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A New Method for Double-Resonance Spectroscopy in a Cold Quadrupole Ion Trap and Its Application to UV-UV Hole-Burning Spectroscopy of Protonated Adenine Dimer

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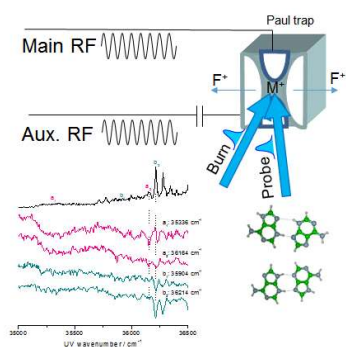
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A novel method for double resonance spectroscopy in a cold quadrupole ion trap is presented, which utilizes dipolar resonant excitation of fragment ions in the quadrupole ion trap. Photofragments by a burn laser are removed by applying an auxiliary RF to the trap, and a probe laser detects the depletion of photofragments by the burn laser. By scanning the wavelength of the burn laser, conformation specific UV spectrum of a cold ion is obtained. This simple and powerful method is applicable to any type of double-resonance spectroscopy in a cold

quadrupole ion trap, and was applied to UV-UV hole-burning spectroscopy of protonated adenine dimer. It was found that protonated adenine dimer has multiple conformers/tautomers, each with multiple excited states with drastically different excited state dynamics.

TOC GRAPHICS



KEYWORDS cold ion spectroscopy, double-resonance, UV-UV hole-burning, quadrupole ion trap, biomolecular ion

Cold ion spectroscopy is drawing much attention as a means to study structure of biological macromolecules since its successful application to protonated amino acids¹ and subsequently to many biomolecular ions.² The essential part of cold ion spectroscopy is a cold ion trap that can accumulate ions and cool them down to cryogenic temperature, such as a 22-pole ion trap³ or a quadrupole ion trap (QIT).⁴⁻⁷ Recently the use of a planar multipole ion trap⁸ or an octopole ion trap⁹ was also reported. Mass spectrometry of a biomolecular ion provides its sequence information through its fragmentation pattern by collision-induced dissociation (CID),¹⁰ but sequence information alone is not enough to understand the structure and function of a flexible biomolecule that has multiple conformers. Spectroscopy can provide detailed information about conformations of flexible molecules, such as intramolecular hydrogen-bonding that stabilizes conformers.¹¹ In this regard, a recently reported hybrid mass spectrometer with a cold ion trap is quite promising for both sequence and conformational information of biomolecular ions.¹²

Double resonance techniques have been used in the spectroscopy of neutral molecules in order to obtain the number of conformers and their respective conformer-specific UV and/or IR spectra.¹¹ The double resonance techniques employ two laser pulses (burn and probe pulses) and usually rely on pulsed detection by time-of-flight (TOF) or laser-induced fluorescence (LIF). Signals from burn and probe laser pulses are separated in time therefore they can be detected separately. The same technique of two temporally separated signals could not be applied to spectroscopy of ions in a cold ion trap, when all ions in the trap were analyzed simultaneously after the two lasers were irradiated. Instead, an IR-UV double resonance technique utilized depletion of ion signal by IR radiation,¹³⁻¹⁵ or an IR-IR double resonance technique employed separation of the parent and fragment ions by a TOF mass analyzer after the first laser was irradiated.¹⁶⁻¹⁸ However, no UV-UV double resonance spectroscopy of a cold ion was performed

until Choi *et al.* have reported a method based on axial instability of low mass ions in a QIT.¹⁹⁻²¹ Féraud *et al.* recently published another UV-UV hole burning method based on TOF-separation of parent and fragment ions and detection of fast neutral fragments.²²

Here we present a novel method of UV-UV hole-burning spectroscopy, which is readily adaptable to any existing cold QIT. Fragment ions from a burn laser are removed from the trap by resonantly exciting its axial micromotion with an auxiliary dipolar RF, then a probe laser determines the depletion of the population. We chose protonated adenine dimer (Ade_2H^+) to demonstrate its capability. Spectroscopy of neutral DNA bases was first reported by Nir *et al.* for guanine²³ and Kim *et al.* for adenine.²⁴ Ultrafast excited state dynamics of DNA bases and their subsequent photostability were studied by many groups.²⁵⁻³¹ Building on the recently reported spectroscopy of protonated DNA bases by Berdakin *et al.*,³² we report UV-UV hole-burning spectroscopy of Ade_2H^+ using the new method.

For double-resonance spectroscopy, the first laser pulse (burn) is fired in the QIT at 30 ms after ion trapping and the second laser (probe) was irradiated in the QIT at 89.995 ms, i.e. 5 μs before extraction from the QIT. Fragment ions produced by the burn laser are ejected from the QIT by dipolar resonant excitation of its axial micromotion by an auxiliary RF waveform ("tickle").³³ A variable-frequency RF waveform from an RF generator (Métrix GX 245) is continuously supplied to the entrance end-cap electrode of the QIT through a 400 pF capacitor, and used as tickle RF. Figure 1 describes the tickle RF connection to the cold QIT. Tickle RF frequency, which is dependent on the QIT geometry, main RF frequency, main RF voltage, and m/z of the ion to be ejected, is calculated using the equation for secular frequency of ions in a QIT.³³ Variation of ion signal intensity as a function of excitation RF frequency gives a range of

m/z for ejected ions as $\Delta m/z \sim 8$ at $m/z = 136$ (See Figure S1 in Supporting Information) i.e., the mass of protonated adenine (AdeH^+).

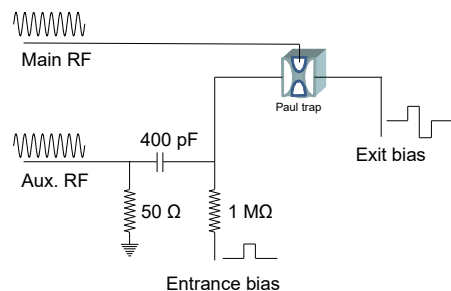


Figure 1. Experimental setup for resonant dipolar ejection of ions in a quadrupole ion trap

Figure 2 shows mass spectra of Ade_2H^+ and its fragment, protonated adenine (AdeH^+), with and without burn laser, probe laser, and tickle RF. Figure 2(a) is a TOF mass spectrum of Ade_2H^+ produced from the ESI, mass-gated, and stored in the cold QIT. Even though only the dimer was chosen for trapping, there is a small amount of monomer present presumably due to CID in the QIT during trapping. Figure 2(b) is a mass spectrum when a burn laser at 276.14 nm (36214 cm^{-1}) was introduced into the QIT 30 ms after ions are being trapped and cooled down. Protonated adenine monomer AdeH^+ is the only photofragment, and the fragmentation yield is more than 50 %. Figure 2(c) shows that when tickle RF (101.24 kHz, 0.7 V (see figure S2 in supplementary information)) is applied to the QIT, the AdeH^+ fragment ions (m/z 136) produced either by CID or laser are completely removed from the QIT, while the parent ion (Ade_2H^+) intensity is not affected. The burn laser is fired at 30 ms after ion trapping but the ions are extracted from the QIT at 90 ms, therefore photofragment ions are trapped in the QIT for 60 ms, which is sufficient for gradual increase in axial motion and subsequent ejection from QIT. The

tickle RF frequency (101.24 kHz) is resonant with the fragment ion AdeH^+ at $m/z = 136$, therefore the motion of the parent ion is not excited. Figure 2(d) shows a mass spectrum when a probe laser at 276.14 nm (36214 cm^{-1}) was irradiated 5 μs before extraction of ions. Photofragment ions by probe laser are not removed by tickle RF, because the time delay between the laser and the extraction is shorter than the time needed for one round-trip along axial direction in QIT. Instead, it is observed that the mass peak for the fragment ion is broadened because the tickle RF is not synchronized to the extraction and its random phase can increase or decrease the speed of ions along TOF axis between laser shots. Thus by averaging ion signal from multiple laser shots the mass peak becomes broad. Probe laser has lower power than that of the burn laser, therefore fragment ion intensity is lower and parent ion intensity is higher than in Figure 2(b). Figure 2(e) shows that the fragment ion from the probe laser is depleted with respect to Figure 2(d) due to the burn laser, and that UV-UV hole-burning spectrum can be measured.

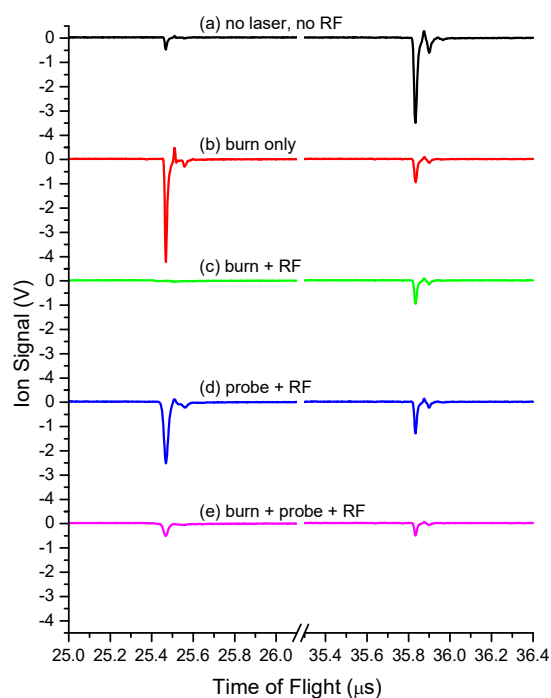


Figure 2. Mass spectra of Ade_2H^+ (35.834 μs) and its fragment AdeH^+ (25.468 μs) (a) without laser nor tickle RF, (b) with burn laser (276.14 nm) only, (c) with burn laser and tickle RF (101.24 kHz, 0.7 V), (d) with probe laser (276.14 nm) and tickle RF, and (e) with burn and probe laser and tickle RF. (The small peak at the right of the main peak is due to ringing of the detection.)

Figure 3(a) is a UV photofragmentation spectrum of Ade_2H^+ taken from 290.00 nm to 265.00 nm at 0.02 nm step (34483 cm^{-1} - 37736 cm^{-1} , $\sim 3 \text{ cm}^{-1}$ step). The protonated adenine monomer had a continuum of absorption that starts from 35460 cm^{-1} and a broad vibronic progression from 36630 cm^{-1} , which were assigned tentatively to two different tautomeric forms, 3H-7H and 1H-9H respectively without excluding the possibility of different excited states.³² The protonated

dimer also has a continuum of absorption from 34820 cm^{-1} , which is red-shifted by 640 cm^{-1} from that of the protonated monomer. The amount of red-shift seems reasonable when solvated by a neutral molecule. A prominent vibronic peak is found at 36214 cm^{-1} (marked b_2), red-shifted from the 36630 cm^{-1} band of the protonated monomer. However the width of the vibronic progression is much sharper than that of the protonated monomer. In the case of protonated adenine monomer, the width of the vibronic peak was 180 cm^{-1} , and AdeH^+ should have 30 fs of excited state lifetime from the uncertainty principle.³² The width of the band at 36214 cm^{-1} for Ade_2H^+ is 20 cm^{-1} , which is slightly larger than the experimental resolution (laser bandwidth and rotational contour). One can conclude that the lifetime is longer than 200 fs from the uncertainty principle. Therefore it can be suspected that the broad absorption of one excited state of Ade_2H^+ is simply red-shifted by solvation but still very broad, while there is a new mechanism in Ade_2H^+ which sharpens the spectral bandwidth and lengthens the lifetime of another excited state. Indeed, *ab-initio* calculations have shown that many electronic states are in the same energy range in both the neutral and protonated adenine,³⁴⁻³⁷ and this should become even more complex in the protonated dimer. To check if the very broad continuous bands and narrow peaks are belonging to different conformer/tautomer or to different electronic states of the same conformer, we performed UV-UV hole-burning spectroscopy of Ade_2H^+ with the new method presented in this paper.

Figure 3(b) is a zoom of Figure 3(a) to better mark the positions of probe laser wavelength used for UV-UV hole-burning spectroscopy and to better compare with the hole-burning spectra in Figure 3(c). The hole-burning spectra marked as a_1 and b_1 were taken with the probe laser tuned at broad absorption, while the ones with a_2 and b_2 were taken at sharp vibronic peaks. Though a_1 and b_1 cannot be completely selective due to overlapping broad absorption, they show

significant difference from each other. The vibronic peak at 36164 cm^{-1} is seen in both a_1 and a_2 but not in b_1 and b_2 . The peak at 36214 cm^{-1} is very intense in b_1/b_2 , which is not the case in a_1/a_2 . Instead a hidden shoulder peak at 36227 cm^{-1} is seen in a_1/a_2 . Also a broad absorption around 35300 cm^{-1} is seen in both a_1 and a_2 , with almost the same intensity as the vibronic bands. Therefore it is confirmed that there are at least two species of Ade_2H^+ (a and b) absorbing in the similar UV region. Moreover, broad and narrow bands do belong to the same species and are supposed to belong to different excited states.

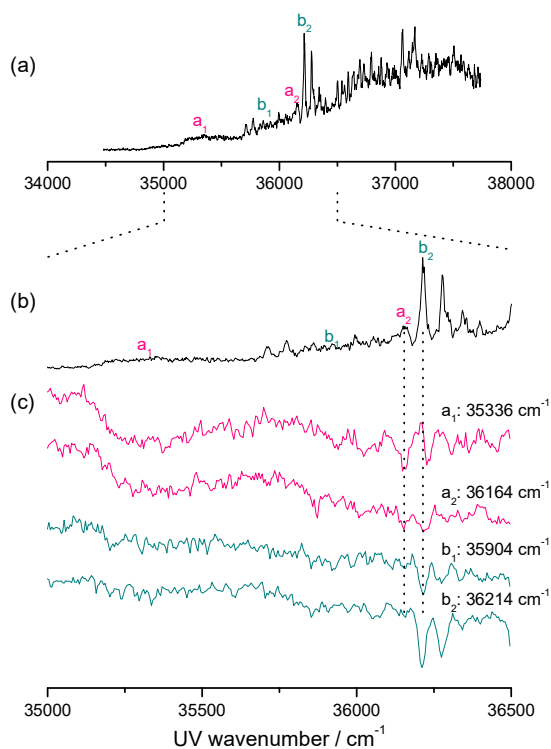


Figure 3. (a) Photofragmentation spectrum of Ade_2H^+ from 34483 cm^{-1} to 37736 cm^{-1} , (b) zoom of the spectrum between 35000 cm^{-1} and 36500 cm^{-1} , (c) hole-burning spectra of Ade_2H^+ by fixing the probe laser at the wavelengths marked a_1 , a_2 , b_1 , b_2 and tuning the burn laser.

The new method for UV-UV hole-burning spectroscopy in a cold QIT has merits over the previously reported methods by Choi *et al.*¹⁹ and Féraud *et al.*²² Compared to the method by Choi *et al.*, it does not require the fragment ion's m/z to be less than half of the parent ion, therefore applicable to a wider range of fragments, e.g. H₂O-loss or NH₃-loss products, which are commonly found in CID of ions. Féraud *et al.*'s method needs modification of a TOF instrument to detect neutral fragments, but the present method can be readily applied to any existing cold QIT without modification of the instrument itself. The neutral detection method requires fast fragmentation of ions between the electrodes at the end of the TOF mass analyzer, while fragmentation can be as slow as a few tens of milliseconds in this new method. This method does not have the problem of overlapping a laser beam with an ion packet in a TOF mass spectrometer, because ions are always confined at the center of the trap. Burn and probe processes are done in the same ion trap while the ions are still trapped at cryogenic temperature, so there is no worry about collisional heating of ions during extraction from the trap. This method is applicable when there is no neutral fragment, e.g. in the dissociation of a doubly charged ion into two singly charged fragment ions. Furthermore, it becomes possible to perform spectroscopy of a photofragment ion by actively isolating the photofragment and doing photofragmentation spectroscopy on it.

One drawback of this method is that it is only applicable to fragment ions with $\Delta m/z > 8$, so loss of hydrogen atom³⁸ or hydrogen molecule⁶ cannot be observed. In those cases, the neutral detection method can be applied to observe the small mass difference. Another drawback is that this is only applicable to quadrupole ion traps, where ions tend to have higher temperature than higher-order multipoles because they are focused at the center of the trap and undergo collisions

between them. Also, as is always the case with any double resonance spectroscopic method, large absorption cross-section and large fragmentation yield are still needed to clearly observe hole-burning effects.

The protonated adenine monomer and dimer systems are quite challenging systems for theoretical studies since the number of excited states nearby the band origin is quite dense and there are many conical intersections between the different states. The hole burning experiment shows that a_1/a_2 belong to the same species and b_1/b_2 to another one. Both species are exhibiting broad absorption together with narrow peaks. Thus one can deduce that, for each conformer/tautomer, there are at least two close lying excited states which have very different non radiative processes. Figure 4 shows two most stable structures of Ade_2H^+ computed at MP2/cc-pVDZ level of theory. Their relative ground state energy at MP2/cc-pVDZ and a few vertical transition energy at ADC(2)/cc-pVDZ are summarized in Table 1. Both structures have 9-H adenine protonated at position 3 and neutral 7-H adenine, but differ in relative orientation of the two moieties. Other possible structures are summarized in Table S1 of Supporting Information. The structure in Figure 4(a) has lower vertical transition energy than that in Figure 4(b). Therefore it was tentatively assigned to a_1/a_2 that has vibronic peaks at lower energy. The structure of Figure 4(b) is tentatively assigned to b_1/b_2 because it has higher transition energy. It should be mentioned that the complexity of system is such that more reliable assignments need higher level calculations as well as more structural information with e.g. IR/UV hole burning spectroscopy.

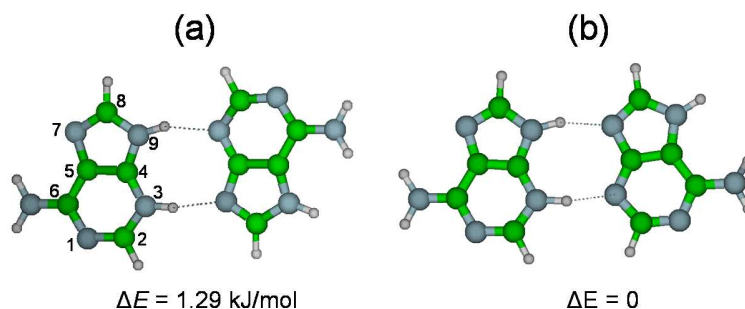


Figure 4. Two most stable structures of Ade₂H⁺ computed at MP2/cc-pVDZ level of theory. Atomic numbering of the purine ring is given. ΔE is relative stability of structures at MP2/cc-pVDZ

Table 1. Relative ground state energy and vertical transition energy of the two most stable Ade₂H⁺ structures.

	(a)	(b)
ΔE (kJ/mol)	1.29	0
S ₁ (eV)	4.86	5.05
S ₂ (eV)	5.04	5.17
S ₃ (eV)	5.13	5.27
S ₄ (eV)	5.30	5.27

ΔE is relative stability of structures at MP2/cc-pVDZ and S_n ($n = 1-4$) are vertical excited state energies at ADC(2)/cc-pVDZ.

One possible explanation for much sharper vibronic bands in Ade₂H⁺ than in AdeH⁺ can be the following. The ultrashort excited state lifetime of AdeH⁺ deduced from its broad vibronic bands can be due to hydrogen atom loss through a $\pi\sigma^*$ state, which has been shown to be a mechanism for ultrafast deactivation of excited states in protonated ions.³⁸⁻³⁹ When the $\pi\sigma^*$ state has another

crossing with the S_0 state, the system returns to the ground state and only CID-like fragments are observed. In Ade_2H^+ , sharp vibronic bands can be seen if the H-loss channel is blocked by the neutral moiety of the dimer, therefore lengthening the excited state lifetime. A way to verify this assumption is to observe the spectra of hydrated clusters of protonated adenine, to see whether the surrounding water molecules can also block the H-loss channel as was seen in protonated tryptophan clustered with water ($\text{TrpH}^+(\text{H}_2\text{O})_{n \geq 2}$).⁴⁰ However a thorough analysis and high-level computation studies are still required to understand the complex spectrum of Ade_2H^+ .

In conclusion, we presented a simple and versatile method for UV-UV hole-burning spectroscopy in a cold quadrupole ion trap, which can be also used for any type of double resonance technique that produces ion fragments with $\Delta m/z > 8$. It is easily and readily adaptable to any existing cold quadrupole ion trap, therefore opening up a new way for conformation-specific spectroscopy of cold ions. We applied this technique to the study of protonated adenine dimer and proved that it has at least two ground state species absorbing in the same UV wavelength region. We also observed that the protonated adenine dimer has sharp vibronic bands in addition to the broad absorption, in contrast to protonated adenine monomer, presumably due to the blocking of the hydrogen atom loss channel in the excited state, which lengthens the excited state lifetime.

Experimental methods

The experimental setup in Marseille has been described previously.^{7, 22, 32, 41} Briefly, ions are produced by electrospray ionization (ESI) and stored in an octopole ion guide before being introduced into a cold ion trap. A mass gate between the octopole and the quadrupole ion trap can coarsely select the m/z range of the ions to be stored in the trap. The 3D QIT (RM Jordan) is

cooled down by a closed-cycle helium refrigerator (Coolpak Oerlikon). The ions are sympathetically cooled for 90 ms by helium gas, which is introduced into the QIT 1 ms before the ions arrive, reaching final ion temperature of around 30 K.²² After extraction from the QIT at 90 ms, the ions are mass analyzed by a home-made time-of-flight mass spectrometer, and detected by a microchannel plate. Ion signal is digitized by a digital oscilloscope and monitored while scanning the laser wavelength to record a photofragmentation spectrum that corresponds to the absorption of the ion. Tunable wavelength laser pulses are provided by two optical parametric oscillators (EKSPLA NT342B), which operates at 10 Hz with 8 cm⁻¹ bandwidth and 10 ns pulse width.

ASSOCIATED CONTENT

Supporting Information. Figure S1. Ejection profile of AdeH⁺ as a function of tickle RF frequency. Figure S2. Ejection profile of AdeH⁺ as a function of tickle RF voltage. Table S1. Structures, relative energy in ground state (in kJ/mol at MP2/cc-pVDZ), and vertical transition energy (in eV at ADC(2)/cc-pVDZ) of Ade₂H⁺. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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