# Infrared Emission Spectra of Formic Acid Adsorbed on $V_2O_5$

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The infrared spectroscopic study of the molecular species chemisorbed on the surface of solids has been markedly advanced since the experimental method developed by Eischens and Pliskin.[1] Recently, it was indicated that an infrared emission method could be used in special cases for the investigation of the surface of solids opaque to infrared radiation.[2,3]

For the investigation of the reaction intermediate adsorbed on the surface of the solid at a high temperature, it is more available to obtain the emission spectra of species adsorbed on the surfaces of solids. Nakada and Matsushita obtained the absorption spectra in the system of $NH_3$-Fe by correcting for the emission effects.[4] However, infrared emission spectra are not commonly used because the experimental methods using them are more difficult than for absorption spectra. Actually, little work has been done with the emission spectra of species chemisorbed on the surface of the solid. In this spectroscopic research, the emission spectra of formic acid ions adsorbed on the surface of $V_2O_5$ could be observed without the use of any special technique.

## Experimental

**Materials.** The sample of vanadium pentoxide ($V_2O_5$) used was of a commercial grade. Formic acid (commercial grade) was purified by dehydration with anhydrous cupric sulfate (97%) and distilled under a vacuum before use.

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[1] R. P. Eischens and W. A. Pliskin, *Advan. Catalysis*, **10**, 1 (1958).

[2] M. J. D. Low and H. Inoue, *Anal. Chem.*, **36**, 2397 (1964).

[3] M. J. D. Low and H. Inoue, *Can. J. Chem.*, **43**, 2047 (1965).

[4] T. Nakada and S. Matsushita, Presented at 19th Annual Meeting of the Chemical Society of Japan, Yokohama, March, 1966, p. 442.

**Infrared Measurements.** $V_2O_5$ supported on the two surfaces of the KBr plate was placed in the infrared cell (Fig. 1). A mixture of formic acid (15 mmHg) and oxygen (30 mmHg) was then placed in the cell and heated for about 2 hr at 200—250°C, after which the cell was cooled to room temperature. About 12 hr later, the absorption spectra were recorded at room temperature (Fig. 2-A-1). After heating, the absorption and the emission spectra were measured at 100, 150, and 200°C (Fig 2-2, 3, 4).

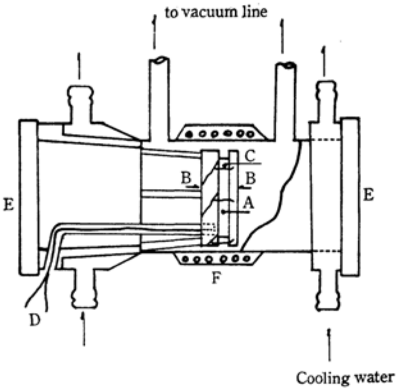

Fig. 1. Schematic diagram of the infrared cell.

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|---|---|
| A | Sample plate (KBr) |
| B | Glass ring |
| C | Glass hook |
| D | Thermocouple |
| E | KBr window |
| F | Heater |

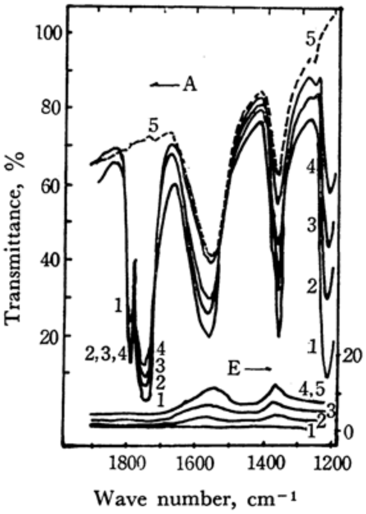

Fig. 2. Absorption and emission spectra of formic acid on $V_2O_5$.

| | |
|---|---|
| A | Absorption spectra |
| E | Emission spectra |
| 1 | At room temperature |
| 2 | At 100°C |
| 3 | At 150°C |
| 4 | At 200°C |
| 5 | After degassing at 200°C |

Eischens and Pliskin proposed[1] to fix the slits of the spectrophotometer at their maximum width. However, it was not necessary to fix the slits of the spectrophotometer at all in this experiment. All the spectra were obtained by the double-beam method.

In the measurements of the emission spectra, the light beam into the cell window was shut out; then the spectra were recorded. All the parts of the cell were made of glass, as is shown in Fig. 1. This cell was fixed in the spectrophotometer and connected with a vacuum line through the ball-joints. The sample plate was fixed between the two glass rings by the use of small glass hooks. All the spectra were recorded in the frequency range from 2000 to 1200 $cm^{-1}$ on a Hitachi EP1-G Model grating infrared spectrophotometer.

## Results and Discussion

The absorption and the emission spectra of formic acid on $V_2O_5$ are shown in Fig. 2. The absorption bands at 1790, 1750, 1570, 1365, and 1210 $cm^{-1}$ appeared at room temperature. No appreciable change in the absorption band at 1570 $cm^{-1}$ was observed upon degassing. The band at 1365 $cm^{-1}$ decreased in intensity, and the other absorption bands completely disappeared upon degassing. The absorption bands of formic acid are found at 1770 (monomer), 1754 (dimer), 1365 (dimer), and 1218 $cm^{-1}$ (dimer).[5,6] From these assignments and the spectral change upon degassing, the band observed at 1790 $cm^{-1}$ is referred to the monomer; those at 1750 and 1210 $cm^{-1}$ to the dimer; that at 1365 $cm^{-1}$ to the dimer and the adsorbed formic acid, and that at 1570 $cm^{-1}$ to the adsorbed species.

The change in intensity with the temperature observed in the bands at 1790, 1750, and 1210 $cm^{-1}$ can be interpreted on the basis of the shift of the thermodynamic equilibrium between the monomer and the dimer of formic acid.

The corresponding bands for the $HCOO^-$ structure, which vary considerably in wave number depending on the formic acid derivatives, were previously observed in the 1310—1390 $cm^{-1}$ and 1540—1610 $cm^{-1}$ [7] regions.

A comparison of the bands of the absorption spectra observed in this work with those reported in the literature indicates that the bands at 1570 and 1365 $cm^{-1}$ in the spectra of chemisorbed species represent formic acid in the form of $HCOO^-$ ions.

The emission spectra could not be observed at room temperature. However, the two broad emission band at *ca.* 1560 and 1365 $cm^{-1}$ appeared at 100—200°C (Fig. 2-E-2, 3, 4). The intensity of these bands clearly increased as the temperature increased. For these emission bands, no change

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5) R. C. Millikan and K. S. Pitzer, *J. Am. Chem. Soc.*, **80**, 3515 (1958).

6) R. C. Millikan and K. S. Pitzer, *J. Chem. Phys.*, **27**, 1305 (1957).

7) J. D. Donaldson, J. F. Knifton and S. D. Ross, *Spectrochim. Acta*, **20**, 847 (1964).

in the spectra could be observed upon degassing. The frequencies of these emission bands were almost the same as those of the absorption bands of formic acid ions. These facts show that these two emission bands can be assigned to formic acid ions chemisorbed on the surface of $V_2O_5$.

In a quantitative investigation of the adsorbed species, it is important to measure not only the emission effect, but also the temperature dependence of the molar absorption coefficient of the species. For this purpose, further analytical and experimental investigations will be necessary. Generally, in the measurements of the emission spectra the observed bands are broad and their intensities are weak. Therefore, the emission method is more difficult than the absorption method. However, in this experiment, the molar absorption coefficient of formic acid was large and the KBr window of the cell seemed to absorb most of the emission beam from the KBr plate on which the $V_2O_5$ sample was placed. Therefore, no change from the routine operation of the instrument was required, and good emission spectra were obtained in this work.