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Photochemistry of adsorbed biacetyl: desorption and photofragmentation

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Abstract

The UV (266 nm) laser-induced desorption and photofragmentation of biacetyl ($CH_3COCOCH_3$), adsorbed on quartz and Ag surfaces at low temperature have been investigated using time-resolved mass spectrometry. On a quartz substrate, the photochemical desorption of $CH_3COCOCH_3$, associated with photofragmentation, is observed. For $CH_3COCOCH_3$ adsorbed on an Ag surface, the major fragments are CH_3CO and CH_3 radicals, but dimeric biacetyl $(CH_3COCOCH_3)_2$ is also observed. These results reveal that the electronic excitation with photofragmentation of adsorbed biacetyl molecules leads to CH_3CO and CH_3 radical formation.

Keywords: $CH_3COCOCH_3$; Laser-induced desorption; Photofragmentation

1. Introduction

In recent years, the photochemistry of adsorbed molecules on solid surfaces has received considerable attention. Because the presence of a solid surface opens up a rich spectrum of electronic excitation and relaxation processes for the adsorbed molecules, the surface photochemistry differs from its counterpart in the gas phase in many fundamental concepts. Pulsed laser-induced desorption and fragmentation offer ways of studying the dynamics of surface photochemistry. In previous studies, UV lasers have been employed to induce the surface photochemistry of adsorbed molecules, involving electronic excitation on a very short time scale, and chemical processes may compete effectively with energy relaxation [1–4]. However, the competition between various photoexcitation, photodesorption and fragmentation processes for the adsorbed polyatomic molecules is still a basic scientific issue which deserves thorough investigation. Recently, several excellent review articles on surface photochemistry have been published [5,6]. In practical applications of surface photochemistry to materials processing, the photofragmentation of multilayer polyatomic molecules by a pulsed laser beam is a useful technique for the generation of a neutral hyperthermal beam of atoms and molecules. Cousins and coworkers [7,8] reported a versatile, repetitively pulsed source of translationally fast and reactive molecules which is suitable for materials processing, e.g. the efficient etching of semiconductor Si surfaces by translationally fast Cl_2 molecules.

In this paper, we chose $CH_3COCOCH_3$ molecules adsorbed on SiO_2 (quartz crystal) and Ag surfaces to investigate the UV-excited surface processes induced by 266 nm laser radiation. Chemically, the quartz and silver substrates are relatively inert. However, the transparency of quartz in the UV facilitates direct excitation of the adsorbate and may lead to dissociation on a shorter time scale than that required for energy transfer to the crystal. Thus the photochemistry of molecules adsorbed on quartz may differ markedly from the corresponding processes on a metal Ag surface. Since the time-of-flight (TOF) method with a quadrupole mass spectrometer (QMS) is a powerful technique for the identification and detection of the desorbed species [9], we used this technique to measure the TOF spectra of the desorbed species from the UV laser desorption of adsorbed biacetyl as well as the effect of the laser fluence. The TOF spectra are simulated with different kinds of Maxwell–Boltzmann distributions. Based on the analysis of the observed TOF spectra of the desorbed species, the mechanisms of UV laser-induced desorption and photofragmentation of $CH_3COCOCH_3$ adsorbed on quartz and Ag are discussed.

2. Experimental details

The experimental set-up used in the present study is similar to that employed for laser-induced etching experiments [10] with modification for surface cooling. Briefly, a main cham-

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ber pumped by a turbomolecular pump (500 l s^{-1}) is equipped with a QMS (ULVAC MSQ-400) for measurements of the mass and velocity distributions of the desorbed species. The sample gas molecules of $CH_3COCOCH_3$ are directed via a stainless steel capillary dosing inlet onto the front side of a quartz or Ag substrate which is maintained on an *xyz* manipulator. The molecular films are deposited continuously onto the substrate which is cooled to 130 K for quartz and 110 K for Ag by a liquid nitrogen cryostat. A quartz crystal microbalance (QCM) is used to monitor the dosing flow rate and estimate the thickness of the molecular films [11].

A 266 nm laser beam is provided by the fourth harmonic frequency from a *Q*-switched Nd:YAG laser (Spectra Physics, Quanta-Ray GCR-150) with a pulse duration of 6 ns and a repetition rate of 10 Hz. The laser beam is focused and introduced from behind, through the quartz substrate first, to irradiate a fraction of the condensed film. In order to minimize direct light scatter into the electron multiplier of the QMS detector, the laser beam is angled approximately 6° off-axis. When Ag is used as a substrate, the laser beam is directed from the front onto the Ag surface at an angle of 45° to the surface normal. The laser intensity is measured by a power meter (Scientech). The desorbed parent molecules and their fragments travel a 19 cm flight path and enter the detection chamber through a 3 mm diameter aperture. The mass and velocity distributions are determined by TOF quadrupole mass spectrometry. The zero time for the TOF measurements is initiated by the laser pulse. Ionization of the neutral desorbed species in the QMS is accomplished by electron bombardment with an impact energy of 70 eV. The ion signal is directly proportional to the density of the desorbed species. The TOF signals are typically averaged for 100–200 laser pulses and corrected for the ion drift time in the QMS.

The TOF spectra of the desorbed species are fitted by a single- or multi-component Maxwell–Boltzmann (MB) distribution [12]. For a single-component MB distribution, the number density of the desorbed species $n(t)$ is given by

$$n(t)=At^{-4}\exp(-t_0^2t^{-2}) \tag{1}$$

where t is the flight time and A and t_0 are adjustable parameters. In addition, the flight time at the peak position of the TOF signal (t_m) is equal to $t_0/\sqrt{2}$ [12].

When the measured TOF signal for a given ion originates from more than one neutral parent component, a multi-component MB distribution can be used with the equation [13]

$$n(t)=\sum_{i-1}^{p}n_i(t)=\sum_{i-1}^{p}A_it^{-4}\exp(-t_{0i}^2t^{-2}) \tag{2}$$

where $p \leq 4$ is the number of neutral parent components and A_i and t_{0i} are adjustable parameters.

3. Results and discussion

A QCM is employed as thickness and rate monitor in thin film deposition using well-established equations relating the decrease in the crystal resonant frequency to the deposited mass [14,15]. The dependence of the deposition rate on the $CH_3COCOCH_3$ dosing pressure measured by the QCM is shown in Fig. 1. It can be seen that the deposition rate increases linearly with the dosing pressure. Using this curve, the deposition rate and film thickness at a given dosing pressure can be estimated roughly.

In the study of the UV laser-induced desorption and photofragmentation of adsorbed biacetyl molecules, a quartz window and an Ag film deposited on a quartz disc are used as substrates. Unlike the situation on optically transparent quartz, silver is relatively inert chemically, but absorbs UV light. It is expected that differences will be observed between the desorption behaviour of biacetyl adsorbed on quartz and Ag surfaces. Fig. 2 presents the TOF spectra of the measured ions obtained from a biacetyl multilayer (approximately 10 monolayers (ML)) adsorbed on a quartz substrate at 130 K

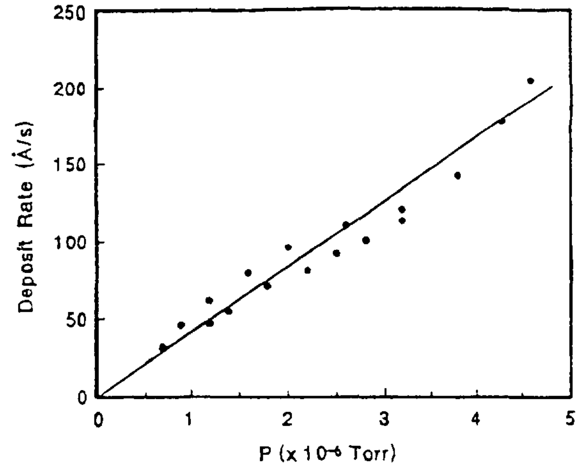

Fig. 1. Deposition rate vs. $CH_3COCOCH_3$ dosing pressure. The line is a least-squares fit to the data.

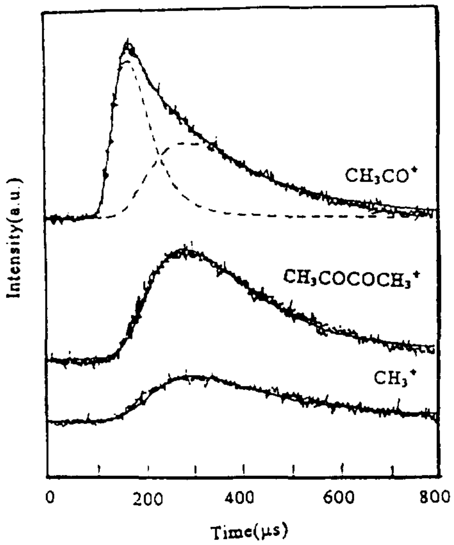

Fig. 2. TOF spectra of fragments and parent molecules desorbed from $CH_3COCOCH_3$ adsorbed on quartz (130 K) irradiated by 266 nm laser pulses at $E_L=65$ mJ cm^{-2}. The full lines are fitted curves to single- or two-component MB distributions.

on 266 nm laser beam irradiation. The TOF spectra of $CH_3COCOCH_3^+$ ($m/e=86$) and CH_3^+ ($m/e=15$) ions can be fitted by a single-component MB distribution, and their flight times (t_m) at the peak position are nearly the same. However, the t_m value for the CH_3CO^+ ($m/e=43$) ion shifts to shorter values and its TOF signal, shown in Fig. 2, apparently consists of two components, a slow component and a fast component. The t_m value for the slow component of the CH_3CO^+ signal is the same (290 μs) as that of the $CH_3COCOCH_3^+$ and CH_3^+ signals. This result implies that the CH_3^+ signal and the slow component of the CH_3CO^+ signal may originate from the cracking fragments of the parent molecule $CH_3COCOCH_3$ in the ionizer of the QMS. However, the fast component of the CH_3CO^+ signal with a t_m value of 180 μs seems to originate from the photodissociation fragment CH_3CO radicals. It is evident that the laser-induced desorption associated with the photodissociation of adsorbed biacetyl on quartz takes place at 266 nm and the major desorbed species are the parent molecules $CH_3COCOCH_3$ and their fragment CH_3CO radicals.

In order to determine the mechanism of desorption and fragmentation, we measured the dependence of the TOF signals on the laser fluence. Fig. 3 shows the TOF spectra of $CH_3COCOCH_3^+$ at different laser fluences in the range 55–130 mJ cm^{-2}. When the laser fluence is less than 90 mJ cm^{-2}, the TOF spectra are similar in shape and have almost the same t_m values. The relative yields of desorbed $CH_3COCOCH_3^+$ ions, obtained by integrating the TOF signals, increase with increasing laser fluence. This characteristic behaviour is expected for a photochemical desorption process involving the detachment of a molecule from a surface by interaction with a single photon [9]. Therefore the desorption of $CH_3COCOCH_3$ from a quartz surface at 130 K on 266 nm laser irradiation at low laser fluence may be photochemical in nature. In contrast, when the laser fluence is higher than 120 mJ cm^{-2}, the TOF signal in Fig. 3 has a faster component with a broader distribution. This indicates that a photon sputtering desorption process [16] may play an important role at high laser fluence. This process is based on a dense electron–hole plasma created by laser light absorption. The non-radiative recombination of electron–hole pairs may energize adsorbed species, which can be desorbed with high kinetic energy and a non-MB distribution. Accordingly, it can be concluded that photochemical desorption is observed for a multilayer of $CH_3COCOCH_3$ at low laser fluence, whereas photon sputtering desorption dominates at high laser fluence.

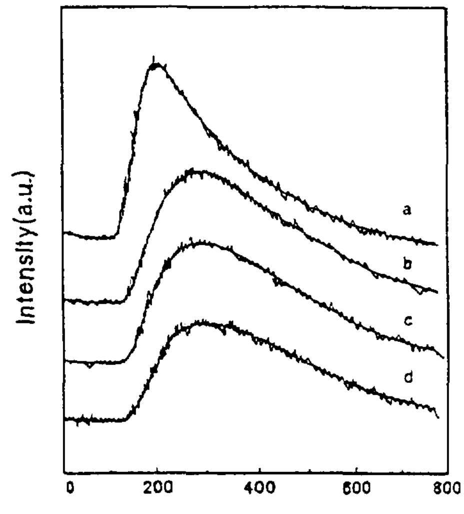

Fig. 3. TOF spectra of $CH_3COCOCH_3$ desorbed from $CH_3COCOCH_3$/quartz at different laser fluences: (a) 130 mJ cm^{-2}; (b) 110 mJ cm^{-2}; (c) 80 mJ cm^{-2}; (d) 55 mJ cm^{-2}.

When biacetyl is adsorbed on an Ag surface instead of a quartz substrate, the measured TOF spectra of the desorbed product ions, shown in Fig. 4, are observed. It can be seen that $CH_3COCOCH_3^+$ ($m/e=86$), CH_3CO^+ ($m/e=43$) and CH_3^+ ($m/e=15$) ions are detected as mentioned above; an ion signal is also observed at $m/e=172$ which corresponds to the dimer of biacetyl $(CH_3COCOCH_3)_2^+$. The TOF spectra of the dimeric biacetyl ion can be fitted satisfactorily by a single-component MB distribution. However, a two-component MB distribution must be used to fit the measured TOF signal of $CH_3COCOCH_3^+$. The slow component in Fig. 4 has a t_m value of 540 μs, which is very close to that of the dimeric biacetyl ion, corresponding to the cracking fragment of the dimer $(CH_3COCOCH_3)_2$; the fast component with a t_m value of 370 μs originates from neutral biacetyl. It should be noted that the TOF signals for both CH_3CO^+ and CH_3^+ ions in Fig. 4 are broader; a three-component MB distribution can be used to simulate these signals. Based on the analysis of the TOF signal and the t_m value of each component, the fastest component can be assigned to the photodissociation fragment

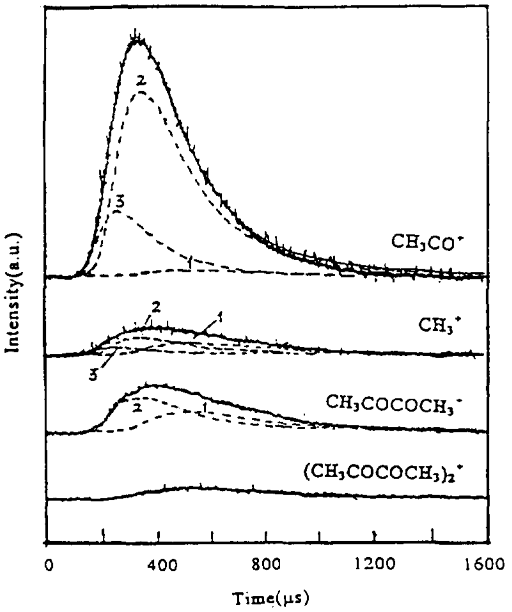

Fig. 4. TOF spectra of biacetyl, its dimer and fragments desorbed from biacetyl adsorbed on Ag (110 K) at $E_L=65$ mJ cm^{-2}. The broken lines are composites obtained from two- or three-component MB distributions. Curve 1, $(CH_3COCOCH_3)_2$; curve 2, $CH_3COCOCH_3$; curve 3, CH_3 or CH_3CO radicals.

CH_3 and CH_3CO radicals; the other two components may originate from the parent molecules $CH_3COCOCH_3$ and $(CH_3COCOCH_3)_2$. Therefore the neutral molecules $(CH_3COCOCH_3)_2$ and $CH_3COCOCH_3$ are the major desorbed species obtained by laser-induced desorption, while CH_3CO and CH_3 radicals are the fragments obtained from laser-induced photofragmentation of biacetyl adsorbed on an Ag surface at 110 K.

The absorption spectrum of biacetyl in the gas phase shows that $CH_3COCOCH_3$ molecules absorb strongly at 266 nm (second absorption region, 220–310 nm) [17]. A vibrationally excited second electronic state (^1A_u or S_2^v) of biacetyl is formed by photoexcitation of a 266 nm photon and photofragmentation takes place on a very short time scale to produce non-thermal equilibrated radicals CH_3CO^*. The mechanism of 266 nm laser-induced desorption and photofragmentation of a biacetyl multilayer adsorbed on a quartz substrate can be proposed as follows

$$CH_3COCOCH_3(S_0, {}^1A_g) \xrightarrow{h\nu} CH_3COCOCH_3^*(S_2^v, {}^1A_u) \rightarrow 2CH_3CO \tag{3}$$

The photofragmentation behaviour of the biacetyl molecule adsorbed on an Ag surface is found to be different from that on a quartz substrate. As mentioned above, both CH_3CO and CH_3 radicals are fragments of adsorbed biacetyl molecules. It appears that the CH_3CO radicals are dissociated to generate CH_3 radicals in the $CH_3COCOCH_3$/Ag system. This result can be explained by laser-induced thermal desorption associated with photochemical fragmentation, since both Ag films and biacetyl multilayers absorb 266 nm UV light. However, dimeric biacetyl is also detected when the 266 nm laser pulse irradiates the front side of the Ag substrate on which about 10 ML of biacetyl are adsorbed. Dimeric biacetyl may be ejected directly from the condensed film on the Ag surface, since it forms easily via hydrogen bonding between two adjacent biacetyl molecules.

In order to examine whether the thermal heating process dominates the desorption and photofragmentation of biacetyl on quartz and Ag surfaces on 266 nm laser irradiation, the laser-induced temperature jump of the substrate surface has been estimated. It is well known that the adsorbed layer and substrate surface can be heated by pulsed laser irradiation on a very short time scale, approximately equal to the laser pulse width (approximately 10 ns). The time interval between the laser pulses (100 ms) in our experiments ensures that the temperature jump induced by a given laser pulse is nearly independent of the previous pulse. From the thermal parameters and adsorption probability of the Ag substrate estimated via the equation given by Domen and Chuang [2], the surface temperature jump (ΔT) can be calculated by the Ready equation [18]. For a 266 nm laser pulse with a duration of 6 ns and a fluence of 130 mJ cm^{-2}, the estimated ΔT value is about 200 K. When quartz is used as substrate, the temperature jump induced by the pulsed laser is certainly less than 200 K, since the absorption probability for quartz is less than that for Ag. Therefore laser thermal heating is not a dominant process in the photodesorption and fragmentation of adsorbed biacetyl at 266 nm.

4. Conclusions

The TOF mass spectrometric technique has been successfully used to identify the desorbed neutral species from the UV laser-induced desorption and photofragmentation of $CH_3COCOCH_3$ molecules adsorbed on quartz and Ag substrates at low temperature. The desorption and dissociation of a biacetyl multilayer adsorbed on a quartz substrate can be induced by 266 nm laser irradiation and the major fragment is the CH_3CO radical. For a biacetyl multilayer on an Ag surface, splashing takes place to generate dimeric biacetyl $(CH_3COCOCH_3)_2$; the most important products in the photofragmentation of biacetyl are CH_3CO and CH_3 radicals.

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