

Multiphoton Ionization of Formaldehyde: Observation of $3p_y$ and $3p_z$ Rydberg States

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Multiphoton ionization (MPI) of CH_2O and CD_2O is reported for dye laser wavelengths between 445 and 470 nm. The ionization pathway starts with three-photon resonant absorption to $3p_y$ and $3p_z$ Rydberg states. One or two additional photons are required, depending on wavelength, to reach threshold. MPI spectra agree well with VUV absorption measurements of the same Rydberg levels. MPI yields are small and photo-acoustic measurements imply the initial three-photon excitation has low probability. Transitions at the four-photon ionization threshold show larger cross sections than the (overall) five-photon ionization bands but hot band transitions were not observed following selective vibrational excitation of ground state molecules.

KEY WORDS: Multiphoton ionization; MPI; Formaldehyde; Rydberg.

Formaldehyde may have the dubious distinction of being the most extensively studied polyatomic molecule in the areas of photochemistry and photophysics.¹ Most work has focussed on the complex interactions among the $\tilde{X}^1A_1(S_0)$, $\tilde{A}^1A_2(S_1)$ and $\tilde{a}^3A(T_1)$ states and the dissociation channels to $\text{H}_2 + \text{CO}$ or $\text{H} + \text{HCO}$. In contrast, high lying electronic states of formaldehyde have not received comparable detailed attention²⁻⁶ despite the advent of non-linear multiphoton spectroscopies that probe energy levels well into the vacuum UV region using visible and near-UV dye laser wavelengths with sub- cm^{-1} resolution.⁷⁻¹⁰ Formaldehyde's absence from the multiphoton ionization (MPI) literature¹¹ is surprising in light of the fact that the next higher

homologue, acetaldehyde, is the subject of thorough MPI study.¹² This note describes multiphoton ionization of CH₂O and CD₂O using dye laser wavelengths between 445 and 470 nm.

The beam from an Nd:YAG-pumped dye laser operating at 10 Hz is focussed into a glass and stainless steel flow cell using a telescope with an effective focal length of 40 cm. The calculated laser spot size is 22 μm. The beam is obviously multimode and astigmatic, therefore, a 150 μm spot size is a more realistic estimate.¹³ Energies of 3–5 mJ in 5 ns pulses are obtained with the dye Coumarin 460 resulting in 3–6 GW cm⁻² peak irradiance. The focal zone is straddled by two electrodes, one biased at -300 V and the other connected to a 1 MHz bandwidth amplifier. Amplified transient photocurrents are measured using a boxcar as the excitation wavelength is varied. The dye laser grating drive was calibrated using the optogalvanic effect. Wavelength uncertainties are ±0.05 nm and the manufacturer's stated laser bandwidth is 0.25 cm⁻¹. Formaldehyde and formaldehyde-*d*₂ (98 at.% D) were prepared continuously by the slow cracking of the corresponding paraformaldehydes at 80°C.

Three-photon resonances to formaldehyde 3*p_y* and 3*p_z* Rydberg states are expected in the wavelength range covered.³⁻⁵ At dye laser frequencies above 21 912 cm⁻¹ (21 942 cm⁻¹ for CD₂O) absorption of one more photon exceeds the 10.87 eV formaldehyde ionization potential (10.88 eV for CD₂O) whereas lower frequencies require two additional photons to ionize the Rydberg states.¹⁴ Figure 1 shows the MPI spectrum of CH₂O (top) and CD₂O (bottom) as a function of three times the laser frequency. Positions of the vibrational levels in 3*p_y* and 3*p_z* Rydberg states reported by Lessard and Moule are also indicated.⁵ Vertical arrows mark energy thresholds for four-photon ionization. All features in the CD₂O MPI spectrum are assigned readily using Lessard and Moule's single photon results.⁵ For CH₂O, the agreement of the three strongest bands is good except the MPI spectrum does not reveal the doublet character of the 3*p_y* origin. Assignment of the two bands between 66 400 and 67 000 cm⁻¹ is not immediately obvious; however, these two bands also appear with similar intensity relative to the 3*p_y*(¹A₁) + 6₀³ transition in the CH₂O VUV absorption spectrum published by Mentall *et al.*³

MPI bands in Figure 1 are blue shifted relative to Lessard and Moule's tabulated values.⁵ In the lower spectrum, the shift is about 30 cm⁻¹ for all major peaks. Shifts appear larger and less uniform for

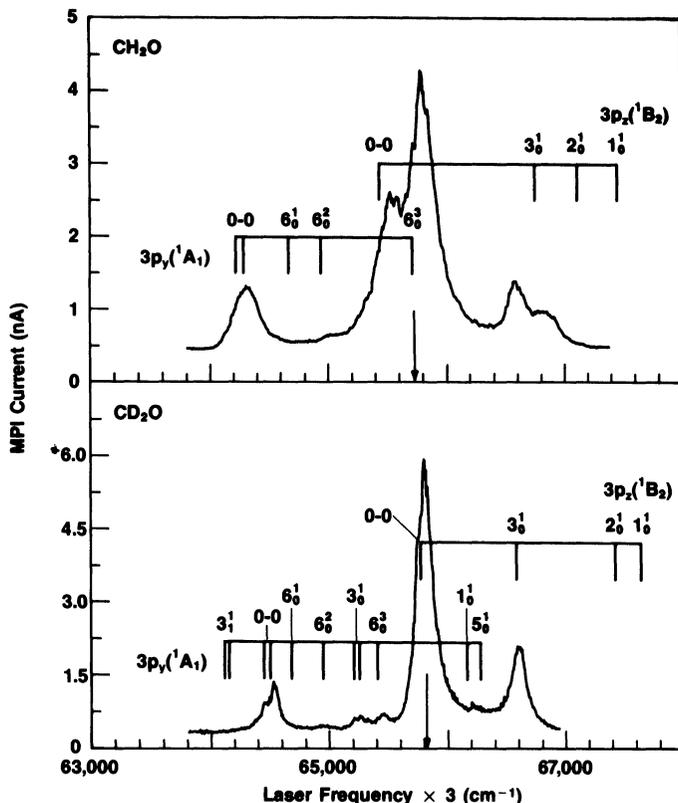


FIGURE 1 MPI spectra of CH_2O (top) and CD_2O (bottom) obtained using 1.0 Torr of gas and dye laser wavelengths between 445 and 470 nm. Vertical lines locate Rydberg levels assigned by Lessard and Moule. Doublets indicate *P* and *R* branches. Arrows indicate four-photon ionization threshold.

CH_2O resulting, in part, from the difficulty of locating accurately the maxima of relatively broad MPI bands. The systematic component of the frequency difference may be attributed to small errors in calibrating VUV spectrometers; at 150 nm, a 0.05 nm error translates to 22 cm^{-1} whereas the same magnitude error in dye laser wavelength measurement equals only 7 cm^{-1} in tripled frequency. The CH_2O $3p_z$ origin is located at $65\,451\text{ cm}^{-1}$ by Lessard and Moule⁵ whereas Allison and Walsh report $65\,494\text{ cm}^{-1}$,³ Mentall *et al.* quote $65\,518\text{ cm}^{-1}$,³ and the MPI value is $65\,548 \pm 15\text{ cm}^{-1}$.

Formaldehyde MPI efficiencies over the wavelength range studied are very low. We conservatively estimate only 1 molecule in 10^6 ionizes at the strongest transitions. This low ionization probability dictates use of irradiances well in excess of 1 GW cm^{-2} which can impose unwanted effects such as power broadening and AC Stark shifting.⁹ Power broadening may explain the lack of definition of the MPI bands, Figure 1, including the inability to resolve the *P* and *R* branches in the $\text{CH}_2\text{O } 3p_y$ origin. Unfortunately, a factor of 2.3 reduction in peak irradiance effected by a 50% increase in the telescope focal length diminishes MPI signals to unusably low levels.

Photoacoustic measurements of CH_2O absorption over the 445 to 470 nm wavelength range fail to produce a signal in excess of noise even with formaldehyde pressures up to 50 Torr and as much as 300 Torr added argon buffer. The photoacoustic cell sensitivity was estimated by comparing a propene $v=5$ overtone spectrum between 13 350 and 14 000 cm^{-1} with Wong and Moore's calibrated spectrum;¹⁵ absorbed energies of 20 nJ were measured with a signal-to-noise rate of ~ 50 implying that a formaldehyde three-photon absorption efficiency of $\sim 1 \times 10^{-5}$ would produce a signal three times the noise level. The combination of the low MPI efficiency and the lack of detectable photoacoustic signal indicates the three-photon absorption cross section is relatively small and that predissociation from the Rydberg levels is not overwhelmingly faster than up-pumping to ionization.

Mentall *et. al.*³ obtained nearly identical extinction coefficients for the formaldehyde $3p_y$ origin and the $3p_z$ origin with the $3p_y(A_1) + 6_0^3$ transition at about 22% lower intensity. The relatively large $3p_y(A_1) + 6_0^3$ MPI band intensity (Figure 1, top) probably occurs because four-photon absorption *via* the 6_0^3 level is sufficient for ionization but both vibrationless transitions require a total of five photons to exceed the CH_2O ionization potential. Similarly, the prominence of the $\text{CD}_2\text{O } 3p_z$ origin (Figure 1, bottom) is attributed to the band's location at the four-photon ionization threshold. Unfortunately, attempts to perturb formaldehyde- d_2 MPI yields by vibrational excitation of molecules in the ground electronic state have not yet been successful. In a two-colour experiment, 850 μJ pulses from a continuously tunable IR laser¹⁶ (0.2 cm^{-1} bandwidth) in resonance with the *Q*-branch of the $\text{CD}_2\text{O } \nu_1$ mode¹⁷ at 2061.3 cm^{-1} did not have any measurable effect on CD_2O MPI yields although photoacoustic measurement indicated

the vibrational transition was saturated. The IR pulse preceded the dye laser pulse by $< 1 \mu\text{s}$. (Deuterated formaldehyde was used in this experiment because it exhibits a strong IR absorption coincident with a high energy output wavelength range of the Raman laser.)

We conclude that formaldehyde MPI yields are primarily limited by the low efficiency of the initial three-photon excitation. The large peak powers required to drive this process lead to line broadening and diminish the amount of spectroscopic information available. CD_2O MPI bands are sharper than CH_2O bands and indicate Lessard and Moule's tabulated values should be increased uniformly by 30 cm^{-1} in the $64\text{--}67\,000 \text{ cm}^{-1}$ region.⁵ Higher resolution data may be possible using two-photon resonant MPI as suggested by Robin for the $2b_2 - 3p_x$ transition.^{2b}

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