

Rapid Communication

UV Laser Photofragment GaCH_3 Detected by Far UV Laser Mass Spectrometry

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Abstract. The GaCH_3 radical has been directly detected by far UV laser mass spectrometry for the first time, as a UV laser photofragment from gaseous trimethylgallium $\text{Ga}(\text{CH}_3)_3$, but not from triethylgallium, $\text{Ga}(\text{C}_2\text{H}_5)_3$. The relative yield $Y(\lambda)$ of GaCH_3 was measured, at various UV photolysis laser wavelengths $\lambda = 193, 210$ and 245 nm, and follows the absorption spectrum of the $\text{Ga}(\text{CH}_3)_3$ precursor molecules.

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Even though the GaCH_3 radical has been considered as one of the main photofragments from UV laser photodissociation of trimethylgallium, no direct evidence has so far been given to identify the existence of this photofragment [1,2]. It is important to detect this radical, not only for finding the mechanism of UV-photodissociation of TMG [1] but also for the understanding of carbon incorporation in the Laser-MOVPE and ALE (Atomic Laser Epitaxy) using Ga-alkyls as precursor of Ga [3]. In the following experiment, which takes advantage of far UV laser mass spectrometry, we succeeded in a direct detection of the photofragment GaCH_3 from TMG molecules exposed to a UV laser pulse.

1. Experiment

The time-of-flight mass spectrometer used has been described elsewhere [4]. The metal-alkyls (Alfa-Ventron) used were the gallium-alkyls (electronic grade) trimethylgallium (TMG), $\text{Ga}(\text{CH}_3)_3$ and triethylgallium (TEG), $\text{Ga}(\text{C}_2\text{H}_5)_3$ and trimethylaluminum (TMA) [5]. Excimer lasers (ArF at 193 nm, KrF at 248 nm) and a frequency doubled (FD) dye laser (Lambda physics, FL3002, 200–250 nm) were used as either the photolysis laser or the probe laser. With a combi-

nation of two of the above lasers, the delay time between them is tunable, and therefore, the role of each laser can be switched from photolysis laser to probe laser, which generates the far UV laser mass spectrum.

2. Results

Figure 1(a) gives typical time-of-flight mass spectra, to show the direct detection of the photofragment GaCH_3 formed in UV laser irradiation of TMG molecules: Ga^+ ($m/e=69$ and 71) and small $\text{Ga}(\text{CH}_3)_2^+$ ($m/e=99$ and 101) ion signals induced by the *first* UV laser at 210 nm (FD dye) alone (top trace), whereas Ga^+ ($m/e=69$ and 71) and GaCH_3^+ ($m/e=84$ and 86) ion signals by the *second* laser at 248 nm (KrF) alone, but with a time delay of $\Delta t = 0.2 \mu\text{s}$ (bottom trace). In the middle trace, a marked enhancement of the GaCH_3^+ signal is caused by the 248 nm laser following the 210 nm laser, due to the first laser induced neutral species [6], i.e. GaCH_3 radicals. To confirm this, TMA was introduced into the chamber. In the middle trace of Fig. 1(b), here again, the (enhanced) AlCH_3^+ signal is induced only by the 248 nm laser following the photolysis laser at 193 nm, demonstrating that the AlCH_3 radicals, identified previously by tunable

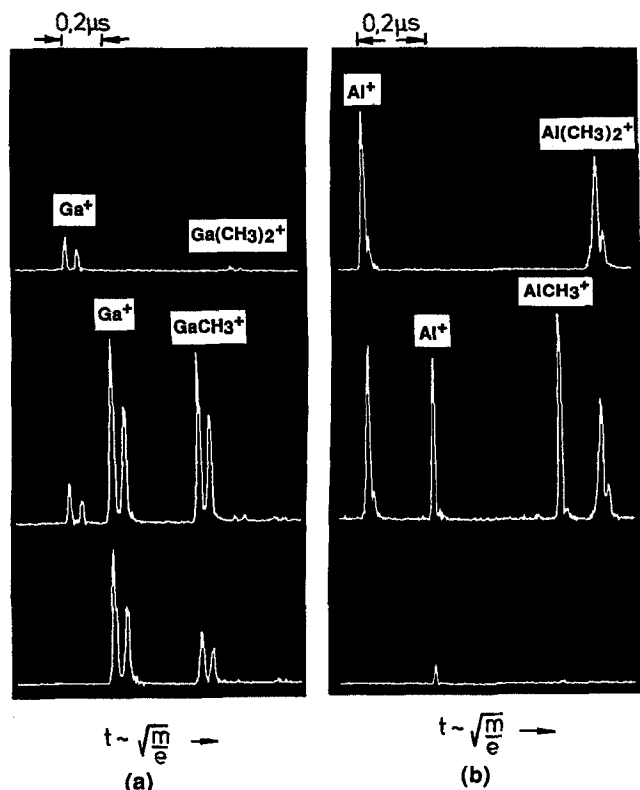


Fig.1. Far UV laser ionization time-of-flight mass spectra of gaseous organometallics, (a) trimethylgallium (TMG), $\text{Ga}(\text{CH}_3)_3$, and (b) trimethylaluminum (TMA), under different experimental conditions:

(top trace): only the photolysis laser at 210 nm (a) and 193 nm (b)

(middle trace): the same photolysis laser, followed by the probe 248 nm laser with delay time $\Delta t = 200$ ns.

(bottom trace): only the probe 248 nm laser. The shift of the second M^+ signal (M: Ga, Al) with respect to the first M^+ signal indicates the time difference ($\Delta t = 200$ ns) between the two lasers

In the middle trace, the enhancement in M^+ and MCH_3^+ ion signal is due to the corresponding first laser induced neutral species, namely, M and MCH_3 (M: Ga, Al)

dye laser mass spectrometry [5], can also be detected by the far UV laser here.

In the middle trace of Fig.1(a) there is only a small increase of the Ga^+ signal due to the detection laser, because 248 nm is an unsuitable wavelength for the detection of Ga atoms [7]. However, the ArF laser can be taken as the probe laser since the energy of 193 nm photons is 6.4 eV, enough to overcome the ionization potential of gallium at 6.0 eV [8]. Actually, simply by only changing the delay time between the two lasers, the 193 nm laser becomes the detection laser and the 248 nm or 210 nm laser becomes the photolysis laser. A considerably

enhanced Ga^+ signal due to the second laser at 193 nm is observed, indicating that free Ga atoms are formed in large abundance from TMG molecules exposed to the laser pulse either at 210 nm or at 248 nm.

It is known from our previous studies [9], that transient GaH photofragment molecules can be formed from TEG molecules under 193 or 248 nm excimer laser irradiation. For comparison, TEG alone was also introduced into the chamber under the same experimental conditions of Fig.1. No GaCH_3 was found from TEG molecules.

Small numbers of metal-dialkyl photofragments, i.e. ML_2 (M=Al, Ga and L= CH_3 , C_2H_5) were detected for 248 nm laser irradiation of the metal-trialkyl precursor, as shown in Fig.2, for TEG as an example.

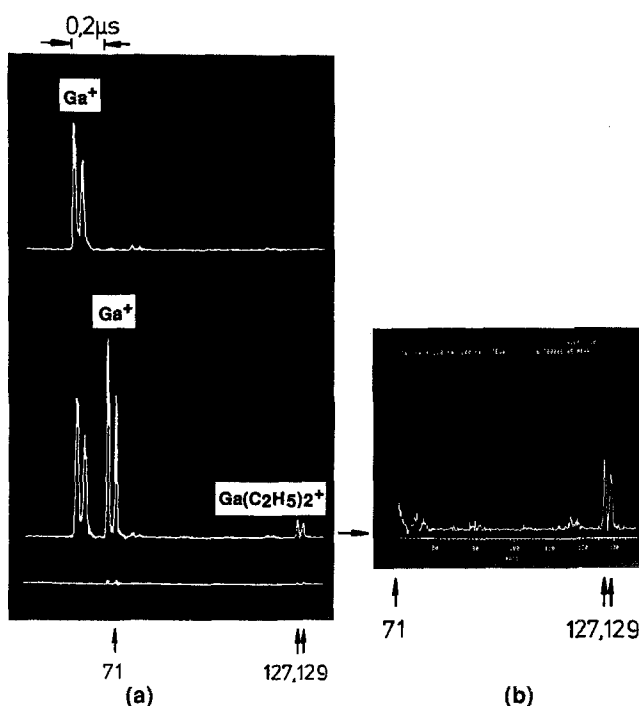


Fig.2. a) Far UV laser ionization time-of-flight mass spectra of gaseous triethylgallium (TEG), $\text{Ga}(\text{C}_2\text{H}_5)_3$, under different experimental conditions (see the text of Fig.1 for details):

(top trace): only 248 nm laser

(middle trace): 248 nm laser + 210 nm laser ($\Delta t = 200$ ns)

(bottom trace): only 210 nm laser

In the middle trace, the (enhanced) $\text{Ga}(\text{C}_2\text{H}_5)_2^+$ ion signal is due to the photofragment $\text{Ga}(\text{C}_2\text{H}_5)_2$ formed in TEG exposed to the 248 nm laser

b) A part of the middle trace of Fig.2a showing that the enhanced ion signals are at $m/e = 71$ (Ga^+) and $m/e = 127, 129$ ($\text{Ga}(\text{C}_2\text{H}_5)_2^+$), see mass calibration

The relative yields of GaCH₃ formation as a photofragment from TMG at different photolysis laser wavelengths were measured, shown in Fig.3, where those of AlCH₃ from TMA are also given under the same conditions. The fact that the yield distribution of AlCH₃ radicals detected by the 248 nm laser coincides with the results with the tunable dye laser [10,11], confirms the measurement for GaCH₃ in Fig.3.

The absorption spectrum of TMG molecules is shown in Fig.4, and is similar to the results given in [12,13].

3. Discussion

Almost nothing is known about the GaCH₃ radical. According to the studies on the closely related radical AlCH₃ [5], we assume that free GaCH₃, as well as the AlCH₃ radical, is detected by *two*-photon ionization at 248 nm. In contrast to AlCH₃, which is detected by the tunable dye laser through *three*-photon ionization at about 440 nm, GaCH₃ is hardly detected [14]. The reason is, that further fragmentation can be induced by the probe laser pulse itself, known from our earlier studies on AlH and GaH [9]. The far UV laser used here as the probe laser needs only two photons to ionize the neutral fragments, and therefore, with the relatively low intensity of the far UV laser, photofragmentation is reduced considerably. Taking advantage of ultrashort laser pulses, fragmentation can also be reduced [15].

The metal-dialkyls, ML₂ (M = Al, Ga, L = CH₃, C₂H₅), are considered as *intermediate* transient fragments, since they are found at 248 nm, and in lower abundance at 193 nm, and since their abundance does not increase with increasing photolysis laser intensity.

It is seen from Fig.3, that the relative yield Y(λ) of GaCH₃, as well as that of AlCH₃, depends on the photolysis laser wavelength λ and follows the order Y(193nm) > Y(210nm) >> Y(248nm). The similarity in the wavelength dependence between the yield Y(λ) in Fig.3 and the absorption spectrum of TMG molecules in Fig.4 suggests that a strong absorption of *one* UV photon at λ < 220 nm will dissociate TMG and efficiently generate GaCH₃ fragments during one laser pulse of 20 ns duration. *No* "bottleneck" [1] in the production of free gallium atoms at 210 - 248 nm was observed, however, since a large abundance of Ga atoms was found from TMG

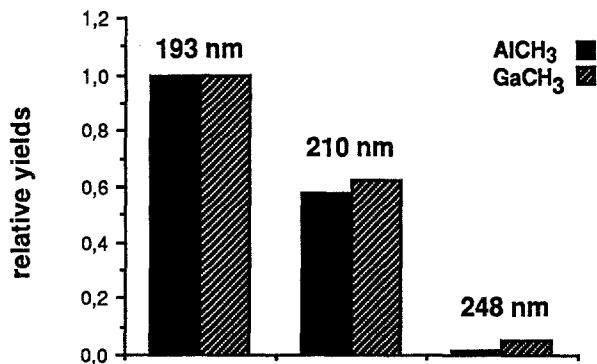


Fig.3. Dependence of the relative yields Y(λ) of GaCH₃ and AlCH₃ on the photolysis laser wavelength at λ = 193, 210, and 248 nm

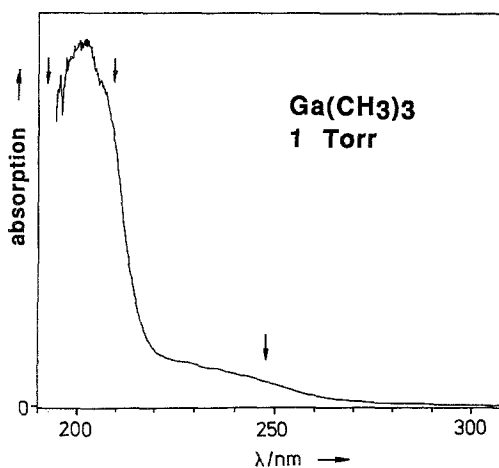


Fig.4. Absorption spectrum of TMG, at a pressure of 1 Torr. The arrows indicate the different laser wavelengths at λ = 193, 210, and 248 nm, respectively

molecules under both 209 nm and 248 nm laser pulses even though few GaCH₃ fragments were produced at 248 nm. This shows that the photofragment GaCH₃ is not the main precursor of free Ga atoms.

In the above results, the dissociation of Ga-alkyls (TMG, TEG) shows some strong analogies with that of Al-alkyls (TMA, TEA) [10]. For these metal-alkyls [12,13], strong absorption starts at about 210 nm (Fig.4, e.g. TMG), where the absorption of *one* photon by the metal-trimethyl precursor will efficiently generate free metal atoms or *metal-monomethyl* fragments, whereas one photon absorbed by the metal-triethyl (or other ligands with β-hydrogen) precursor will induce free metal atoms or *metal-hydride* fragments. Further, a weak *one-photon* absorption at 220-260 nm (Fig.4) can still efficiently generate free metal atoms, which might result from a vib-

ronically allowed quadrupole transition to a totally dissociative potential surface [16], and abundant metal-hydride fragments if the precursor molecule has β -hydrogen [6], but only few metal-monomethyl radicals.

4. Conclusion

The GaCH_3 radical - as a photofragment of UV laser induced dissociation of gaseous trimethylgallium $\text{Ga}(\text{CH}_3)_3$ - has been detected for the first time by far UV laser mass spectrometry. Also $\text{Ga}(\text{C}_2\text{H}_5)_2$ was detected from TEG for the first time. GaCH_3 radicals are not the precursor for Ga atoms, but rather are generated from TMG through a reaction channel competing with the generation of Ga atoms. The relative yield $Y(\lambda)$ of GaCH_3 obeys $Y(193\text{nm}) > Y(210\text{nm}) \gg Y(248\text{nm})$, which follows the absorption spectrum of the $\text{Ga}(\text{CH}_3)_3$ precursor molecules.

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