CHEMISTRY LETTERS, pp. 1431-1434, 1981.

OPTOACOUSTIC STUDY OF THE INFRARED MULTIPHOTON EXCITATION OF SF_6

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The optoacoustic effect was used to detect the infrared multiphoton excitation of SF_6 as a function of laser wavelength and laser energy fluence. The red shift of the multiphoton excitation specra was observed and from the laser fluence dependence of the intensity of optoacoustic signals, this phenomenum was found to be arised from the resonance of multiquantum transitions to the overtone levels of SF_6.

The infrared multiphoton excitation spectra of polyatomic molecules have been known to be quite different from the conventional infrared absorption spectra.[1-3] The red shift of the infrared multiphoton spectra of SF_6 has been reported by several investigators.[1,2,4] Similar anormaly of infrared multiphoton excitation spectra was also observed in ethylene.[1,3] In the latter case, the anormaly was found to arise from the resonance of the double quantum transitions to the overtone levels of

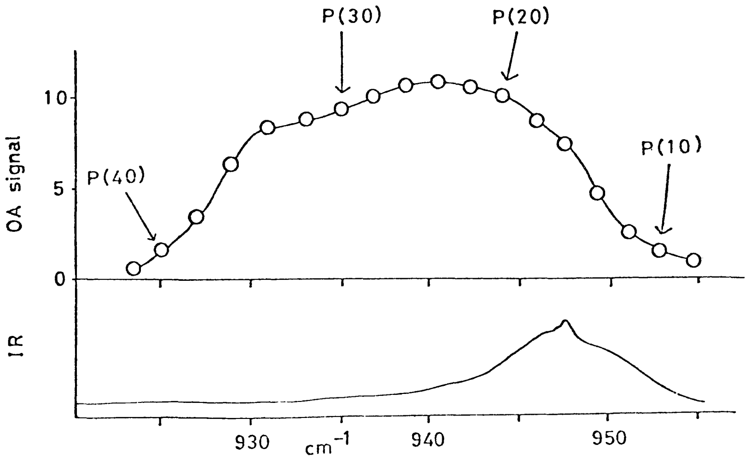

Fig.(1) Multiphoton excitation spectrum in the top and illustration of IR spectrum at the bottom.

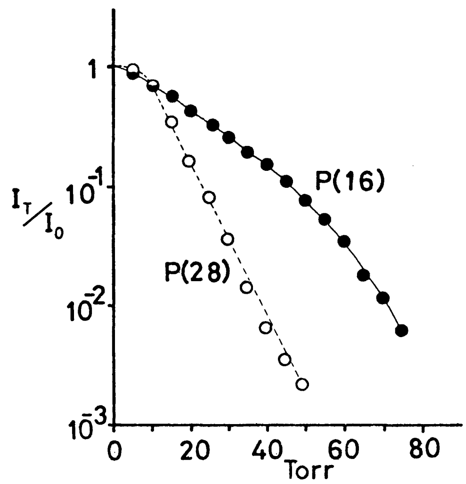

Fig.(2) Energy absorption by SF_6 at the laser wavelength indicated above.

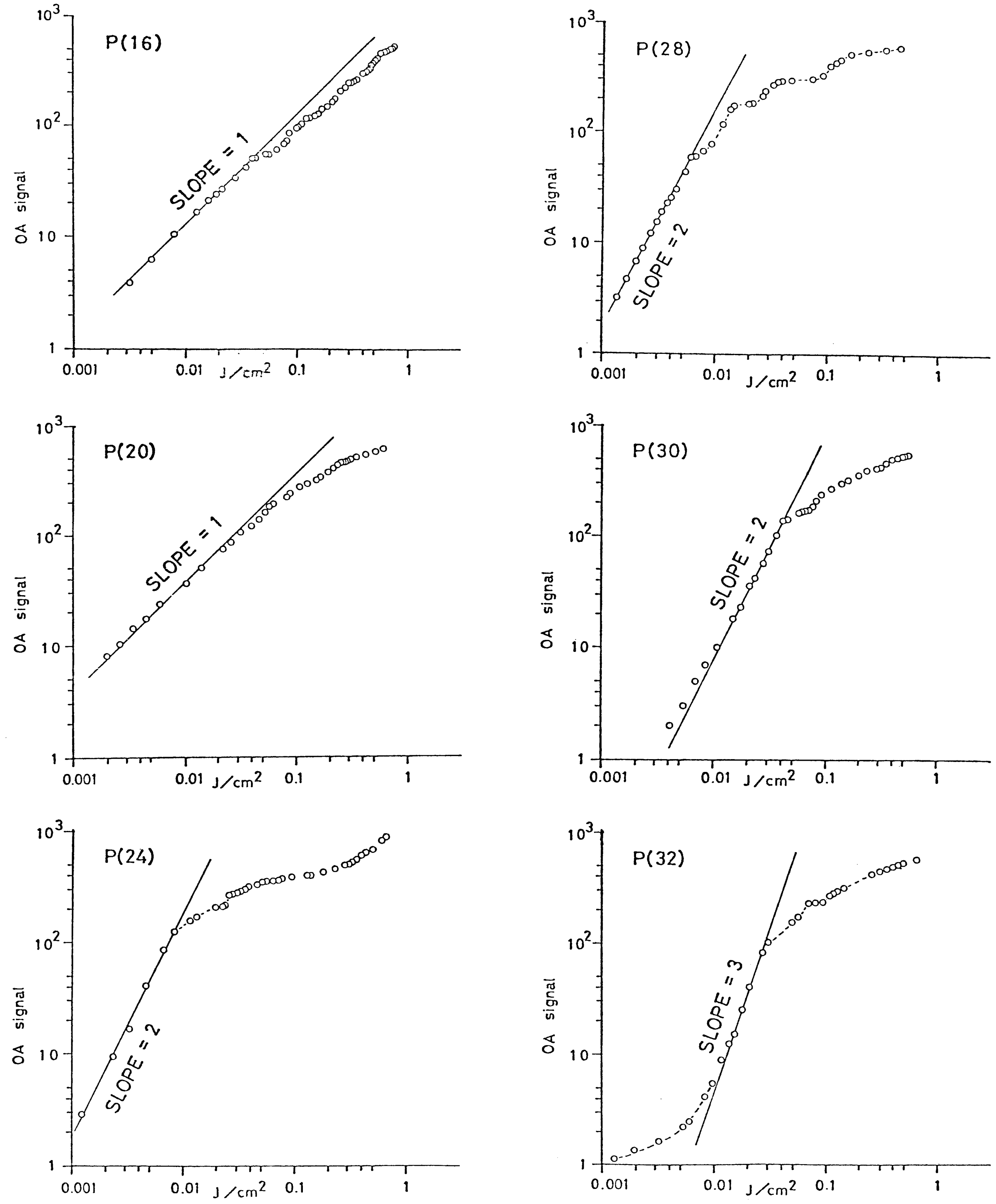

Fig.(3) The dependence of the optoacoustic signals(in milli volts) on the laser energy fluence at the wavelength indicated in the figure.

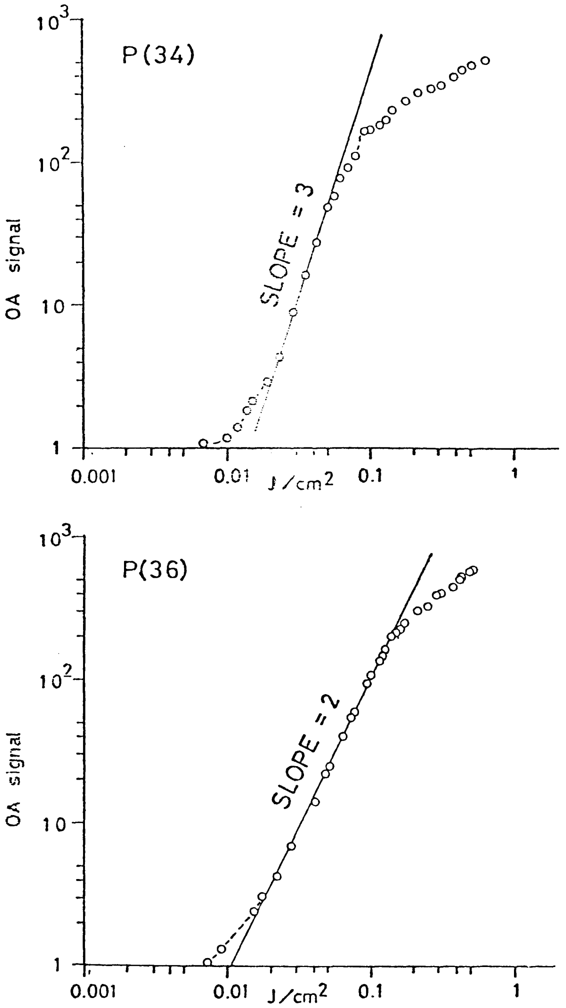

Fig.(3) Continued.

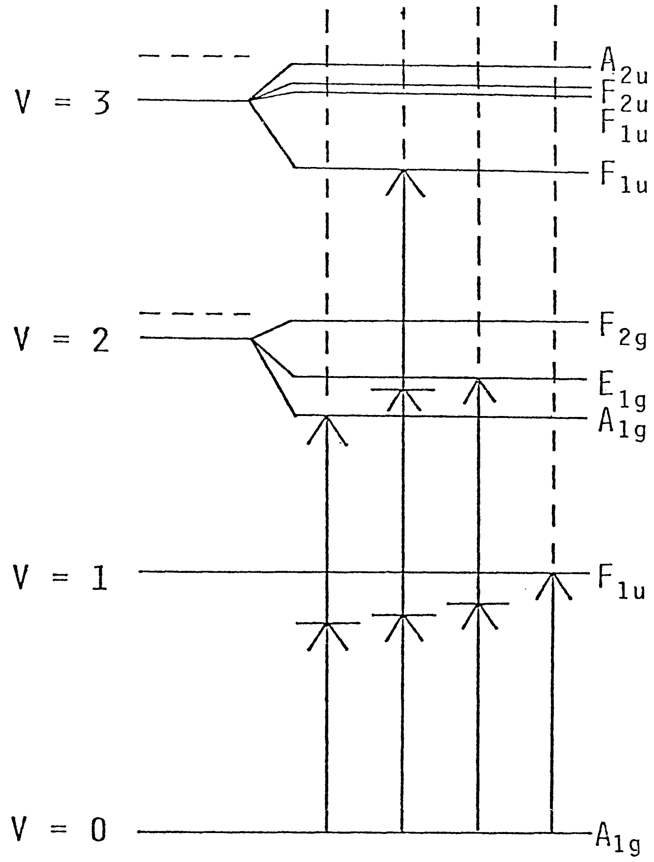

Fig.(4) The schematic of the multiphoton resonances.

out of plane bending modes of ethylene where the Fermi resonance plays a role in shifting the vibrational levels.[3] In those studies, the optoacoustic effect has been used as a useful tool to elucidate the mechanism of the infrared multiphoton excitation.[1-5] In the present study, the behavior of energy absorption by SF_6 under the intense infrared laser radiation was examined in detail as a function of laser wavelength and energy fluence.

The experimental set up was same to that already reported.[3] Briefly, a Lumonics type 103 TEA CO_2 laser was used as an infrared radiation source operating in the multimodes. The laser energy was attenuated by passing through a cell which contained SF_6. The attenuation characteristics are shown in Fig.(2). The optoacoustic cell was a stainless steel cylinder fitted by NaCl windows with a capacitance microphone at the center of the cylinder. The optoacoustic signals were amplified and stored in a strage scope. The fluctuation of the optoacoustic signals from pulse to pulse was within 10 %. All the experiments were performed at 0.4 torr SF_6 pressure in the optoacoustic cell. At this pressure, energy absorption by the optoacoustic cell was negligibly small as shown in Fig.(2). As the poor vacuum must lead to the false experimental results, care was taken to keep low pressure of the optoacoustic cell. The overnight pumping down was found to be necessary for this type of experiment.

Fig.(1) shows the multiphoton excitation spectrum of SF_6 obtained at about 0.3 J/cm^2 along with the illustration of the conventional IR spectrum. The red shift of the multiphoton excitation spectrum is clearly indicated in this figure. In order to elucidate the mechanism of the origin of this red shift, the dependence of the optoacoustic signals on the laser wavelength and laser energy fluence was examined in detail and the results are summerized in Fig.(3).

Fig.(3) clearly shows the anormalous features of energy absorption by SF_6 under the intense infrared laser radiation. At the frequencies of P(16) and P(20), the intensity of the optoacoustic signals was found to increase linearly to the laser energy fluence. This indicates that the energy absorption is due to the single quantum transitions and obviously corresponds to the linear IR absorption spectrum. However, at the lower frequency side, the energy absorption depends on the higher powers of the laser energy fluence and this suggests that the resonance of the multiquantum transitions must play a role in determining the mechanism of the energy absorption. It is easy to see that at the wavelength of P(24) $\sim$ P(30) and P(36) the two photon resonance must play a role and the wavelength of P(32) and P(34) must match to the three photon resonance.

Referring the vibrational energy diagram of the overtone levels of SF_6 calcurated by Cantrell et al.[6] we can easily assign the multiphoton resonances as shown in Fig.(4).

However, the interpretation described above is preliminary and tentative, because there is a serious difficulty in that the behavior of the energy absorption at the wavelength longer than P(30) line shows a curious feature that it has a foot at the lower energy side if we try to interpret these data in terms of simple perturbation theory. So, more detailed theoretical analysis must be necessary to clarify the the mechanism of the infrared multiphoton processes in SF_6.

References

1. V.N.Bagratashvilli, I.N.Knyazev, V.S.Letokhov, and V.V.Lobko, Optics Commun., 18 (1976) 525.
2. T.F.Deutch, Optics Lett., 1 (1977) 25.
3. T.Fukumi, Optics Commun., 30 (1979) 351.
4. J.G.Black, E.Yabronovich, and N.Bloembergen, Phys.Rev.Lett., 38 (1977) 1131.
5. D.M.Cox, Optics Commun., 24 (1978) 336.
6. C.D.Cantrell, H.W.Galbraith, and J.Acherhalt, in "Multiphoton Processes" ed. J.H.Eberly and P.Lambropoulos, John Wiley & Sons (1978) p307.

(Received June 19, 1981)