the 90° mass analyzer is to prevent the light in the ion source from directly entering the scattering chamber. After being refocused and decelerated with a series of einzel lenses, the C^{2+} ions enter the scattering chamber with an energy determined by the potential difference between the anode of the ion source and the scattering chamber.

The beam currents are monitored by a Faraday cup placed behind the scattering chamber. Typical C^{2+} currents were about 5×10^{-10} A. Target pressure was held at 8×10^{-3} Torr. The kinetic energy spread of C^{2+} ion beams was about 2.4 eV, which was determined by a stopping potential method. The fraction of metastable states that might be involved in the incident beams was determined by means of a beam attenuation method.[3] The result leads us to the conclusion that only a metastable state C^{2+}(perhaps ^3P) is involved in the primary beams by an amount of 30 % for a discharge voltage of 100 eV and 15 % for 60 V.

Light emitted from the excited reaction products is observed through a quartz window perpendicularly to the beam axis by a scanning monochromator (Jobin Ybon, H-20) equipped with a photomultiplier (Hamamatsu TV, Type R585S) cooled below 0°C. The light intensity was measured by a pulse-counting method with a multichannel analyzer (Canberra, Series 30) drived by a microcomputer. Emission spectra were obtained by accumulating the pulses for 700 sec per channel by repeated sweep over 512 channels. One channel corresponds to 1.7 Å of the spectrum.

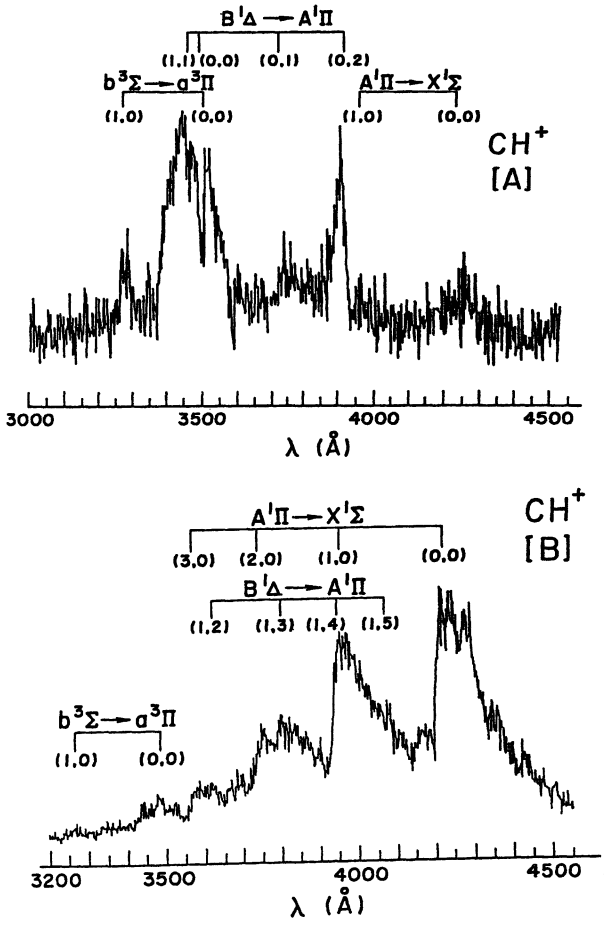

Fig. 1. Emission spectra of CH^+ observed in collision of [A] C^{2+} with H_2 and [B] C^+ with H_2. The profiles of the two spectra are distinctly different from each other. The resolution is 20 Å.

Emission spectrum observed at the relative energy of 7 eV is shown in Fig. 1, in which the emission spectrum produced in the collision of C^+ with H_2 are also exhibited for comparison.[4] No correction was made for quantum yield and spectral efficiency of the instrument. Observed bands are ascribed to the emission from excited states of CH^+($B\,^1\Delta \rightarrow A\,^1\Pi$ and $b\,^3\Sigma^- \rightarrow a\,^3\Pi$) as indicated in the figure.[5] There are also seen very weak bands around

4250 Å. This may be due to $CH^+(A\,^1\Pi \rightarrow X\,^1\Sigma)$, though it is not certain. Assignment of these bands to the emission from excited CH^{2+} ions is precluded because excited states of CH^{2+} ions are supposed to be unstable from the theoretical calculation[6] and have not been found experimentally up to the present.

The incident C^{2+} ion beams contain two states ^1S and ^3P as described above. If $C^{2+}(^1S)$ reacts with H_2, two excited states and the ground state of the singlet system of the ion CH^+ can be produced by spin and orbital symmetry conservation, i.e.,

$$C^{2+}(^1S) + H_2(X\,^1\Sigma_g^+) \rightarrow CH^+(X\,^1\Sigma^+) + H^+ + 9.9\text{eV} \quad (1)$$

$$\rightarrow CH^+(A\,^1\Pi) + H^+ + 7.0\text{eV} \quad (2)$$

$$\rightarrow CH^+(B\,^1\Delta) + H^+ + 3.5\text{eV}. \quad (3)$$

The metastable state ^3P of C^{2+} ions produces CH^+ ($b\,^3\Sigma^-$) as well as $CH^+(a\,^3\Pi)$ by the following exothermic reactions,

$$C^{2+}(^3P) + H_2(X\,^1\Sigma_g^+) \rightarrow CH^+(a\,^3\Pi) + H^+ + 15.3\text{eV} \quad (4)$$

$$\rightarrow CH^+(b\,^3\Sigma^-) + H^+ + 11.9\text{eV}. \quad (5)$$

Present experimental results show that the processes (3) and (5) of the five reactions above certainly take part in the chemiluminescence of C^{2+} ions in collision with H_2 molecules. The emission from $CH^+(A\,^1\Pi)$ was expected to appear in the spectral region longer than 3950 Å owing to the process (2) or, at least, owing to the cascade from $CH^+(B\,^1\Delta)$. It was not observed, however, except for the questionable bands near 4250 Å. This is a striking contrast to the chemiluminescent reaction of $C^+ + H_2$ (Fig. 1[B]). The reason is not known at present, but may have some connection with the closed-shell structure of the C^{2+} ion. The reactions which lead to the ground state ($X\,^1\Sigma^+$) and the metastable state

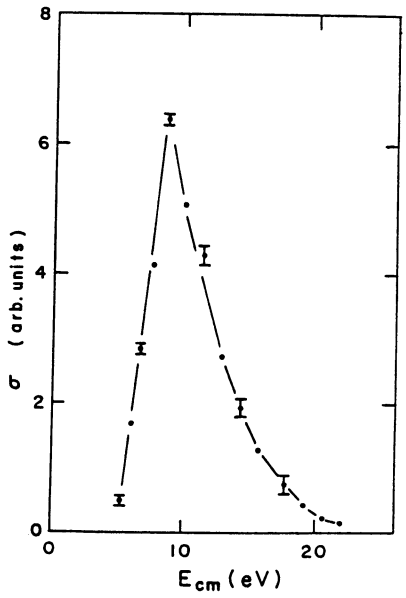

Fig. 2. Energy dependence of relative cross sections σ of the emission around 3500 Å. σ is in units of photon counts per unit time normalized to the beam intensity.

(a $^3\Pi$) are not observable in the present optical experiment.

Although the observed reactions are all exothermic, they appear to have a threshold at about 5 eV, as shown in Fig. 2.[7] The cross section decreases rapidly with increasing beam energy in the region above 10 eV. Occurrence of the chemiluminescent reactions of C^{2+} with H_2 seems to be restricted within the beam energy range 5 - 20 eV in the CM frame.

References and Notes

1) A. A. Viggiano, F. Howorka, J. H. Futrell, J. A. Davidson, I. Dotan, D. L. Albritton, and F. C. Fehsenfeld, J. Chem. Phys., 71, 2743 (1979).

2) T. Ishikawa and H. Inouye, J. Phys. Soc. Jpn., 62, 935 (1979).

3) B. R. Turner, J. A. Rutherford, and D. M. J. Compton, J. Chem. Phys., 48 1602 (1968).

4) Observation of CH^+ emission in collision of C^+ with H_2 was made with the same experimental set up, but the accumulation time of photon counts was 50 sec per channel owing to an order stronger intensity of C^+ beams.

5) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra" (Capman and Hall, London, 1976) p. 91.
K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structures IV. Constants of Diatomic Molecules" (Van Nostrand Reinhold Co., New York, 1979) p. 144.

6) A. J. Lorguet, J. C. Lorguet, H. Wankenne, J. Momigny, and H. Lefebvre-Brion, J. Chem. Phys., 55, 4053 (1971).

7) The bands around 3500 Å are likely to be composed of the 3503 bands of the singlet system and the 3490 bands of the triplet system (Ref. 5). Owing to very low intensity of the emission, we observed the bands en bloc, reducing the resolution of our optical instrument (80 Å in this measurement).

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