Two-Photon $\tilde{C}\ ^1B_2$(n, 4s) ← $\tilde{X}\ ^1A_1$ Absorption of Thioformaldehyde as Observed in (2+2) Resonance Enhanced Multiphoton Ionization Spectroscopy[1]

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Two-photon $\tilde{C}\ ^1B_2$(n, 4s) ← $\tilde{X}\ ^1A_1$ absorption of methanethial (thioformaldehyde) H_2CS has been probed by (2+2) resonance enhanced multiphoton ionization spectroscopy (REMPI) for the first time. The REMPI spectrum has a well developed rotational structure with O, P, Q, R, and S branches, which has been simulated using rotational constants reported by Moule and co-workers.

Continued interest is on methanethial (thioformaldehyde) H_2CS, a transient molecule which plays an important role in many astronomical systems. It plays an important role in photochemical evolution of sulfur-containing molecules on Jupiter.[2] It is found in comets, translucent molecular clouds, and interstellar matter.[3] Its spectroscopy has been studied experimentally by Moule's group,[4–7] and Clouthier and Ramsay.[8] Excited state decay dynamics were studied by the authors' group,[9,10] Bruno and Steer,[11] and Clouthier and coworkers.[12,13] Potential energy curves were obtained theoretically by Harchey and Grein.[14,15] Among singlet–singlet transitions only the S_1—S_0 ($\tilde{A}\ ^1A_2$ — $\tilde{X}\ ^1A_1$) transition is observed in the visible (610–440 nm) region. The other transitions are located in the UV region. While the former is extensively studied, not much progress has been made in UV after the works made in the early 80's by Moule and coworkers.[5–7]

In the present paper, two-photon $\tilde{C}\ ^1B_2$(n, 4s) ← $\tilde{X}\ ^1A_1$ absorption has been measured by (2+2) resonance-enhanced multiphoton ionization (REMPI) spectroscopy. Microwave-optical double resonance (MODR) works on rotational bands in the $\tilde{A}\ ^1A_2$ — $\tilde{X}\ ^1A_1$ transition were reported.[16,17] IR–IR, IR–radio frequency and IR–MW double resonance experiments were made.[18] However, no visible–visible double resonance mearsurements have been reported to the best of our knowledge.

Thioformaldehyde H_2CS was prepared by pyrolysis (820 °C) of thietane $(CH_2)_3S$, and flowed between two planar Ti electrodes (1 cm ϕ) in a vacuum chamber. The gas pressure was ca 0.9 Torr (1 Torr = 133.3 Pa). Pulsed laser light from an excimer laser-pumped dye laser (Lambda Physik) was focused by a quartz lens (f = 100 mm) into the volume between two electrodes. DC voltage of ca. 350 V was applied between the electrodes. Ion current was amplified, intergrated by a boxcar integrator (PAR 162/164), and fed to a chart recorder.

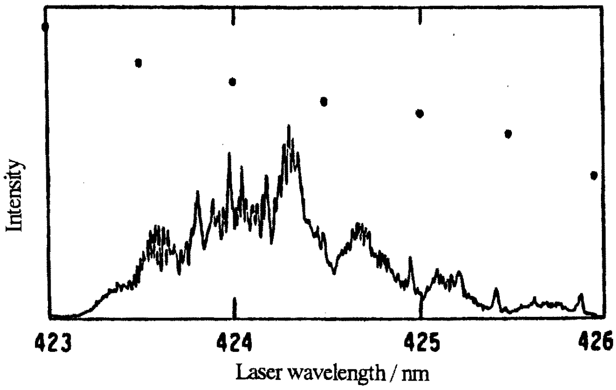

Figure 1. Observed MPI spectrum. The laser power is shown by small open circles.

The obtained MPI spectrum is shown in Figure 1. The spectrum is composed of several bands together with some sharp spikes. Moule and coworkers observed a 4s ← n Rydberg transition near 212 nm.[5–7] Drury and Moule reported high-resolution study of the transition.[5] Our MPI spetrum centered at ca. 424 nm can be assigned to a two-photon transition to the (4s ← n) Rydberg excited state. It was assumed that the observed spectrum corresponds to the rotational structure of a single vibrational band. A simulation of the observed band was performed

Table 1. Rotational constants (cm^{-1}) used in the simulation[a]

	$\tilde{X}\ ^1A_1$[b]	$\tilde{C}\ ^1B_2$[c]
A	9.7294	8.5575
B	0.5904	0.6033
C	0.5555	0.5619

[a] $(B+C)/2$ was used instead of B and C in the simulation. [b] From Ref. 4. [c] From Ref. 7.

Table 2. Placzek-Teller factors $b^{JK}_{J'K'}$ (from Placzek[19])

K' \ J'	J	J+1	J+2
K	$\frac{[J(J+1)-3K^2]^2}{J(J+1)(2J-1)(2J+3)}$	$\frac{3K^2[(J+1)^2-K^2]}{J(J+1)(J+2)(2J+1)}$	$\frac{3[(J+1)^2-K^2][(J+2)^2-K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$
K+1	$\frac{3(2K+1)^2(J-K)(J+K+1)}{2J(J+1)(2J-1)(2J+3)}$	$\frac{(J-2K)^2(J+K+1)(J+K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
K−1	$\frac{3(2K-1)^2(J+K)(J-K+2)}{2J(J+1)(2J-1)(2J+3)}$	$\frac{(J+2K)^2(J-K+1)(J-K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$

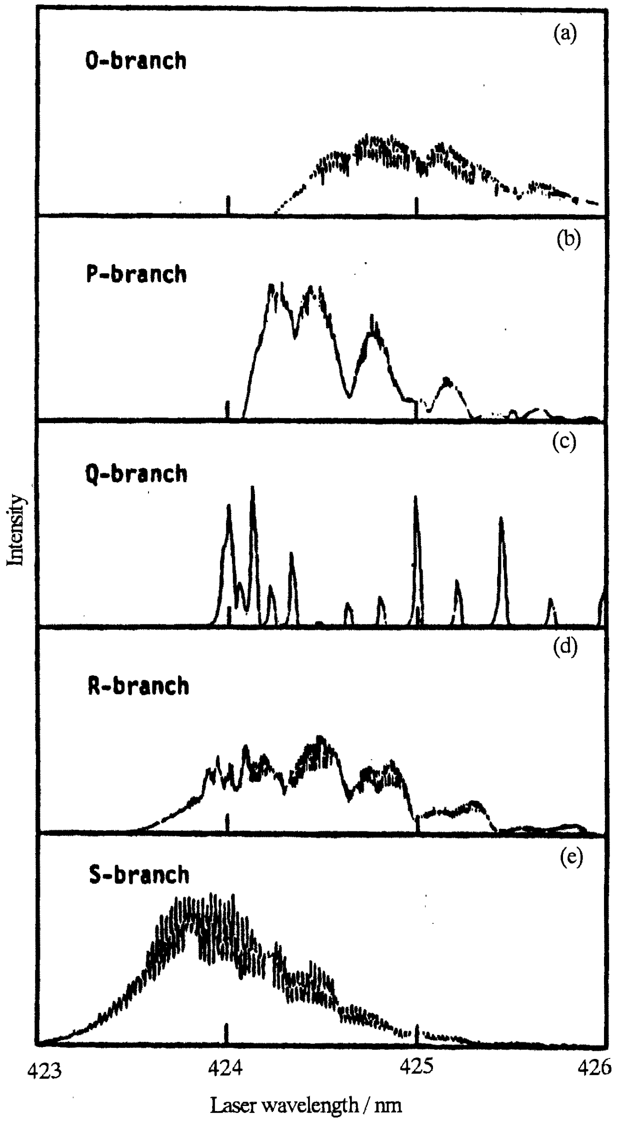

Figure 2. Simulated component spectra. (a)-(e) is for the O-, P-, Q-, R-, and S-branch, respectively.

using the rotational constants reported by Moule and coworkers (Table 1).[4,7] Although thioformaldehyde is an asymmetric top, our simulation was made for a symmetric top, using the average of $B + C$ in stead of two constants B and C. The selection rule for the two-photon absorption is $\Delta J = 0, \pm1, \pm2$ and $\Delta K = \pm1$. The ground-state molecules were assumed to obey a Boltzmann distritution (T = 298 K). Intensities of each rotational line are given using Placzek–Teller factors $b_{J'K'}^{JK}$ reproduced in Table 2 for convenience.[19] The factors for $J' = J - 1$ and $J - 2$ are obtained using the relationship

$$(2J+1)b_{J'K'}^{JK} = (2J'+1)b_{JK}^{J'K'} \qquad (1)$$

Figure 2(a)–(e) is simulated results for O-, P-, Q-, R- and S-branch, respectively. Their sum is shown in Figure 3. As shown, the simulation essentially reproduces the observed spectrum. There remain, however, some spikes not reproduced. They may come from different origin(s).

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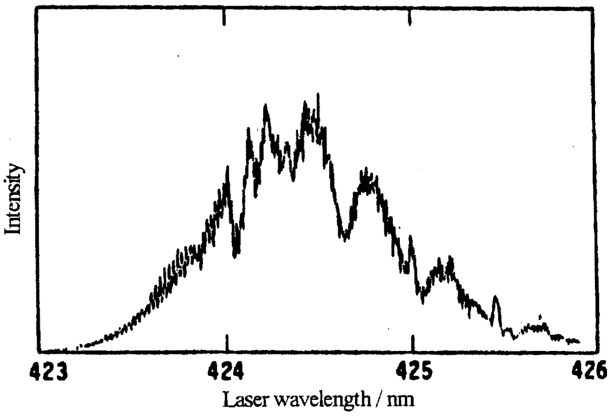

Figure 3. Total simulated spectrum (sum of (a)-(e)).

References and Notes

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