

VIBRATIONAL SPECTRUM OF THE THIOMETHOXY (CH₃S) RADICAL INVESTIGATED WITH INFRARED-VACUUM ULTRAVIOLET PHOTOIONIZATION

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We produced methylthio (or thiomethoxy, CH₃S) radicals by photodissociation of CH₃SH in a supersonic jet at 248 nm. The CH₃S⁺ ions were subsequently produced with the 1+1 IR-VUV photoionization and detected with the time-of-flight (TOF) technique. The IR spectrum of CH₃S was obtained on tuning the wavelength of the IR laser in the range 2780–3280 cm⁻¹ while monitoring the intensity of the CH₃S⁺ signal; the frequency of the VUV laser was maintained at 134.8 nm, 200 cm⁻¹ below the ionization threshold of CH₃S (IE = 9.225 eV). This technique has an advantage over other IR-absorption techniques because its mass selectivity eliminates interferences from the precursor and other photolysis products such as H₂CS, CH₃, or CH₃SS. Absorption bands near 2820, 2904, and 3215 cm⁻¹ were observed and tentatively assigned as transitions from the ground vibrational state to the 1¹, 4¹ (a₁), and 5¹6² states, respectively. These bands are in agreement with those reported for CH₃S produced via in situ photolysis of CH₃SH, CH₃SCH₃, and CH₃SSCH₃ isolated in solid p-H₂.^[1] A new band near 2970 cm⁻¹ that is consistent with that observed in photoelectron spectrum^[2] might be assigned to the transition from the ground vibrational state to the a₁ component of the 5¹6² state.

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