

Supersonic Expansion and LIF – Fluorescence Excitation Study of the CH₃O Radical and Selected CH₃O Based Clusters

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Abstract: In this work we describe importance of supersonic expansion for the laser initiated fluorescence study of CH₃O radicals. We manifest this importance on our results obtained at laser induced fluorescence (LIF) spectroscopy of CH₃O radicals and CH₃O(Ar) and CH₃O(CH₄) clusters in a supersonic beam. The CH₃O is produced by photolysis of the CH₃ONO precursor at 266 nm. We study laser induced fluorescence from higher vibronic levels of CH₃O* that have not been studied before. We observe fluorescence from CH₃O(CH₄) cluster vibronic states: $\bar{3}^1$, $\bar{3}^2$, $\bar{2}^1$ and also $\bar{3}^3$, $\bar{2}^1\bar{3}^1$ of the first excited electronic state of CH₃O(CH₄). The intensity is weaker for the latter two high energy vibronic states than for the lower vibronic states. This is in contrast to CH₃O monomers for which the fluorescence intensity is stronger for higher vibronic states. Surprisingly, the fluorescence lifetimes are very similar for different vibronic states of both the monomer and the clusters. Possible causes for this intensity difference between monomers and cluster will be discussed.

1. Introduction

1.1. Production of radicals and their clusters

Supersonic jet techniques have revolutionized spectroscopy studies over the past 20 years [1]. One is now able to study isolated molecules and clusters in the gas phase with unprecedented resolution, flexibility, sophistication, and ease. Especially important for the study of radicals and clusters by laser and mass spectroscopy are outlined subjects of supersonic jet techniques: The gas expanded cools because the expansion is adiabatic ($dq = 0$) and the gas does work against its own internal potential energy of attraction and the final pressure in the chamber (ca. 10^{-6} torr). Thus, the translational temperature of the final expanded beam of gas can be below 0.1 K. This cooling has two important consequences: ¹⁾ individual molecules become internally cold (i.e., vibrational temperature ~ 10 K and rotational temperature ~ 2 K); and ²⁾ at these low external and internal temperatures, molecules condense to form clusters.

Other advantages of these sample handling and preparation techniques are as follows:

1. Radicals and transient species can be generated from molecular beam (MB) either:

a) thermally/pyrolysis: MB (precursor and carrier gas) passes through ceramic tube inserted to the resistive heated SiC tube where radicals are produced at sufficient temperature (in case of higher temperatures molecular decomposition can occur).

b) or photolytically before the expansion: if MB is parallel to laser beam focused to the inner part of capillary, then the laser beam hits MB and radicals are produced.

Afterwards in both above mentioned cases radicals are cooled as the expansion progresses.

2. This beam of species for spectroscopic study is well suited to laser and mass spectroscopy.

3. Detection of species can be accomplished by spectroscopic and/or mass signatures.

4. Dynamics, mechanisms, and rates can be determined for reactions as one controls energy content and excitation timing for species in the supersonic beam.

Clusters, aerosols, and nanoparticles are made in the supersonic expansion as the gases cool coming out of the nozzle. Cluster size seems only limited by expansion gas composition and nozzle temperature. Three or more component clusters are readily made by appropriate sample composition and expansion conditions. For the study of radical chemistry there is an advantage (if species do not react in the ground state in the nozzle before clustering e.g.: CH_3O and CH_4 , CH_3O and H_2O etc.) that species are coupled with van der Waals forces together and form clusters. Afterwards, excitation (e.g. by laser) causes breaking of couplings in cluster [e.g.: $\text{CH}_3\text{O}(\text{CH}_4)$, $\text{CH}_3\text{O}(\text{H}_2\text{O})$ etc.], remained species in excited state are placed close together and can react, thus their reactivity can be studied. For the spectroscopic study of photoinitiated reactivity of species, which cannot be mixed prior the expansion (because of their reactivity, e.g.: Cl_2 and CH_3OH), commonly used supersonic pulsed nozzle (e.g.: based on General valve, or Jordan valve) needs to be replaced with newly developed late mixing pulsed nozzle source [2]. Clustering of molecules can be also generated by supersonic expansions achieved in two chamber differentially pumped vacuum systems, which are not used for radical study but this arrangement is commonly used for studying electron-molecule interactions [3]. In the molecular beam environment, both isolated radicals and their reactive and not reactive clusters with other species are available for the study.

1.2. Detection and spectroscopy of radicals and their clusters

Species in the supersonic expansion/molecular beam environment can be detected in the following ways:

1. by laser spectroscopy of the species for known small radicals or radical/solvent clusters (e.g., OH, CN, NCO, CH_3O , $\text{C}_6\text{H}_5\text{CH}_2$, etc., and their small clusters), typically this is an emission spectroscopy like laser induced fluorescence (LIF);

2. by resonance enhanced, multiphoton, mass resolved excitation spectroscopy (MRES) in which molecules and clusters are ionized at threshold through an intermediate electronic transition that is characteristic of the species.

Both LIF and MRES detection techniques can be used to study molecules, radicals, and clusters. Disadvantage of MRES is the necessity to ionize species in order to detect them by mass spectroscopy. Advantage of MRES is that we can analyze also species which we cannot detect by LIF. In this work we focus on spectroscopy of monomers and clusters of CH_3O since this radical is involved in important reactions in combustion chemistry and interaction dynamics and kinetics may yield important data for a better understanding of the combustion process. We have studied laser induced fluorescence spectroscopy of CH_3O radicals and $\text{CH}_3\text{O}(\text{Ar})$ and $\text{CH}_3\text{O}(\text{CH}_4)$ clusters cooled by a super-

sonic expansion prior to laser excitation. CH_3O^* has been produced by a photolysis of CH_3ONO precursor at 266 nm. The CH_3O^* can be also produced by a photolysis or pyrolysis of other precursors (e.g.: CH_3OH [4]). For photolysis, the excimer lasers with wavelengths 193 nm [4] or 248 nm [5–7] have been used previously.

2. Experiment

2.1. Precursor synthesis and radical generation

CH_3ONO was produced according to the following chemical reaction: $2\text{NaNO}_2 + 2\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{CH}_3\text{ONO} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$. Our synthesis arrangement schematically viewed on Fig. 1a. was slightly modified than that published by Blatt [9]. 33 % H_2SO_4 drops to stirred solutions of NaNO_2 , CH_3OH , H_2O placed in the 1st three neck flask. Reaction product is neutralized passing through CaCl_2 to the 2nd three neck -trapped flask. Reaction by products: CH_3OH has lower vapor pressure; NO_x have higher vapor pressure. In the 3rd storage flask after synthesis we get CH_3ONO .

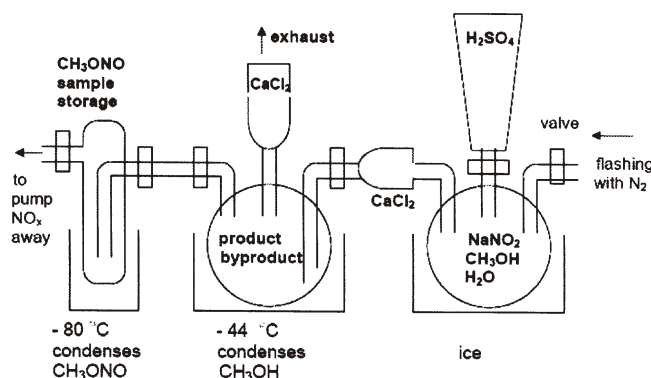


Fig.1a. Schematic view to synthesis of CH_3ONO .

CH_3ONO is a yellowish color liquid at -80°C and transparent gas at 0°C . The CH_3ONO photolysis occurs inside the capillary (before supersonic expansion) and the CH_3O expands from the capillary to vacuum, being cooled by supersonic expansion and clustered with Ar or CH_4 . Experimental system is shown in Fig. 1b.

2.2. Radical excitation and detection of LIF

The photolysis and the excitation beams (see Fig. 1) are from two different pulsed lasers (Nd-YAG with ~ 10 ns pulse duration). Photolysis beam is 4th harmonics of Nd-YAG at 266 nm. Excitation beam is from a tunable dye laser doubled by KDP crystal and pumped by 2nd harmonics of Nd-YAG at 532 nm. The dye laser fundamental (588–625 nm) is filtered out. To cover our wavelength region we used Exciton laser dyes: R640, R610 (solved either in methanol or ethanol) and their mixtures. Signal is collected by

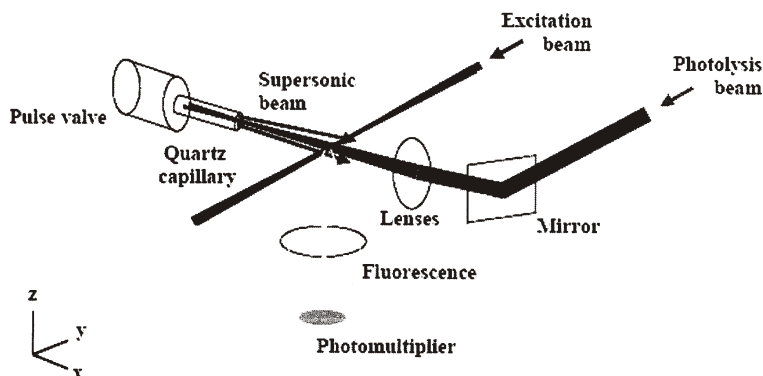


Fig.1b. Schematic view of the experimental setup.

Hamamatsu photomultiplier tube (PMT); (we used: UV340 and pyrex filters) and amplified by an amplifier and integrated by a Boxcar unit.

Proper timing of both lasers and nozzle opening allows us to synchronize the following events:

1. to generate a gas pulse (CH_3ONO + Carrier gas) from the nozzle to a quartz tube;
2. to photolyse CH_3ONO by 266 nm inside the quartz tube and to allow supersonic expansion of the CH_3O product;
3. to excite CH_3O or CH_3O based clusters cca 2 cm downstream after pulsed expansion by an excitation laser and to detect the fluorescence spectra (using PMT) by scanning the excitation laser.

3. Results and Discussion

3.1. Spectroscopy of CH_3O

Evidence of reaction $\text{CH}_3\text{ONO} + h\nu \rightarrow \text{CH}_3\text{O}$ as a product of photolysis is illustrated by obtained CH_3O spectra (Fig. 2a and Fig. 3a). Identity of CH_3O is also verified by its proper lifetime [6]. Prior this experiment the system was calibrated in accordance with the well known spectrum of aniline [8]. When measuring aniline the photolysis laser was set up. During this step proper timing of photolysis laser resulted in decomposition of aniline. This timing served as a preliminary estimate of timing for the setup of measuring CH_3O spectrum.

3.2. Spectroscopy of CH_3O based clusters

If we are using, as a carrier gas, a mixture of Argon or Methane in a Helium, we can clearly see, from the obtained set of spectra, formation of the corresponding clusters $\text{CH}_3\text{O}(\text{Ar})$ and $\text{CH}_3\text{O}(\text{CH}_4)$ displayed in Fig. 2b and Fig. 3b, respectively. We observed the following features:

- a) $\text{CH}_3\text{O}(\text{Ar})$ and $\text{CH}_3\text{O}(\text{CH}_4)$ cluster fluorescence excitation exhibit a red spectral shift of 29 cm^{-1} and 110 cm^{-1} , respectively.

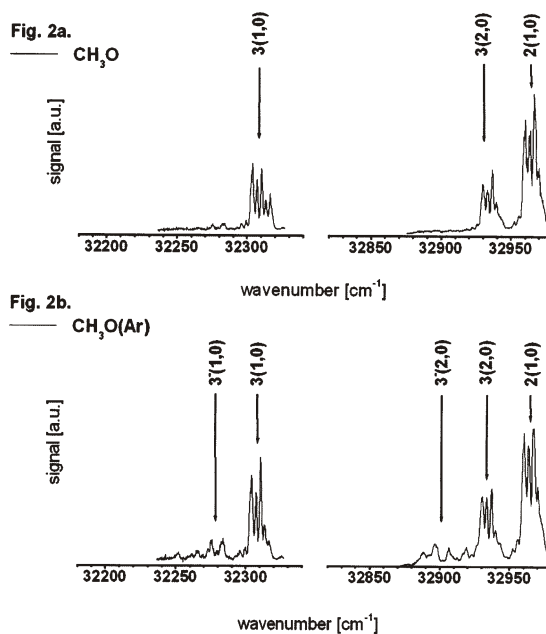


Fig. 2. Comparison of spectra for various vibrational levels of CH_3O^* and $\text{CH}_3\text{O}(\text{Ar})$ clusters. The same red spectral shift 29 cm^{-1} for all vibrational levels of $\text{CH}_3\text{O}(\text{Ar})$ cluster (in Fig. 2b).

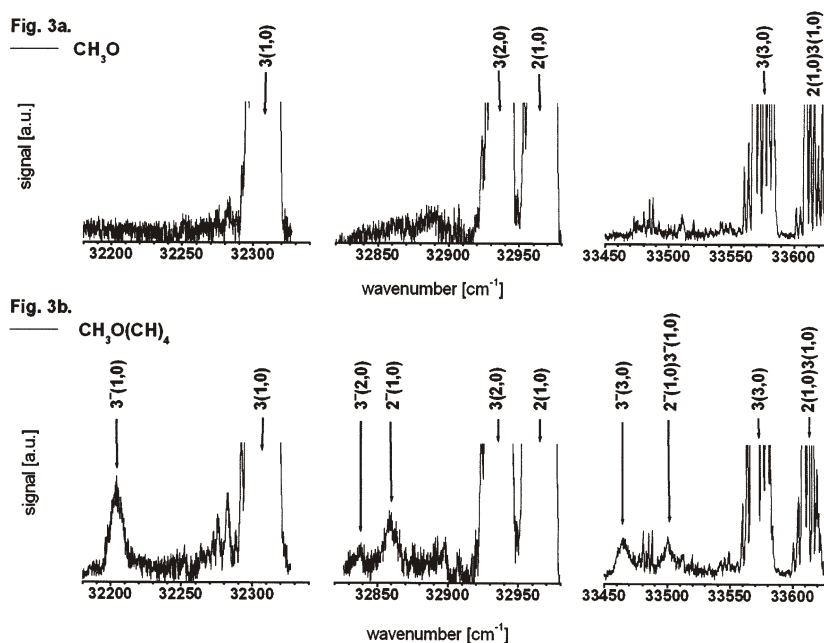


Fig. 3. Comparison of spectra for various vibrational levels of CH_3O^* and $\text{CH}_3\text{O}(\text{CH}_4)$ clusters. The same red spectral shift 110 cm^{-1} for all vibrational levels of $\text{CH}_3\text{O}(\text{Ar})$ cluster (in Fig. 3b).

pend on the vibrational state, we know that this does not happen. Therefore, we suggest that both channel 1 and channel 2 occur.

4. Conclusion

Photolysis of CH_3ONO at 266 nm yields CH_3O in high concentrations. Clusters of CH_3O can be formed with Ar and CH_4 . Cluster dynamics and reactions can be studied in this system because interfering species are kept to a minimum and the chemistry is unique.

Here presented results and experiment serve as a basis for our further investigation/detection of the OH as a product of the chemical reaction: $\text{CH}_3\text{O}^* + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{OH}$ by LIF technique as we (V. Foltin and E. R. Bernstein) announced with preliminary results [10]. For this study CH_3ONO is optimal precursor; cooling by supersonic expansion and clustering plays a crucial role. In case of investigation/detection of the CH_3 as a product of the chemical reaction: $\text{CH}_3\text{O}^* + \text{CH}_4 \rightarrow \text{CH}_4\text{O} + \text{CH}_3$ the CH_3 cannot be detected directly by LIF and REMPI technique needs to be used. In REMPI experiment the following steps will be inevitable: photolysis of precursor, excitation to form CH_3 , ionization of CH_3 which allows us to detect product by a mass spectrometer.

In order to use radical spectroscopy for investigation of reaction kinetics (e.g.: reaction constants and cross sections) in excited states, close distance between reactant species must be achieved, so that after excitation reaction can occur. This distance can be achieved in both cases: a) if species are clustering (described above), b) if concentration in a gas phase during the lifetime of species involves enough collisions, and so the reaction in the excited state can occur (described shortly below).

In study of kinetics of the above displayed or other reactions of interest, we can use, for radical generation instead of supersonic expansion and photolysis (or pyrolysis), the flowing afterglow technique in the following way: In a microwave discharge in helium He^+ ions and electrons are formed. When these ions and electrons are in the gas flowing out of the discharge region, they are cooled to low temperature. In certain distance from the discharge a precursor for production of radical is injected into the flowing gas. Through charge exchange He^+ ions react with CH_3ONO and produce CH_3ONO^+ , CH_3O^+ , etc. ions. These ions recombine with the cooled electrons in the process of dissociative recombination and produce excited CH_3O^* , CH_3^* , NO^* , etc. molecules. Excited molecules emit photon and convert to the ground state. In certain distance, in which all the molecules are in the ground state, the reactant (H_2O , CH_4 , etc.) is injected into the flowing gas. After state selective excitation of CH_3O by laser, reaction occurs and the fluorescence from possible products of reaction (OH, etc.) is observed. Without this excitation no fluorescence is observed. As described above both $\text{CH}_3\text{O}^* + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{OH}$ and $\text{CH}_3\text{O}^* + \text{CH}_4$

$\text{CH}_4\text{O} + \text{CH}_3$ chemical reactions occur only in case of excited CH_3O^* , because the reactant species are inert in the ground state. By investigating the dependence of fluorescence on the concentration of CH_3ONO and H_2O or CH_4 , respectively, it can be proved that two-molecular reaction occurs (i.e. reaction in which only one collision between CH_3ONO and H_2O or CH_4 , respectively, occurs). By comparing intensity of fluorescence for the same reaction product in investigated and in other known reaction, the reaction constant can be obtained. Such a reaction constant can be used in a process of modelling reactions in the atmosphere or in combustion.

By choosing other radicals and reactants a huge variety of unique chemistry can be observed with the above outlined experimental methods.

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