LASER-INDUCED FLUORESCENCE OF HCF AND HCCI *

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We report the first observation of the laser-induced fluorescence excitation spectrum of the $\tilde{A}^{1}A''(000)-\tilde{X}^{1}A'(010)$ vibronic band of HCF and some subbands of the $\tilde{A}^{1}A''(030)$ and $\tilde{A}^{1}A''(040)-\tilde{X}^{1}A'(000)$ vibronic bands of HCCl, using the technique of molecular beams.

1. Introduction

Carbenes play a very important role in some reactions of organic syntheses. It is a new trend of research in carbene chemistry to study chemical reactions of electronically excited carbenes, of which the results are bound to promote applications of carbene reactions in organic chemistry. Thus spectroscopic studies of carbenes are significant for carving a new path of research in organic chemistry.

Merer and Travis reported the first spectroscopic observation of HCF [1] and HCCl [2]. Later, Jacox and Milligan reported a low-temperature matrix study of HCF [3] and HCCl [4]. Recently, Patel et al. observed the chemiluminescence spectrum of HCF [5], and several groups reported laser-induced fluorescence (LIF) studies on HCF [6–9] and HCCl [10] successively. In this Letter we report the first observation of the LIF excitation spectrum of the $\tilde{A} {}^{1}A''(000) - \tilde{A} {}^{1}A''(010)$ vibronic band of HCF and some subbands of the $\tilde{A} {}^{1}A''(030)$ and $\tilde{A} {}^{1}A''(040)$ $-\tilde{X} {}^{1}A'(000)$ vibronic bands of HCCl with the technique of molecular beams.

2. Experimental

Fig. 1 shows a schematic diagram of the experimental apparatus. HCF and HCCl were synthesized by reactions of F atoms with CH₃F and CH₃Cl respectively. The F atoms were produced by a microwave discharge of 2450 MHz in CF₄ diluted in Ar. The discharged gas mixture effused into the vacuum vessel through a quartz tube. Fluoromethane effused into the vessel through a stainless steel tube and crossed with the F beam perpendicularly at the center of the vessel. The vacuum vessel was evacuated by a mechanical pump. The vacuum of the vessel was about 0.1 Torr during the measurements. The light source was a ring dye laser (Changchun Institute of Optics and Fine Mechanics, model 801B) pumped by an argon ion laser (Nanjing Electron Tube Factory, model 360). Continuous scanning of the wavelength was achieved by rotating a three-plate



Fig. 1. Schematic diagram of the experimental apparatus.

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birefringent filter with a synchronous motor and a gear drive. The wavelength of the laser light was measured with a monochromator calibrated by a sodium lamp. The fluorescence was detected by a photomultiplier (RCA 31034A) cooled to -40° C by a refrigerator. The photons of the fluorescence were counted by a photon counter (Brookdeal 5Cl, 5C41). Variation in the intensity of the laser as a function of wavelength was monitored by a power meter and plotted synchronously with the analog output of the photon counter by an x-y recorder.

3. Results and discussion

3.1. HCF

Both chemiluminescence and LIF excitation spectra of the reaction product HCF were observed. The chemiluminescence studies of the reaction will be reported separately. The carrier of the LIF excitation spectrum obtained was initially identified to be HCF by chemical evidence and by a comparison between observed (not shown) and literature (fig. 1 of ref. [6]) spectra around 579 nm, which correspond to the subbands of the $\tilde{A}^{1}A''(000)-\tilde{X}^{1}A'(000)$ vibronic band.

Fig. 2 shows the LIF excitation spectrum of the $\tilde{A}^{1}A''(000)-\tilde{X}^{1}A'(010)$ vibronic band of HCF. The laser scanning speed used to obtain the spectrum was



Fig. 2. The LIF excitation spectrum of the $\tilde{A}^{1}A''(000)$ - $\tilde{X}^{1}A'(010)$ vibronic band of HCF. The spectrum is not corrected for variations in the intensity of the laser as a function of wavelength which is indicated.

Table 1		
Frequencies of the Q	heads of the subbands of HCF ((cm^{-1})

<i>K'</i> - <i>K</i> "	Frequencies	
	measured	calculated
7-6	16464	16461
6-5	16341	16338
5-4	16226	16224
4-3	16122	16120
3-2	16031	16028
2-1	15955	15953
1-0	15896	15895
0-1	15856	15856

about 0.15 nm/s. Six well-resolved c-type subbands with $\Delta K = +1$ on the violet side of the band were observed. Their Q heads and the degradation to the violet of the K structure are prominent in the spectrum. The center of the band is very complicated because of the overlap of numerous subbands. However, their Q heads can be definitely identified. The spectrum obtained with a laser scanning speed of about 0.06 nm/s was used to determine the positions of the Q heads of the subbands. The frequencies of the Q heads were obtained by averaging the results from repeated measurements. The results are listed in table 1. The errors were typically ± 3 cm⁻¹ and arose mainly from the instability of the laser power and the hopping of the laser frequency. Within the error limit of the measurements the frequencies of the O heads were in agreement with those calculated from the rotational energy formulas for nearly symmetric tops using the term values of K-rotational levels and constants of the $\tilde{A}^{1}A''(000)$ state reported by Merer and Travis [1] and rotational constants of the $\tilde{\mathbf{X}}^{1}\mathbf{A}'(010)$ state reported by Hakuta [9].

In our experiment HCF molecules were produced by the secondary reaction of the reaction of F atoms with CH_3F . The secondary reaction leads to a chemically activated molecule, which can unimolecularly eliminate HF:

$$F + CH_3F \rightarrow CH_2F + HF,$$

$$\Delta H_0^0 = -34 \text{ kcal/mol},$$

$$F + CH_2F \rightarrow CH_2F_2^* \rightarrow HCF + HF,$$

$$\Delta H_0^0 = -49 \text{ kcal/mol}.$$

The available reaction energy populates the \tilde{X} ¹A'(010) state. The density of the reactants formed as beams in the reaction zone is large compared to a flow system at the same background pressure, and there are no wall effects in the molecular beam apparatus. Those are the reasons why the \tilde{X} ¹A'(010) state can be detected by us. It is significant for determining the nascent internal state distributions of the reaction products and studying the reaction dynamics.

3.2. HCCl

Fig. 3 shows a part of the LIF excitation spectrum of the $\tilde{A} A''(030)$ and $\tilde{A} A''(040) - \tilde{X} A'(000)$ vibronic bands of HCCl in the 570-670 nm wavelength region. According to Merer and Travis [2] we assigned nine Q heads of the subbands of HCCl in



Fig. 3. Part of the LIF excitation spectrum of HCCl in the 570-670 nm wavelength region. The spectrum is not corrected for variations of the laser intensity as a function of wavelength.

Table 2
Frequencies of the Q heads of the subbands of HCCl (cm ⁻¹)

K'-K"	Frequencies	
	$v_2'=3, v_2''=0$	$v_2' = 4, v_2'' = 0$
4-5	15436	16460
3-4	_	16258
2-3	15111	-
0-1	-	15699
2-1	15234	_
3–2	15471	16437
4-3	-	16701

the observed wavelength region. The frequencies of the Q heads are listed in table 2. The errors are typically ± 3 cm⁻¹. Within the error limit of the measurements the frequencies of the Q heads are in agreement with those given by Merer and Travis [2].

It is seen that the appearance of the spectrum of HCCl is quite different from that of the isoelectronic molecules HCF (see fig. 2), as the bands do not show the clearly defined K structure characteristic of transitions of near-symmetric top molecules. The spectrum of HCCl consists of a progression of simple subbands with many weak irregularly spaced features in between. The intensities of the subbands K' = 0-K'' = 1 are rather high, but those of the other subbands are very much lower.

We also observed the LIF excitation spectrum of HCF simultaneously with that of HCCl (see fig. 3). This indicates that a recombination reaction exists in the secondary reaction of F atoms with CH_3Cl , and there are two channels for eliminating hydrogen halides:

 $F+CH_{3}Cl\rightarrow CH_{2}Cl+HF,$ $\Delta H_{0}^{0} = -35.4 \text{ kcal/mol},$ $F+CH_{2}Cl\rightarrow CH_{2}ClF^{*}\rightarrow HCCl+HF,$ $\Delta H_{0}^{0} = -33.6 \text{ kcal/mol},$ $F+CH_{2}Cl\rightarrow CH_{2}ClF^{*}\rightarrow HCF+HCl,$ $\Delta H_{0}^{0} = -40.5 \text{ kcal/mol}.$

References

^[1] A.J. Merer and D.N. Travis, Can. J. Phys. 44 (1966) 1541.

- [2] A.J. Merer and D.N. Travis, Can. J. Phys. 44 (1966) 525.
- [3] M.E. Jacox and D.E. Milligan, J. Chem. Phys. 50 (1969) 3252.
- [4] M.E. Jacox and D.E. Milligan, J. Chem. Phys. 47 (1967) 1626.
- [5] R.I. Patel, G.W. Stewart, K. Casleton, J.L. Gole and J.R. Lombardi, Chem. Phys. 52 (1980) 461.
- [6] M.N.R. Ashfold, F. Castaño, G. Hancock and G.W. Ketley, Chem. Phys. Letters 73 (1980) 421.
- [7] M. Kakimoto, S. Saito and E. Hirota, J. Mol. Spectry. 88 (1981) 300.
- [8] T. Suzuki, S. Saito and E. Hirota, Can. J. Phys. 62 (1984) 1328.
- [9] K. Hakuta, J. Mol. Spectry. 106 (1984) 56.
- [10] M. Kakimoto, S. Saito and E. Hirota, J. Mol. Spectry. 97 (1983) 194.