

Near UV multiphoton dissociation of organosilanes with picosecond and nanosecond laser pulses

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Abstract

Multiphoton dissociation undergone by the organosilanes 2-chloroethenylsilane and phenylsilane upon irradiation with laser pulses of 20 ps and 4 ns duration at 290 nm has been studied through detection of their spontaneous fluorescence. Atomic Si ($4s\ ^1S_0$) emissions are reported, together with the Swan bands of C₂. Additionally, SiH₂ formed in a two-photon process was observed by laser-induced fluorescence techniques in the photolysis of 2-chloroethenylsilane. The results show a strong selectivity when compared to those obtained previously for far UV irradiation around 200 nm and provide insight into the nature of the photodissociation mechanisms, where the SiH₂ fragment plays a central role. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Over the last decade, there has been a considerable effort devoted to understanding the photodissociation mechanisms undergone by organosilanes [1–4] due to the industry-triggered interest in chemical vapour deposition processes (CVD) for the manufacture of silicon semiconductors. The phenylsilane molecule (C₆H₅SiH₃) has been receiving intense attention [5–7], as it was found to be an efficient precursor for Si film formation. The molecule of 2-chloroethenylsilane (H₃SiCH=CHCl, or CES in the following) has been the subject of recent investigations both in the IR [8,9] and the far UV [4,9,10] and it has been observed that it can yield Si/H/C and SiC deposits, with relative contents depending on irradiation conditions.

Previous photodissociation studies on CES and phenylsilane have been performed, either in the IR, or through excitation of the lowest lying singlet states. In the case of CES, the first excited singlet state is situated at around 6.4 eV [4,9], which corresponds to excitation in the region of 200 nm. In analogy with other haloethylenes [11], the broad absorption band is expected to be followed by a mixture of valence and

Rydberg states as the excitation energy is increased. The absorption spectrum of phenylsilane, in its turn, shows three absorption bands around 260, 210 and 185 nm, which correspond to excitation to the S₃, S₂ and S₁ states, respectively [12]. Once more, Rydberg series are reported for higher energies. Both in the IR and in the far UV, silylene (SiH₂) has been shown to be one of the primary products of the photodissociation of CES [4,13] and phenylsilane [7,14]. In fact, SiH₂ has been identified as a key intermediate in the decomposition of silanes and organosilanes [1,15] and has been shown to play an important role in the CVD processes to form hydrogenated amorphous silicon (a:Si–H). From a theoretical point of view, the low-lying electronic states of silylene have been the subject of numerous ab initio calculations [16–18], and the dissociation channels into Si+H₂ or SiH+H have also been tackled [19]. Experimentally, silicon (³P) has been observed following state-selected excitation of $\tilde{A}\ ^1B_1$ silylene [20].

In this work, we have studied the multiphoton dissociation of CES and phenylsilane using near ultraviolet irradiation at 290 nm through the detection of spontaneous and laser induced fluorescence (LIF). The initial process must necessarily involve the absorption of two photons, since none of the molecules possesses resonances at the one-photon level. A two-photon absorption, in its turn, will produce a molecular excitation to the Rydberg region in either molecule. For this work, we have used a laser system providing 290 nm

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pulses of 20 ps duration with maximum intensity around $10^{11} \text{ W cm}^{-2}$ in the focal region. Additionally, it was found that fluorescence emissions could also be observed when using less intense laser pulses ($5 \times 10^8 \text{ W cm}^{-2}$) of 4 ns and the same wavelength. Therefore, comparison was possible between the emission characteristics observed with 20 ps and 4 ns laser pulses, which tend to favour, respectively, photon absorption following the molecular pathway or ladder switching mechanisms where intermediate species are responsible for the formation of the fluorescence emitting fragment [21]. Performing a comparative study of the effect of using pulses of different length has proven useful in the past in order to study the competing mechanisms of radiation absorption and dissociation [22–24]. The results obtained shed further light on the understanding of the photodissociation mechanisms undergone by these two organosilanes, with special emphasis on the role played by the silylene product.

2. Experimental details

The experimental set-up has been described in previous works [23,24] and only a brief summary will be given here. The experiments were carried out with a laser system capable of providing 20 ps and 4 ns laser pulses with similar energy and spatial characteristics. In the picosecond experiments the train of laser pulses is provided by a synchronously pumped mode-locked dye laser (Rhodamine 6G) pumped by an active mode-locked Ar^+ laser. Some of the pulses in the train are selected for amplification in a dye amplifier (Kiton Red), the latter being pumped by a frequency doubled Nd:YAG laser that operated at 10 Hz. In this regime, the system provides 20 ps, 580 nm pulses with a bandwidth of 1 nm. Alternatively, this laser system could be made to pro-

duce pulses of 4 ns duration by switching off the RF signal in the mode-locker of the Ar^+ pump laser. This leads to a CW output in the dye oscillator, and thus the final amplified pulse acquires a duration that is close to that of the Nd:YAG pump laser. The energy of the linearly polarised output beam was controlled by propagation through a half-wave plate and a polariser. Frequency doubling in a BBO crystal produced up to $50 \mu\text{J}$ of 290 nm laser radiation with duration similar to that of the fundamental beam. In most experiments, a cut-off filter (Schott UG5) was used to eliminate the 580 nm radiation at the output of the doubling crystal.

Photolysis radiation was focused by a quartz lens ($f = 15 \text{ cm}$) at the centre of a glass cell fitted with quartz windows that contained the vapour samples. Photofragment fluorescence detection was made perpendicularly to the laser propagation direction by an EMI 9816 QB photomultiplier. The spectral selection was performed by a high luminosity low resolution Bausch & Lomb monochromator.

The fluorescence cell was connected to a vacuum system typically operating at 10^{-5} Torr. Working pressures of the samples ranged between 0.1 and 3 Torr and were measured by a capacitance manometer (MKS Baratron 0.01–10 Torr).

CES ($\text{H}_3\text{SiCH}=\text{CHCl}$) was synthesized according to the method described in [8]. Its purity was found to be 95% through gas chromatography. Phenylsilane ($\text{C}_6\text{H}_5\text{SiH}_3$), from ABCR, had a stated purity of 99.4%.

3. Results

Spontaneous fluorescence emitted upon 290 nm irradiation was recorded and spectrally analysed in the 200–700 nm range. Fig. 1 shows the results obtained with a sample of 1.5 Torr of phenylsilane when 20 ps or 4 ns irradiation was

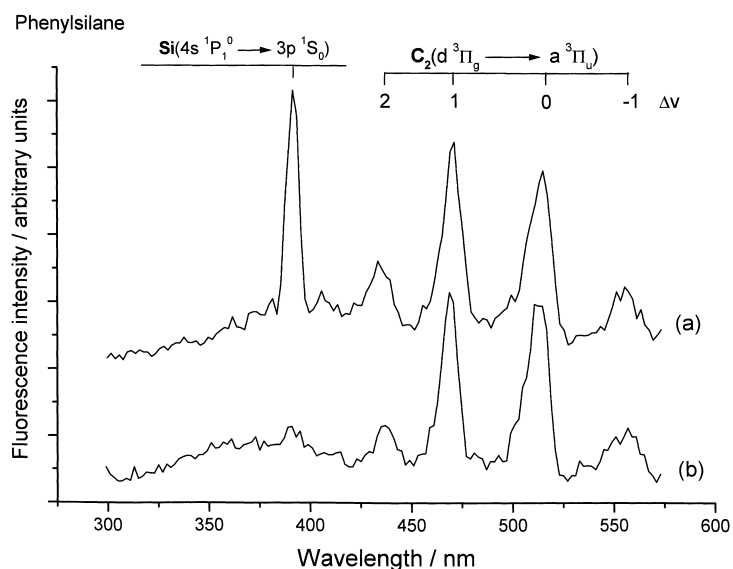


Fig. 1. Spontaneous emission spectra obtained by irradiation of a sample of 1.5 Torr of phenylsilane with 290 nm pulses. Laser fluence 10^{18} photons cm^{-2} . Resolution 8 nm. (a) Pulses of 20 ps duration. (b) Pulses of 4 ns duration.

employed. Several emission bands are detected and can be readily assigned to the Swan bands of the diatomic fragment $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$, $\Delta v = 2, 1, 0, -1$, centred at 430, 470, 515 and 550 nm, respectively, and to an atomic line of Si ($4s^1P_1^0 \rightarrow 3p^1S_0$) at 390.5 nm. This latter atomic emission is almost undetectable for long pulse (4 ns) irradiation. An additional fluorescence emission that overlaps with the stray light of the photolysis laser at 290 nm, not shown in Fig. 1, could only be noticed by observing the effect of emptying the fluorescence cell. It was unequivocally assigned to emission in the Si ($4s^1P_1^0 \rightarrow 3p^1S_0$) transition at 288.2 nm. Both emissions at 390.5 and 288.2 nm are originated from the $4s^1P_1^0$ state. The same pattern of spontaneous fluorescence, consisting of C_2 and Si emissions, was observed for the CES molecule, but signals levels were around six times less intense for the same working pressure. It must be noted that no $SiH(A^2\Delta \rightarrow X^2\Pi)$ emission, centred at 415 nm, was observed for CES or phenylsilane. This observation is in marked contrast with the data obtained for far UV irradiation around 200 nm [9,10,25], where intense $SiH(A^2\Delta \rightarrow X^2\Pi)$ fluorescence was detected both for CES and for phenylsilane. Another remarkable absence is that of the triplet state of Si, $4s^3P^0$, situated 1300 cm^{-1} below the $4s^1P_1^0$ state, and indeed of a multitude of other excited singlet ($3d^1D_2^0$, $3d^1P_1^0$, $3d^1F_3^0$) and triplet ($3p^3D^0$) states of Si which were easily detected in the far UV photolysis of both CES and phenylsilane through their emission lines in the 200 to 300 nm region [9,25].

An analysis of the behaviour of the fluorescence signals as a function of laser energy was performed in order to get insight into the nature of the multiphoton processes that are responsible for the formation of the fragments. An example of such an experiment is shown in Fig. 2, where fluorescence intensity is represented as a function of laser energy on a

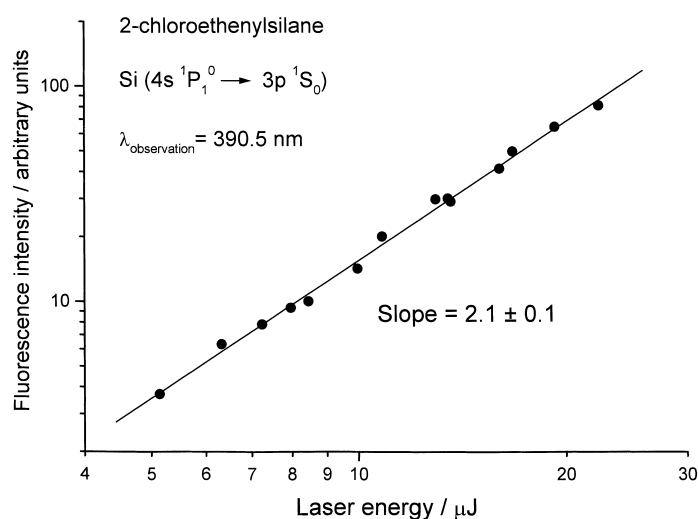


Fig. 2. Log–log representation of the dependence of the Si($4s^1P_1^0 \rightarrow 3p^1S_0$) fluorescence signal at 390.5 nm on laser energy, obtained upon 290 nm, 20 ps photolysis of a sample of 1.8 Torr of CES.

Table 1

Intensity of $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$, $\Delta v=0$ emissions for phenylsilane and CES in the two laser pulse duration regimes used. Their values are given relative to the largest signal

	Phenylsilane	CES
20 ps irradiation	1	$(1.6 \pm 0.2) \times 10^{-1}$
4 ns irradiation	$(1.6 \pm 0.2) \times 10^{-2}$	$(2.6 \pm 0.7) \times 10^{-3}$
Ratio (20 ps/4 ns)	62 ± 8	68 ± 17

log–log plot. As can be seen in the figure, in the case of the Si ($4s^1P_1^0 \rightarrow 3p^1S_0$) emission detected in the 290 nm, 20 ps photolysis of CES, a slope consistent with a quadratic dependence was measured. On thermochemical grounds, all processes leading to the formation of electronically excited Si and C_2 require at least the absorption of three 290 nm photons. The measurements, yielding slopes ranging from 2.0 to 3.0 in all cases are, therefore, an indication of the existence of a partial degree of saturation.

The behaviour exhibited by the fluorescence signals as a function of sample pressure was also measured. In all cases examined, they showed a linear behaviour for low pressure, followed by saturation above 1 Torr. The linearity indicates that collisional processes are not playing an important role in the process. Additionally, this type of measurement allows the comparison of fluorescence intensities detected for equal laser fluence but different molecules or irradiation conditions (20 ps or 4 ns pulses), for the ratio can only be safely measured when the comparison is made within the linear regime. The result of such an analysis for the emission of the C_2 Swan bands is presented in Table 1. As can be seen in the table, changing the pulse duration from 20 ps to 4 ns produced a decrease of the C_2 signal by a factor of around 65, CES and phenylsilane yielding the same value within the error bars.

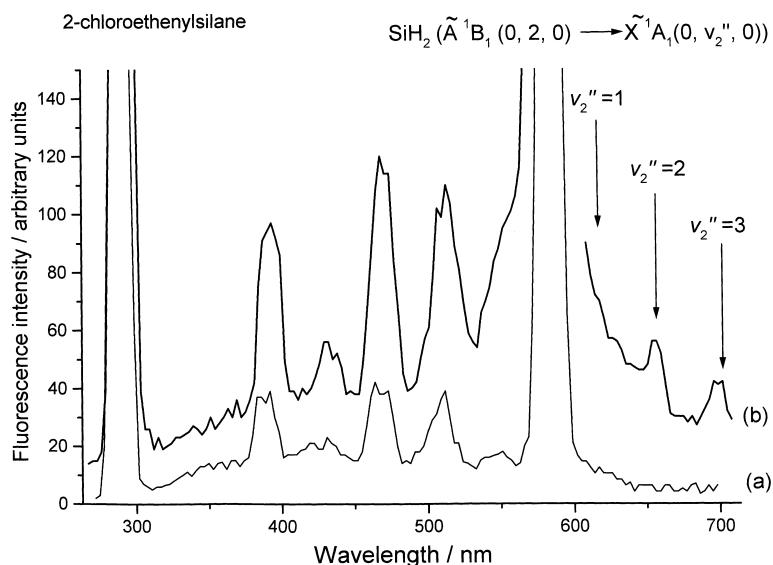


Fig. 3. Spontaneous and induced fluorescence spectra obtained upon irradiation of a sample of 1.0 Torr of CES with 20 ps pulses. (a) Simple irradiation at 290 nm (b) Double irradiation: both fundamental (580 nm) and frequency doubled (290 nm) beams.

Additional experiments were carried out allowing both the fundamental (580 nm) and the frequency doubled (290 nm) beams into the chamber. A relevant result of such experiments for the case of the fluorescence spectra of CES for 20 ps pulse irradiation is shown in Fig. 3. In the figure, both the single irradiation (at 290 nm) and double irradiation (at 290 and 580 nm) fluorescence spectra are shown. The increase observed in the already described emission bands is only due to the larger amount of UV laser energy into the chamber as a result of removing the cut-off filter. However, additional features were observed in the long wavelength region (>600 nm). Those can be readily assigned to fluorescence emissions induced by the 580 nm beam in the SiH₂ fragment. Radiation at 580 nm is resonant with the SiH₂($\tilde{A}^1B_1(0, 2, 0) \leftarrow \tilde{X}^1A_1(0, 0, 0)$) transition, whose origin is at 580.3 nm [26]. De-excitation from the $\tilde{A}^1B_1(0, 2, 0)$ state gives rise to the vibrational progression observed.

4. Discussion

Studies based on the identification of solid deposits and gaseous products resulting from the photolysis of CES, both upon IR [8,13] and far UV [4] irradiation, have established the existence of the following decomposition paths:



The relative importance of the reaction of chloroethene elimination (1) to dehydrochlorination followed by decomposition of ethynylsilane (2) depends upon the wavelength and

fluence conditions. In a recent publication [10], we identified an additional channel consisting of a β -elimination, probably into ethyne and chlorosilane, through the identification of the HSiCl product with LIF techniques when 193 nm irradiation was employed

SiH₂ produced in the IR photolysis of CES has been observed previously through the detection of both its spontaneous and LIF [9,13], although in neither case was it possible to assert whether it had been formed in process (1) or (2). An attempt to observe its formation after far UV irradiation failed [10] and the HSiCl radical was observed instead under those conditions, which led to the conclusion that the additional β -elimination played an important role with respect to SiH₂ yielding mechanisms. Observation of SiH₂(\tilde{X}^1A_1) upon 290 nm photolysis gives supporting evidence of the existence of SiH₂ elimination processes, extending their validity to the Rydberg region around 69 000 cm⁻¹ that is probed by two-photon absorption. Additionally, the fact that it is possible to detect the LIF signal when pump and probe beams overlap temporally within the 20 ps duration of the laser pulse, indicates that SiH₂(\tilde{X}^1A_1) formation is a process that takes place in a relatively short time (<20 ps). As CES does not possess any molecular resonance at the one-photon level, the mechanism for SiH₂ formation must involve the absorption of at least two photons. By using the value of $\Delta H_f^0(\text{CES})=5350 \text{ cm}^{-1}$ [9], the energy balance of the process is



$$\Delta H = 20\,600 \text{ cm}^{-1}$$

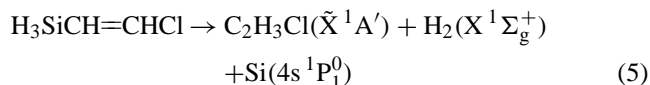
Upon two 290 nm photon absorption, the reaction is highly exothermic, since the excess energy that can be channelled

into internal degrees of freedom of the fragments and translational energy is as high as $48\,350\text{ cm}^{-1}$.

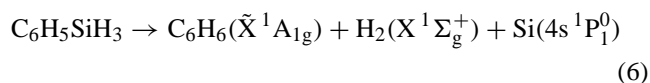
The fast appearance of SiH_2 in the process of fragmentation of CES makes it a possible candidate to be the precursor of the excited Si atoms whose emission was described above. The same applies to phenylsilane, where it is expected that the formation of SiH_2 will be taking place through the primary dissociation mechanism [7,27,28].



As regards the formation of excited Si atoms, the most striking feature, and one where the behaviour has proven opposite to that observed in the far UV photolysis [9,25], is the selectivity in the excited states of the atom that can be populated in the process. A possible explanation for that selectivity would be the presence of a resonant absorption step that would produce a significant population of the Si ($4s\ ^1P_1^0$) state. In fact, the presence of the Si ($4s\ ^1P_1^0 \leftarrow 3p\ ^1D_2$) transition at 288.3 nm, within the bandwidth of the 290 nm photolysis laser, could seem to indicate that this is the case. To check this point, photolysis was also studied upon 291.5 nm excitation, where the laser wavelength is no longer resonant with the Si transition, and no appreciable differences concerning the intensity of the Si fluorescence emission were observed when compared to excitation at 290 nm. Therefore, the contribution of a resonant process by the Si atom can be safely discarded. Rather, we are led to think that Si atoms are formed either by multiphoton absorption and subsequent dissociation of the parent molecule or, as suggested earlier, in a process where the SiH_2 intermediate species plays a role. A closer look at the energy requirements that Si ($4s\ ^1P_1^0$) formation demands in the photolysis of both CES and phenylsilane will help distinguish between these two situations. In each case, the lowest energy mechanism would proceed as follows:



$$\Delta H = 76\,400\text{ cm}^{-1}$$



$$\Delta H = 76\,800\text{ cm}^{-1}$$

As can be seen, the energy requirements are analogous. Together with the extremely similar behaviour of the Si emissions for these two molecules regarding selectivity, dependence on laser energy and on laser pulse duration, this is an indication of the presence of parallel mechanisms in CES and phenylsilane.

The energy required for processes (5) and (6) corresponds to the absorption of at least three 290 nm photons, which would provide $103\,500\text{ cm}^{-1}$. With such an amount of energy, it would be possible, in principle, to populate all Si

singlet and triplet states mentioned above, and the observed selectivity would remain unexplained. We will, therefore, consider the intervention of an intermediate species in the process. This species should undoubtedly be SiH_2 , since it is the only silicon containing fragment that is a primary photolysis product of both CES and phenylsilane. Moreover, dissociation of SiH_2 from its different states into $\text{Si} + \text{H}_2$ is extremely selective as to the states of Si that may be formed. In particular, according to ab initio calculations [19], the $2\ ^1B_2$ state of SiH_2 correlates with the dissociative path that leads to $\text{Si}(4s\ ^1P_1^0) + \text{H}_2(X^1\Sigma_g^+)$. The calculations also show that $\text{SiH}_2(2\ ^1B_2)$ does not correlate with the dissociation paths leading to $\text{SiH}(A^2\Delta)$. Production of $\text{Si}(4s\ ^1P_1^0)$ and absence of $\text{SiH}(A^2\Delta)$ would therefore suggest the participation of a $\text{SiH}_2(2\ ^1B_2)$ intermediate. The information gathered with our experiments suggests that the mechanism for $\text{Si}(4s\ ^1P_1^0)$ formation is the following: dissociation of the parent molecule after a two-photon absorption leads to the formation of SiH_2 through processes (1) and (4), respectively, for CES and phenylsilane. Subsequent resonant absorption by this fragment produces excitation to its $2\ ^1B_2$ state, from which dissociation proceeds into $\text{Si}(4s\ ^1P_1^0)$. The quadratic behaviour observed in the dependence of fluorescence signal on laser energy is consistent with this scheme: at the range of fluences used ($\sim 10^{17}$ – 10^{18} photons cm^{-2}), a resonant absorption step by SiH_2 is likely to be saturated, and therefore the quadratic dependence just reflects the initial two-photon process with no intermediate resonances undergone by the parent molecule. The dramatic decrease of excited Si production upon lengthening the pulse duration to 4 ns is the expected effect: the efficiency of purely multiphoton, as opposed to stepwise, processes tends to be very critically dependent on laser intensity, the maximum intensity reached by the 20 ps pulses being more than two orders of magnitude higher than that for 4 ns pulses.

The suggested mechanism for $\text{Si}(4s\ ^1P_1^0)$ formation being the same for both CES and phenylsilane, we are led to attribute the higher fluorescence intensity of the Si emission in phenylsilane than in CES, with a ratio of around 6, to their different two-photon absorption cross-sections in the $69\,000\text{ cm}^{-1}$ region. To this respect, our results would indicate that the cross-section for two-photon absorption for phenylsilane is around six times larger than it is for CES.

Less can be said about the formation of the $\text{C}_2(d\ ^3\Pi_g)$ fragment, as it involves the absorption of a higher number of photons (at least 4 in the case of phenylsilane). It can be mentioned, however, that the mechanism must proceed through some slow dissociation step, since the diminution of the efficiency of the process when long (4 ns) pulses are used is of lower magnitude than it is for the Si emission. As the first step in the process is a pure two-photon absorption by the parent molecule, only a slow dissociation process can somehow compensate for the critical intensity dependence. Similar effects were observed in the formation of $\text{C}_2(d\ ^3\Pi_g)$ in the photolysis of the ketone molecule in the near UV [23].

5. Conclusions

As has been shown above, a completely different panorama concerning the formation of excited silicon-containing fragments arises after 290 nm photolysis of CES and phenylsilane as compared to results in the far UV around 200 nm [10]. Thus, while multiphoton dissociation at 290 nm yields only $\text{Si}(4s\ ^1P_1^0)$ and $\text{C}_2(d\ ^3\Pi_g)$, the equivalent interaction around 200 nm additionally produces a set of singlet and triplet silicon states, and a highly populated $\text{SiH}(A^2\Delta)$ radical. This critically wavelength-dependent behaviour is most likely related to the different states of silylene that are populated in the process. In this respect, it would be interesting to direct further efforts to experiments similar to those reported by Knight et al. [20], where direct observation of $\text{Si}(^3P)$ was correlated with state-selected photoexcitation of $\text{SiH}_2(\tilde{A}^1B_1)$. In practical terms, this strongly wavelength-dependent behaviour provides a simple tool to selectively produce silicon fragments, which can prove useful in either production or diagnosis of CVD processes. Work is in progress to study the photolysis of these two molecules under irradiation with intermediate wavelength values from 193 to 290 nm, particularly at the threshold of one-photon excitation for each molecule.

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