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Visible Photodissociation Spectra of Gaseous Rhodamine Ions: Effects of Temperature and Tagging

Rafael Navrátil,[‡] Juraj Jašík,[‡] and Jana Roithová*[‡]

[‡]Department of Organic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, 12843 Prague 2, Czech Republic

Abstract

The paper reports on the effect of helium, argon, and nitrogen tagging on photodissociation spectra of Rhodamine 123 ions. We show that the effect of tagging is negligible as far as determination of the 0-0 transition in the electronic spectra is concerned. In contrast to the photodissociation spectra of the bare ions, the tagging method provides resolved Franck-Condon envelopes. Ar and N₂ tagging spectra revealed minor blue shifts (~0.5 nm) for some maxima in the Franck-Condon envelope with respect to the helium tagging spectrum. The N₂ tagging VisPD spectrum was less resolved compared to He- and Ar tagging spectra. Further, the effect of temperature on photodissociation spectra of bare rhodamine ions was investigated. It is shown that at room temperature the absorption spectrum is dominated by the absorption of vibrationally excited ions. The vibrationally relaxed ions start to be dominantly sampled at about 150 K. In average, three to four photons are required to induce photodissociation of the rhodamine ions and it slightly depends on the wavelength. We ascribe it to the fluorescence process.

Keywords: Cryogenic ion trap, Fluorescence, Gas-phase, Helium tagging, Ion spectroscopy, Mass spectrometry, Photodissociation

1 Introduction

Rhodamine dyes are useful because of their luminescence properties [1]. They have ample of applications as fluorescence labels [2,3]. Fluorescence of the rhodamine ions was also studied in the gas phase [4-8]. They can be used as a fluorescence label to study conformations of mass-selected ionized biomolecules [9]. Recently, Wellman and Jockusch compared fluorescence spectrum of mass-selected Rhodamine 110 ion with its photofragmentation spectrum [10-12]. They found out that the photofragmentation spectrum has slightly red-shifted maximum and a narrower profile [13].

We have investigated photofragmentation spectra of several rhodamine ions with helium tagging spectroscopy at 4 K [14,15]. We were able to obtain vibrationally resolved absorption spectra and interpret them based on the calculation of the Franck-Condon envelope for the electronic transition of the bare ions. We have determined the energy of the 0-0 transition. The value was considerably blue-shifted with respect to the absorption maximum previously published by Wellman and Jockusch (by 5.8 nm with respect to their photodissociation spectra and by 3.3 nm with respect to their fluorescence excitation spectra). The question arose whether it was due to the temperature difference or whether it was the effect of helium tagging.

In order to unravel the origin of the discrepancy, we have to first investigate the mechanism of helium tagging UV-Vis spectroscopy. The spectra are measured for mass-selected ions trapped and cooled down in an ion trap using helium buffer gas. Sufficiently relaxed ions form complexes with the present helium. Absorption of a Vis photon is detected by detachment of the helium atoms from these complexes. There can be several mechanisms leading to the helium detachment. Firstly, the detachment can happen, if the helium tag is not bound in the excited state (see Figure 1b). In such a case, the 0-0 transition would be slightly blue-shifted with respect to the 0-0 transition of the bare ion (Figure 1a). The shift would be related to the binding energy of the helium atom in the ground state (the energy of ground state is shifted by the binding energy with helium, whereas the excited state is not influenced). Another scenario would be that the helium atom is bound in the ground as well as the excited state. The 0-0 transition could then result from a fluorescence transition to a vibrationally excited ground state (Figure 1c). Alternatively, the transition from the excited state could be non-radiative and lead to either the hot triplet state or again to the hot ground state (intersystem crossing). Provided that the helium binding energy is similar in the ground state and the excited state, the detected 0-0 transition would reflect the 0-0 transition of the bare ion.

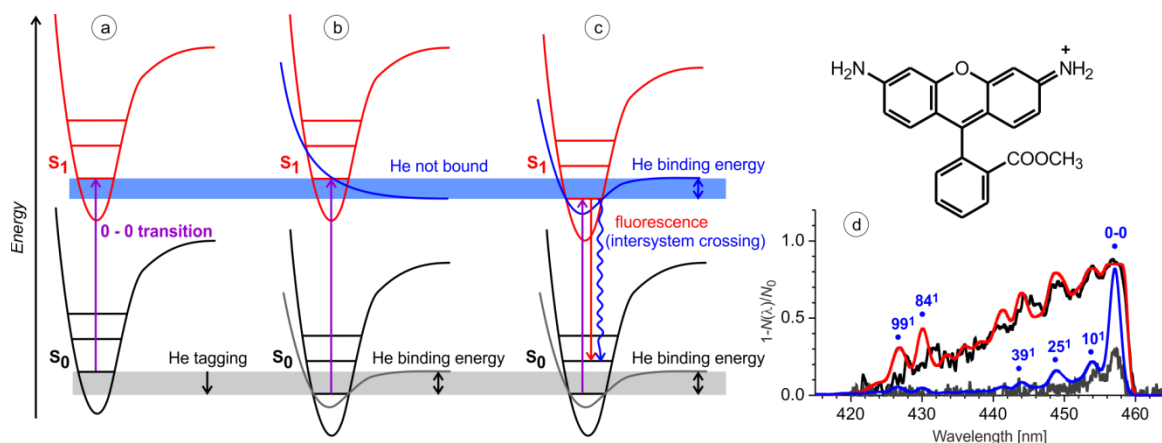


Figure 1. Simplified scheme of the effect of helium tagging on the ground and the excited state of a molecule and a possible mechanism of the detection of the 0-0 absorption by helium tagging Vis spectroscopy: (a) unperturbed system; (b) helium atom is not bound in the excited state; (c) helium is bound also in the excited state, the excitation is followed by fluorescence or thermal transition to a vibrationally excited ground state. (d) Helium tagging Vis spectrum of Rhodamine 123 ion (full laser power – black line; 30% laser power – gray line). The blue line is a simulation of Franck-Condon envelope; the red line is the same simulation normalized to the laser power with which the black experimental spectrum was measured. For details see ref. [14].

In this contribution, we will address possible scenarios by measurements Vis spectra of Rhodamine 123 with different tags and by plain photodissociation at different temperatures.

2 Experimental and theoretical details

The experiments were performed with the ISORI instrument [16]. ISORI is based on the combination of a low-temperature ion trap with a commercial TSQ 7000 instrument [17]. In its original design TSQ 7000 has a quadrupole-octopole-quadrupole geometry [18]. The original ion source vacuum chamber is connected to the main instrument via a customized flange. It preserves all of the ionization options provided by TSQ – here the electrospray ionization equipment is used [19-21]. The new ultra-high vacuum chamber consists of three additional differentially pumped regions: 1) the region with the first quadrupole (4P₁), and the quadrupole bender (QPB), 2) the octopole (8P), 3) the region with the ion trap (w4PT), the second quadrupole (4P₂) and the detector. The ion trap has a linear quadrupole geometry where the hyperbolic shape of each electrode is approximated by six wires [22]. It is mounted into a copper box, which is screwed onto a Sumitomo cold head (RDK 101 E). The copper box reaches minimum temperature of 2.6 K. The temperature of the box, surrounding the trap,

and of the heat shield is measured by silicon-diode sensors (LakeShore DT-670B1-CU). In case of measurements at elevated temperature up to 50 K the trap was heated using a certain current flowing through a resistor attached to the copper trap box. Measurements at temperatures higher than 50 K were performed simply by stopping the cooling-down phase at the given temperature. Cooling of the ions is achieved by collisions with helium buffer gas. The buffer gas is injected by a custom-made piezo valve, situated in vacuum, directly into the trap with a straight Teflon tube. The presence of the He buffer gas leads to elevation of the minimum trap temperature via convective heat transfer by several tens of Kelvin.

The Rhodamine ions were obtained by electrospray ionization of methanolic solutions of Rhodamine 110 chloride or Rhodamine 123 chloride (purchased from Sigma Aldrich and used without further purification). The ions of interest were mass-selected by the 4P₁, deflected by the QPB, and guided by the 8P to the w4PT. During the first part of the 1 Hz trapping cycle the ions were guided into the trap and simultaneously, He buffer gas has been injected. The maximum He number density was on the order of 10¹⁵ cm⁻³. In order to create He-tagged complexes, the trap was maintained at lowest possible temperature. Simultaneously, N₂-tagged complexes were produced because of traces amount of N₂ impurity. For formation of Ar-tagged complexes we used 10% Ar/He mixture as the buffer gas.

The injection times were typically 100 – 200 ms. After injection phase of the trapping cycle, the trapped ions were irradiated. The irradiation time was controlled by electrical signal gating the supercontinuum laser. For the measurements of photofragmentation spectra of bare ions we have used 50 ms injection time and subsequent 150 ms interval for cooling the ions with helium. The laser was admitted only after the cooling period, when helium background pressure dropped. This timing was necessary in order properly relax the ions and in order to hinder the collisional cooling during the irradiation time. The exit electrode of the trap was opened at 980 ms, the ions were mass-analyzed by the 4P₂, and detected by a Daly type detector operated in ion-counting mode. After the extraction, the RF voltage of the trap was switched off for 10 ms in order to banish possible not-extracted ions.

The Vis spectra of the tagged ions are presented as the reduced signal $[N_0 - N(\lambda)]/N_0$, where $N(\lambda)$ and N_0 are the numbers of the tagged complexes determined in every other trapping cycle either with or without irradiation by the laser. The photodissociation spectra of bare ions are plotted as number of the given fragment ions. The spectra shown in Figure 4a were normalized to the fragmentation efficiency measured at 460 nm. The spectra shown in Figure 4b are normalized to the maximum intensity 1.

To generate tunable Vis radiation, we used supercontinuum laser NKT Photonics SuperK Extreme (78 MHz seed laser repetition rate) connected to acusto-optic tunable filter (AOTF) SuperK Select (range 400 – 650 nm, FWHM from 1.8 nm at low wavelengths to 8.5 nm at high wavelengths). According to the manufacturer’s test report, the accuracy of the AOTF is in the range of +/- 0.2 nm of the nominal value over the whole wavelength domain. The light from the filter was focused into the trap region by CaF₂ lenses from the QPB side. The diameter of the focal spot was approximately 0.5 mm. Power of the Vis laser was measured right before entrance window of the instrument (after focusing lens) using power meter Thorlabs PM100A with detector Thorlabs S120C. Dependency of fragmentation yield on the laser power was measured by changing the nominal emission of the supercontinuum laser in discrete steps which were afterwards calibrated by the power meter.

3 Results

3.1 Effect of tagging

We have first measured the photodissociation spectra using alternative tags. Next to the original helium tagging, we have applied also tagging by argon and the nitrogen molecule. We have assumed that argon as well as N₂ will be much stronger bound to the Rhodamine ion than the helium atom and therefore the eventual changes in the position of the 0-0 transition will be more distinct. Figure 2 shows a comparison of helium tagging with argon and N₂ tagging. The maximum of the band that most probably corresponds to the 0-0 transition (denoted as 0-0 transition in the following) is located at 457.1 nm for the helium tagging and at 457.3 nm for the argon tagging as well as the N₂ tagging. The relative shift corresponds to the energy difference on the order of 0.1 kJ mol⁻¹.

The smallest energy of the 0-0 transition was found for the helium tagging and it slightly increased for argon and nitrogen. The differences in theoretical binding energies (see Table S1 in the Supporting Information) are however two orders of magnitude larger. We therefore exclude the rationale based on Figure 1b. Small shifts in energy are expected for mechanistic possibilities depicted in Figure 1c. The energy shifts could reflect the differences in binding energies of a tag in the ground state and in the excited state (*i.e.* differences in the heights of the gray and blue panel in Figure 1).

All tagging photodissociation spectra were measured at the temperature of the trap set to 4 K. The internal energy relaxation of the trapped ions depends not only on the temperature of the trap, but also on the number of the collisions between the ions and helium buffer gas (which is in order 10⁴ – 10⁵ for our conditions). We kept the same density of the buffer gas

and therefore we assume that we have always prepared an ensemble of the ions with a very similar internal energy distribution. Nevertheless, the helium complexes will be formed only with the ions with the lowest internal energy, whereas argon and nitrogen will be probably forming complexes also with the ions that are not completely vibrationally relaxed. This might be the reason of the small shift in the 0-0 transition that we have observed. In addition, we can see an effect of the tagging on the Franck-Condon envelope (cf. the vertical lines in Figure 2). The position of the 10^1 transition (predicted theoretically) is considerably shifted to larger wavelengths when He, Ar, and N_2 tagging are compared. In addition, the N_2 tagging spectrum shows less resolved Franck-Condon envelope. This suggests that the Ar and N_2 tagging surely influence the molecular structure of the Rhodamine ion. We cannot exclude that He tagging has an effect as well, but a comparison with classical photodissociation spectra measured at 10 K shows at least for the second maximum on the Franck-Condon envelope a good agreement.

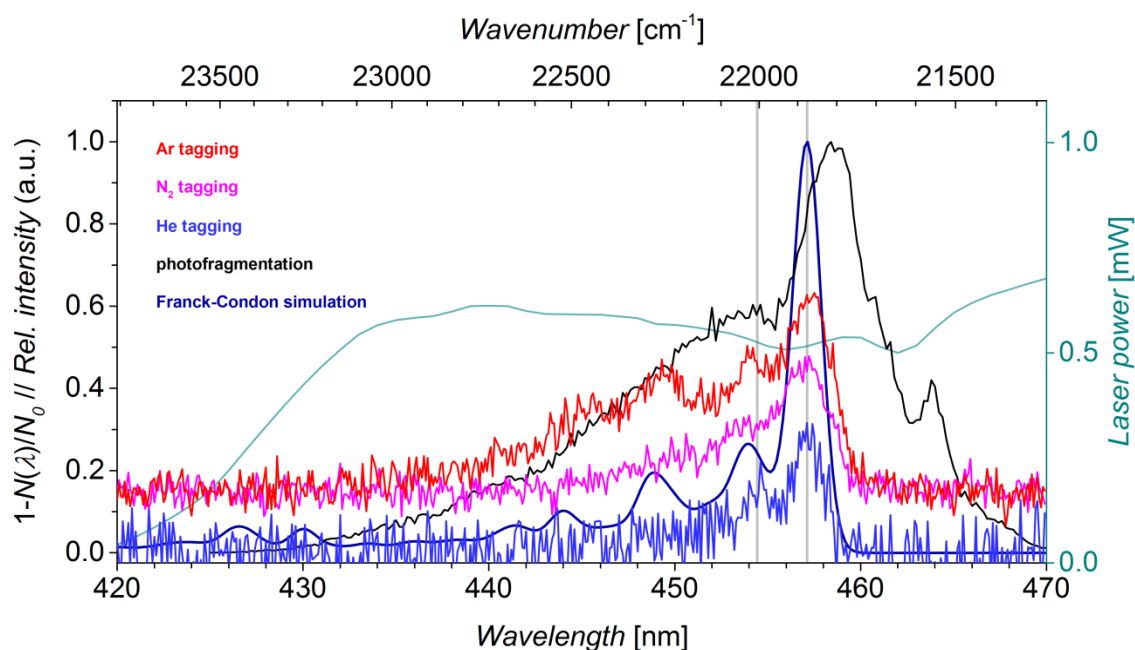


Figure 2. Comparison of He-, Ar-, and N_2 tagging photodissociation spectra of Rhodamine 123 ion measured at 4 K. The spectra were measured with a reduced laser power in order to avoid saturation. Argon tagging spectra with a larger laser power and at higher temperature (10 K) can be found in the Supporting Information (Figure S1). The black spectrum shows a standard photodissociation spectrum measured at 10 K; the fragment with m/z 285 was monitored. The vertical lines denote the 0-0 transition and 10^1 transition determined from the helium tagging VisPD spectrum.

3.2 Effect of temperature on photodissociation spectra

Further, we have compared the Vis spectra obtained by the tagging method and by the photodissociation of bare ions at 10 K (Figure 2 and 3). The photofragmentation mass

spectrum of bare Rhodamine 123 ion (m/z 345, Figure S2) is dominated by the peak at m/z 285 ($\Delta M_r = - 60$) that is accompanied by less abundant peaks at m/z 328 ($\Delta M_r = - 17$), m/z 313 ($\Delta M_r = - 32$), m/z 298 ($\Delta M_r = - 47$) and m/z 270 ($\Delta M_r = - 75$). The dominant fragmentation probably corresponds to the elimination of the whole methylester group and one hydrogen atom (*i.e.* methylformate). The loss of mass 17 is most probably caused by the elimination of ammonia. The remaining channels probably correspond to combined losses of ammonia and parts of the methyl ester group.

Clearly, all photofragmentation channels possess the fragmentation maxima at the same wavelength ($\lambda = 459.1$ nm). This maximum is shifted by ~ 2 nm with respect to the maxima obtained from the tagging experiments. The notable difference is that the photofragmentation spectrum contains hot-band features at ~ 464 nm and ~ 468 nm. Formation of loosely bound tagged ions, in particular the helium tagged complexes, requires that the bare ions are internally relaxed to the ground vibrational state. If we sample the whole population of the bare ions in the bare photofragmentation experiments, we can see that a part of the ions is still vibrationally excited even at 10 K. Interestingly, we can detect the hot bands even for argon-tagged complexes (see Figure S1).

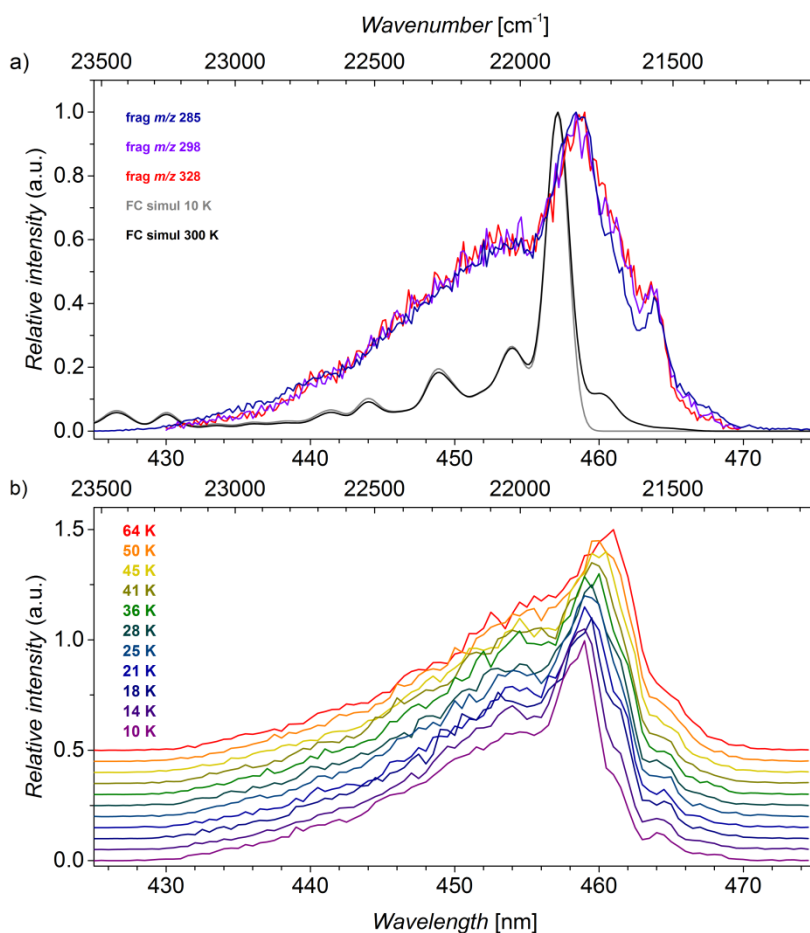


Figure 3. a) Comparison of photodissociation spectra of Rhodamine 123 ion measured at 10 K (full laser power) obtained by monitoring different fragments (m/z 285, m/z 298, and m/z 328). The gray line shows Franck-Condon envelope simulation at 10 K and the black line is the simulation at 300 K (computational details can be found in the Supporting Information). b) Photofragmentation spectrum of Rhodamine 123 ion at variable temperatures (fragment with m/z 285 was monitored; the total yield of photofragmentation was $\sim 5\%$).

We have tested the effect of temperature on the photofragmentation spectra in a more detail (Figure 3b). It was impossible to obtain a resolved Franck-Condon envelope for bare photofragmentation spectra. Further, in the temperature range from 10 K to 64 K, we can see a clear shift of the maximum corresponding to the 0-0 transition and increasing population of the hot bands. At $T = 45$ K (yellow) the separation of the 0-0 transition and the first hot band becomes indistinguishable. We note in passing that analogous temperature changes are known for fluorescence spectra and some rhodamine molecules are used as sensitive temperature sensors [23,24].

We have continued with the temperature dependent study also at a higher temperature range (Figure 4). The results clearly show that the photodissociation spectrum measured at

room temperature actually reflects mainly photoexcitation of vibrationally excited parent ions. The maximum of photofragmentation at 300 K is at 467 nm. The spectrum is not resolved, which means that we sample a broad population of vibrationally excited ions. With decreasing temperature, some of the internal degrees of freedom are relaxed and the maximum of the first peak shifts to 465 nm ($T = 150$ K). With further decreasing temperature, the spectrum starts to resemble the spectra measured at the low temperature range (Figure 3b).

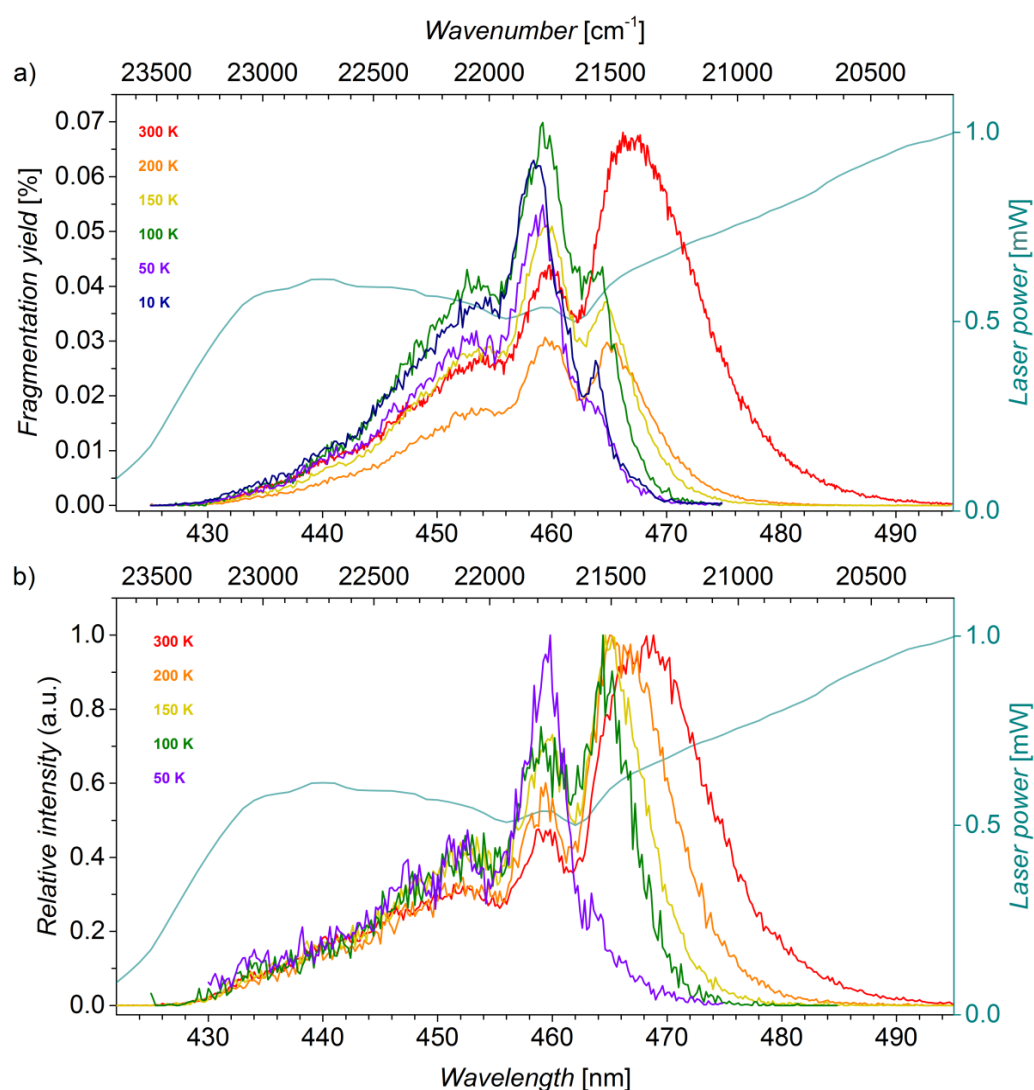


Figure 4. Photodissociation spectra of a) Rhodamine 123 ion and b) Rhodamine 110 ion (fragments with m/z 285 were monitored for both parent ions) measured at variable temperatures. The fragmentation yield for Rhodamine 123 was determined at 460 nm as 3.0 – 6.5 % and the spectra are normalized to the given fragmentation yield. The error for the determination of the fragmentation yield was about 20 % - it is probably the reason for the low intensity of the spectrum measured at 200 K. For Rhodamine 110, all spectra are normalized to maximum intensity 1.

In order to make a comparison with the previous results of Wellman and Jockusch [13], we have also measured temperature dependent photodissociation spectra of Rhodamine 110 (Figure 4b). We can see precisely the same effect as for Rhodamine 123. The maximum of the absorption spectrum at 300 K is at 468 nm. Wellman and Jockusch reported a value of 465 nm which is in the range of the band due to absorption of vibrationally excited parent ions. The shift in the reading can be given by some temperature differences and by a lower spectral resolution in the previous measurements [13].

3.3 Multi-photon character of VisPD spectra

The number of photons required for bringing about the photodissociation can be determined from the laser power dependence of the fragmentation. We have compared these results for spectra measured at room temperature and the data clearly show that 2 to 4 photons are necessary for inducing the photofragmentation (Figures 5a – 5e). The numbers were determined from the power function fits of the data (see Figure 5). The exponents reflect the number of the photons required for the occurrence of the photofragmentation. The estimate of the number of the photons is in agreement with the previous results of Wellman and Jockusch [13].

Slightly larger exponents were obtained by fitting the analogous measurements at 50 K (Figures 5f – 5h) and 10 K (Figures 5i and 5j). The power dependences are not only dependent on the temperature, but also on the wavelength at which they were determined. At wavelengths, where the vibrationally excited ions absorb (467 nm and 475 nm), less photons in average are necessary for the fragmentation. We have performed the experiments under the conditions that exclude collisional cooling as a competing process to photofragmentation (see the experimental details). We propose that the multiphotonic nature of the photofragmentation spectra of rhodamine ions is given by their efficient fluorescence. The emission of a photon can lead to differently vibrationally excited S_0 state. There is only a certain probability that sufficiently internally excited S_0 state will be populated so that the fragmentation would occur. At higher temperature, we start with a broader distribution of states which can lead to the observed effect.

We note in passing that we have previously demonstrated that helium tagging VisPD spectra are indeed single-photon absorption spectra [14].

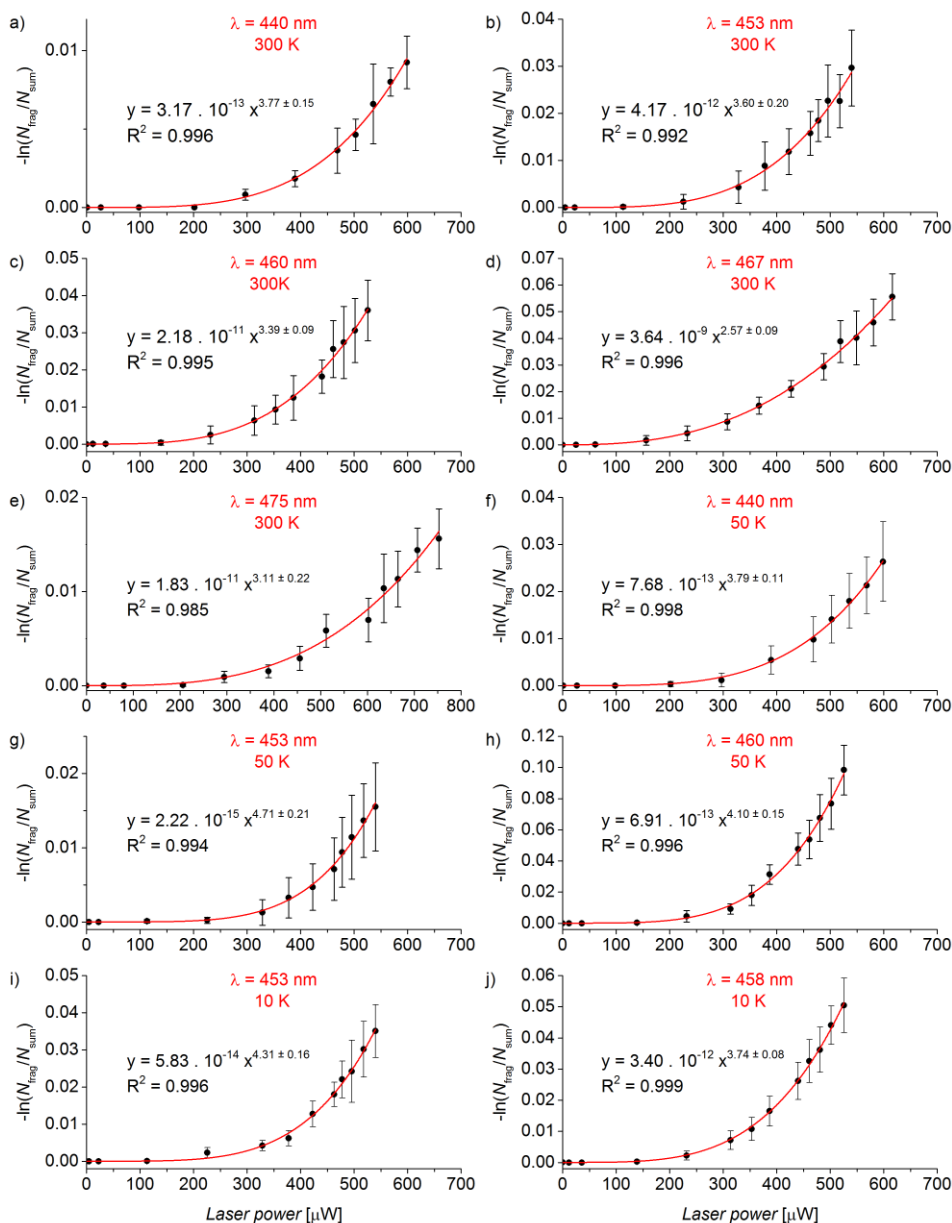


Figure 5. Dependence of the photofragmentation efficiency on the laser power measured at the indicated wavelengths at 300 K (a – e), at 50 K (f-h) and at 10 K (i,j). The error bars denote standard deviation of the experimental data and the red lines are fits of the experimental data given by the inserted equation.

4 Discussion

4.1 Effect of tagging

Measurements of tagging photodissociation spectra in the visible spectra range showed that the energy of the 0-0 transition depended on the tag only negligibly. We can therefore exclude that the mechanism of the tagging UV-Vis photodissociation spectroscopy for these ions would be based on the fact that helium would not be bound to the ion in the excited state. Instead, the excited state relaxes either by fluorescence or by thermal conversion to a vibrationally excited ground state (event. triplet state). The internal energy is then sufficient

for the elimination of the tag. We can also estimate that the binding energies of the tags investigated here (He, Ar, N₂) are very similar in the ground state and in the excited state.

The tagging method, however, clearly has an effect on the measured Franck-Condon envelopes in going from He to Ar and to N₂ tagging. Transitions to the vibrationally excited S₁ states are associated with increasing blue shifts in absorption for the tagging with: He < Ar < N₂. In analogy to the ground electronic state, it can be expected that loosely bound tags will not be bound in highly vibrationally excited S₁ states. These states will be therefore less influenced by the tag. The relative shifts of the maxima in Franck-Condon envelopes could be thus related to the binding energies of the tags in the ground electronic state. The estimated differences based on the shifts of the 10¹ maxima between helium tagged ions on one hand and argon and nitrogen tagged ions on the other correspond to 0.3 kJ mol⁻¹ and 0.6 kJ mol⁻¹, respectively. These amounts of energy are again much smaller than the expected binding energies of argon and nitrogen based on DFT calculations (Table S1).

Comparison of the helium and argon tagging spectra with the bare photodissociation spectra show that the tagging provided an access to the Franck-Condon envelope of the electronic transition. Photofragmentation spectra of the bare ions were always unresolved even when recorded at the same temperature as the tagging spectra (cf. Figure S1).

4.2 Effect of temperature

We can see that the photofragmentation yield in the range of the 0-0 transition only marginally depends on temperature (Figure 4a). The overall photofragmentation yield however increases with temperature because of the efficient absorption of the vibrationally excited ions that starts to play a role at 150 K and prevails at room temperature. We should keep in mind that at high temperatures more ions are vibrationally excited and therefore a lower population of the ions in the ground state is expected together with a decrease of the fragments yield at 459 nm. The experimental data reveal exactly this trend (cf. Figure 4). We note in passing that it was impossible to get the data under the exactly same conditions, because several experimental parameters are changing with temperature (trapping conditions and overlap of the ion cloud with the laser beam). The absolute intensities in Figure 4a are therefore measured with ± 20 % accuracy. The data in Figure 4b were intentionally normalized to the maximum intensity of 1.

We have shown that the photofragmentation yield for the bare rhodamine ions increases with the third to fourth power of the laser power. It can be translated as that on average three to four photons are required in order to induce the fragmentation of the ion.

Previously, we have shown that helium tagging VisPD spectroscopy is a single-photon process. Multiphoton nature of the plain VisPD spectra leads to a lower resolution when compared to the helium tagging spectra and this holds even if the ions are internally relaxed at a low temperature. It has been proposed that the multiphoton character of these spectra is due to competition with collisional cooling with a buffer gas [13]. We irradiate the ions after the buffer gas is pumped off, therefore most probably the multiphoton character is due to the efficient fluorescence of the rhodamine ions and is inherently associated with this type of molecules.

Conclusions

We have compared helium tagging photodissociation spectra of Rhodamine 123 in the visible range of the spectrum with analogous spectra obtained by argon and nitrogen tagging at 4 K and with bare photodissociation spectra at variable temperatures. The results show that the effect of tagging is rather modest. The energy of the 0-0 transition is influenced only negligibly and we thus conclude that the binding energy of the tags is rather similar in the ground state and in the excited state.

We further show that the tagging has an effect on the Franck-Condon envelope of the electronic transition. The argon and N₂ tags have a significantly larger binding energy to the rhodamine ions than helium. It is reflected in small blue-shifts of the preferred transitions. We can therefore conclude that tagging is not completely “innocent” for electronic spectra.

We show that previously published absorption spectra of rhodamine ions are dominated by the absorption of the ion in vibrationally excited ground state. The temperature dependent study revealed that the spectrum is significantly influenced by the absorption of vibrationally excited ground states at temperatures above 150 K. The question about the origin of the differences between our previously published helium tagging spectra and the spectra obtained at room temperature by photodissociation or fluorescence of bare ions [13] can be thus unequivocally answered: The reason is the different temperature and internal energy of the ions sampled in the experiments.

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Author Information

Corresponding Author: *Phone: (420) 221951322, E-mail: roithova@natur.cuni.cz

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