



Photoelectron Spectroscopy

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Tautomer-Specific Resonant Photoelectron Imaging of Deprotonated Cytosine Anions

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Abstract: Tautomers of the nucleobases play fundamental roles in spontaneous mutations of DNA. Tautomers of neutral cytosine have been studied in the gas phase, but much less is known about charged species. Here, we report the observation and characterization of three tautomers of deprotonated cytosine anions, [trans-keto-amino-N3H-H8b] (tKAN3H8b⁻), [cis-keto-amino-N3H-H8a] (cKAN3H8a⁻) and [keto-amino-H] (KAN1⁻), produced by electrospray ionization. Excited dipole-bound states (DBSs) are uncovered for the three anions by photodetachment spectroscopy. Excitations to selected DBS vibrational levels of cKAN3H8a⁻ and tKAN3H8b⁻ yield tautomer-specific resonant photoelectron spectra. The current study provides further insight into tautomerism of cytosine and suggests a new method to study the tautomers of nucleobases using electrospray ionization and anion spectroscopy.

As fundamental building blocks of DNA and RNA, nucleic acid bases are involved in the transmission and encoding of genetic information. Tautomerism is crucial to the structure and proper function of DNA because the formation of rare tautomers can cause mismatches in base pairing, resulting in spontaneous mutagenesis.^[1,2] The tautomers of cytosine, one of the pyrimidine bases, have been studied in different environments. Theoretical calculations have shown that the isolated neutral cytosine molecule can adopt six tautomers, as shown in Scheme S1 (Supporting Information), where their relative stabilities in aqueous solution^[3] and gas phase^[4] are also given. The canonical tautomer of keto-amino-N1H (KAN1H) predominantly exists under physiological conditions and it is the tautomer that forms the Watson-Crick pair with guanine via hydrogen bonding.^[1] Other rare tautomers have also been observed by various spectroscopic techniques.^[5-11] Additionally, the effect of water molecules on the structural dynamics and tautomerism of cytosine have been investigated,^[12,13] showing that water can facilitate tautomerization from the canonical form to the rare tautomers by lowering the activation barriers of the prototropic process. The high stability of the keto-amino tautomers in solution is derived from their large dipole moments.^[3,14] Early thermodynamic and kinetic studies showed that the major KAN1H and minor KAN3H forms (Scheme S1a) are in equilibrium in aqueous solution.^[15] Additionally, various tautomeric forms of the radical anion and cation of cytosine as well as the protonated cytosine have been studied.^[16–20]

However, relatively little is known of the deprotonated cytosine anion ([Cy-H]⁻),^[21-23] despite its potential role in DNA damage. The ionization of DNA bases by low-energy electrons is a crucial process for DNA damage after radiation.^[24] Dissociative-electron-attachment experiments have shown that $[Cy-H]^{-}$ is the most abundant anion fragment^[25] and it can pair with guanine to form anionic complexes.^[26] The cytosine tautomers can be deprotonated at different sites to produce a plethora of negative ions (Scheme S2). Luo et al.^[21] calculated the structures of five different [Cy-H]⁻ anions generated by deprotonation of the canonical KAN1H tautomer and computed the electron affinities (EAs) of the corresponding neutral [Cy-H] radicals. Considering the deprotonation of other rare tautomers and searching for 95 initial structures, Vázquez et al.^[22] found that the six most stable $[Cy-H]^-$ anions were, in the order of stability, tKAN3H8b⁻ > cKAN3H8a⁻ > KAN1⁻ > $cEAOH8a^- > cKAN1H8a^- > tEAOH8a^-$ (Table S1).

For the current study, we recalculated the structures and relative energies of these six anions and a seventh anion tKAN1H8b⁻ (Scheme 1) generated by deprotonation of KAN1H. The computed EAs and dipole moments of their corresponding radicals are presented in Table S1. The three most stable $[Cy-H]^-$ anions are similar to those described by Vázquez et al.^[22] It is interesting that the most stable anion tKAN3H8b⁻ is not stemming from the deprotonation of the canonical KAN1H cytosine (Scheme S2). Parsons et al.^[23] reported a low-resolution photoelectron imaging (PEI) study on the $[Cy-H]^-$ anion produced by a pulsed discharge method. A congested broad band was observed and the



Scheme 1. The seven most stable tautomers of deprotonated cytosine anions in the gas phase. Relative energies (below the structures) are given in kcalmol⁻¹.

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spectrum was assigned to the KAN1⁻ anion with a measured EA of 3.037(15) eV for the neutral KAN1 radical, compared with the theoretical values of 3.00 eV by Lou et al.^[21] and 3.37 eV by Vázquez et al.^[22] However, no other tautomeric forms of the $[Cy-H]^-$ anion have been disclosed.

Anions with dipolar neutral cores ($\mu > \approx 2.5$ D) can support dipole-bound states (DBSs) near the electron-detachment thresholds,^[27,28] which have been observed as resonances in photodetachment spectra of anions^[29] and studied by rotational autodetachment.^[30-32] We have investigated autodetachment from the vibrational levels of DBS more recently for cryogenically cooled anions and obtained highly non-Franck–Condon resonant photoelectron spectra.^[33-35] The corresponding radicals of the seven anions in Scheme 1 all have dipole moments larger than 2.5 D except for the cEAOH8a radical (Table S1). Hence, excited DBSs are expected to be observed, allowing tautomer-specific resonant PEI to be performed.^[36,37]

Here, we report a high-resolution PEI and photodetachment spectroscopy study of [Cy–H]⁻. The experiment is done on an electrospray–PEI apparatus,^[38] which is equipped with an electrospray ionization (ESI) source, a cryogenically cooled ion trap,^[39] and a high-resolution PEI system.^[40] More experimental details are provided in the Methods section (Supporting Information). Three tautomeric deprotonated cytosine anions, tKAN3H8a⁻, cKAN3H8b⁻, and KAN1⁻, were observed. The photodetachment spectrum shows strong DBS resonances due to autodetachment from vibrational levels of the excited DBSs of the tKAN3H8a⁻ and cKAN3H8b⁻ anions. Several weak resonant peaks were tentatively assigned to a third deprotonated anion KAN1⁻, which is expected to have a weak ion abundance due to its low stability.

Figure 1 shows the non-resonant photoelectron image and spectrum of $[Cy-H]^-$ at 354.7 nm. The complexity of the vibrational structures suggests the possible presence of different tautomeric anions. To assist the spectral assignments, we performed Franck–Condon simulations for all the seven low-lying anions using the FC-LabII program^[41] and compared them with the spectrum. Figure 1 shows that the simulated spectrum of tKAN3H8b⁻ is in good agreement with the spectral features at higher binding energies (above the peak ^T0), while the simulated spectra of the other anions are not (Figure S1). This means that the peaks at higher binding



Figure 1. Non-resonant photoelectron image and spectrum of $[Cy-H]^-$ at 354.7 nm. The peak ^c0 is due to detachment from cKAN3H8a⁻, while the peaks above ^T0 are from tKAN3H8b⁻. The Franck–Condon (FC) simulation data of tKAN3H8b⁻ are presented as dots. The double arrow below the image shows the direction of the laser polarization.

energies are due to photodetachment from tKAN3H8b⁻, which is the most stable tautomeric anion according to our calculations (Table S1) and the previous study by Vázquez et al.^[22] The peak labeled ^T0 defines the EA of the neutral tKAN3H8b radical, which is more accurately measured to be 3.0870(5) eV in the near-threshold resonant photoelectron spectra (see below). The measured EA is in perfect agreement with our computed value for tKAN3H8b, which also represents the largest EA among the first seven tautomers (Table S1). Peaks C and D, shiftes by 373 cm^{-1} and 575 cm^{-1} from peak ^T0, represent the most Franck-Condon-active vibrational modes ${}^{T}v_{21}$ (376 cm⁻¹) and ${}^{T}v_{18}$ (583 cm⁻¹) of tKAN3H8b (Table S2), respectively. Both modes involve inplane H-atom vibrations (Figure S2b). The peak labeled ^C0 at a lower binding energy should come from another tautomer, most likely the second most stable cKAN3H8a⁻ species (see below). The EA of the cKAN3H8a radical defined by peak ^C0 was measured to be 3.0471(5) eV, which agrees well with our computed value (Table S1).

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The cKAN3H8a and tKAN3H8b radicals are calculated to have dipole moments of 3.35 D and 5.55 D (Table S1), respectively, which are large enough to support excited DBSs for the corresponding anions. We performed photodetachment spectroscopy by monitoring the total electron yield while scanning the laser wavelength across the detachment thresholds, as shown in Figure 2. The arrow (^CEA) at 24577 cm⁻¹ and the arrow (^TEA) at 24898 cm⁻¹ indicate the detachment thresholds of cKAN3H8a⁻ and tKAN3H8b⁻, respectively, which are consistent with the measured EAs from the photoelectron spectra (Figures 1 and 3). Around 24300 cm⁻¹, the peaks labeled ^C0' and ^T0' represent the ground vibrational levels of the DBSs of cKAN3H8a⁻ and tKAN3H8b⁻, respectively. These peaks are below the respec-



Figure 2. Photodetachment spectrum of $[Cy-H]^-$. The spectrum was obtained by measuring the total electron yield as a function of the photon energy across the detachment thresholds of cKAN3H8a⁻ and tKAN3H8b⁻, indicated by the arrows below ^CEA and ^TEA, respectively. The intensity below 24 900 cm⁻¹ is multiplied by a factor of 10. Peaks ^C0' and ^T0' represent the ground DBS vibrational levels of cKAN3H8a⁻ and tKAN3H8b⁻, respectively. Peaks ^C1-^C3 are due to autodetachment from vibrational levels of the DBS of cKAN3H8a⁻, while peaks ^T1-^T7 are from tKAN3H8b⁻. Peaks α , β , and γ at lower photon energies are assigned to DBS levels of KAN1⁻. The outermost ring in the inset shows the PE image obtained with a photon energy corresponding to peak ^T0' due to resonant two-photon detachment. The double arrow below the image indicates the direction of the laser polarization.

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Figure 3. Tautomer-specific resonant photoelectron images and spectra at a) 406.04 nm, b) 403.55 nm, c) 402.63 nm, d) 401.57 nm, e) 400.82 nm, f) 399.22 nm, g) 398.70 nm, and h) 398.23 nm and non-resonant images/spectra at i) 400.22 nm and j) 392.11 nm. (a–c) correspond to autodetachment from fundamental vibrational levels of the DBS of cKAN3H8a⁻, while (d–h) are from the DBS of tKAN3H8b⁻. The peak numbers in the parentheses correspond to the DBS resonances in Figure 2 and the assignments are also given. Peaks labeled in bold face indicate the enhanced final neutral vibrational levels due to vibrational autodetachment from the DBS. The double arrows below the images show the directions of the laser polarization.

tive detachment thresholds by 325 \mbox{cm}^{-1} ($^{C}0'$ below $^{C}\mbox{EA})$ and 577 cm⁻¹ (^T0' below ^TEA), representing the binding energies of the DBSs of the two anions. The larger DBS binding energy of tKAN3H8b⁻ is consistent with the larger dipole moment of the corresponding neutral tKAN3H8b radical. The belowthreshold peaks ^C0' and ^T0' are due to resonant two-photon detachment. The resonant two-photon photoelectron image corresponding to peak $^{T}0'$ is shown in the inset of Figure 2. The p-wave angular distribution of the two-photon signals is consistent with a detachment from an s-type dipole-bound orbital of tKAN3H8b⁻, as previously observed.^[33-35] Above ^cEA, the peaks ^c1 to ^c3 correspond to vibrational levels of the DBS of cKAN3H8a⁻ as a result of vibrational autodetachment. The peaks ^T1 to ^T7 represent the DBS vibrational levels of tKAN3H8b⁻. The weaker peaks ^T1 and ^T2 below ^TEA are due to resonant two-photon detachment, while the strong peaks ^T3 to ^T7 are due to autodetachments from vibrational levels of the DBS of tKAN3H8b⁻.

At even lower photon energies in Figure 2, three weak peaks, labeled α , β , and γ , are also observed, which are not stemming from cKAN3H8a⁻ or tKAN3H8b⁻. They could be from the DBS of the KAN1⁻ anion, whose neutral core has a very large dipole moment of 7.79 D (Table S1). The energy shifts of peaks β and γ relative to peak α are 255 cm⁻¹ and 594 cm⁻¹, respectively. We also calculated the vibrational frequencies of all the other neutral radicals with dipole moments larger than 2.5 D (Table S2). The shifts of 255 cm⁻¹ and 594 cm⁻¹ are found to agree well with the fundamental

vibrational modes ${}^{KA}v_{28}$ (231 cm⁻¹) and ${}^{KA}v_{22}$ (593 cm⁻¹) of KAN1, respectively (Figure S2 c). This indicates the presence of a third tautomer in the ion beam (Scheme 1). The intensity of the KAN1⁻ anion is very weak because of its relatively high energy, so that no clear spectral features are observed for this tautomer in the photoelectron spectra.

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The photon energies, shifts from the respective ground vibrational levels of the DBS, and assignments of the observed resonances are given in Table S3. The assignments of all the resonances are based on the calculated vibrational frequencies (Table S2) and the vibrational autodetachment in the resonant photoelectron spectra (Figures 3a–h), which yield tautomer-specific information. We have previously shown that vibrational frequencies in the DBS are the same as those in the neutral states,^[33–35,42–44] that is, the diffuse dipole-bound electron has little effect on the neutral cores.

By tuning the detachment laser wavelengths to the abovethreshold peaks (^C1-^C3 and ^T3-^T7), we have obtained eight high-resolution resonantly enhanced photoelectron images and spectra (Figures 3 a–h). As discussed previously,^[33–37] two detachment channels contribute to the resonant photoelectron spectra: the non-resonant detachment represented by the baseline in Figure 2 and the resonantly enhanced vibrational autodetachment via the DBS resonances. Autodetachment from DBS vibrational levels generally follows the mode selectivity^[33] and $\Delta v = -1$ propensity rule,^[45,46] which results in highly non-Franck–Condon photoelectron spectra.

The resonant photoelectron spectra involving autodetachment from vibrational levels of the DBS of cKAN3H8a⁻ or tKAN3H8b⁻ are essentially tautomer-specific, because resonant excitations to the DBSs have much higher cross-sections than the non-resonant photodetachment processes, which are not tautomer-specific. In comparison with the non-resonant spectra in Figures 3i and 3j, the resonant spectra in Figures 3a and 3c that show spectral features of the cKAN3H8a⁻ tautomer display an enhancement of peak ^C0, which should be due to autodetachment from fundamental vibrational levels of the DBS of cKAN3H8a⁻ according to the $\Delta v = -1$ propensity rule. The photon energies used in Figures 3a, c, corresponding to the DBS resonances of ^C1 and ^C3 in Figure 2, are 375 cm⁻¹ and 585 cm⁻¹ above the DBS ground vibrational level (C0') of cKAN3H8a-, in good agreement with the calculated frequencies of the fundamental vibrational modes of ${}^{C}\nu_{21}$ (375 cm⁻¹) and ${}^{C}\nu_{18}$ (581 cm⁻¹) of cKAN3H8a, respectively (Table S2 and Figure S2a). Hence, the DBS resonances of $^{\rm C}\!1$ and $^{\rm C}\!3$ should be assigned to the $^{\rm C}\!21'^1$ and ^C18^{'1} DBS vibrational levels of cKAN3H8a⁻. The good agreement of the frequencies of the neutral radical and the dipole-bound anions is consistent with the weakly-bound nature of the extra electron in the DBS, as shown previously.^[33–37] The highly enhanced peak A (°30¹) in Figure 3b is due to excitation to the combinational DBS vibrational level of $^{C}29'^{1}30'^{3}$ of cKAN3H8a⁻ followed by the $\Delta v = -3$ vibrational autodetachment, indicating a breakdown of the $\Delta v =$ -1 propensity rule due to anharmonic effects involving the low-frequency bending mode. Similarly, Figures 3d-h all display a strongly enhanced peak ^T0 due to resonant excitations to the DBS vibrational levels of ^T18'¹, ^T27'¹, ^T25'¹, ^T17^{'1}, and ^T23^{'1} of tKAN3H8b⁻, followed by a $\Delta v = -1$

vibrational autodetachment. The tautomer specificity of the resonant spectra is vividly revealed in these spectra, as can be seen by the almost negligible intensity of the ^C0 peak due to the cKAN3H8a⁻ tautomer. A schematic energy level diagram showing the autodetachment processes for the eight resonant photoelectron spectra is displayed in Figure S3.

The photon energies and assignments of all the observed DBS resonances of the $[Cy-H]^-$ anions are summarized in Table S3. The measured vibrational frequencies for the neutral cKAN3H8a and tKAN3H8b radicals are compared with the calculated frequencies in Table S4.

The observed ion abundance suggests the order of stability for the three anions as tKAN3H8bcKAN3H8a⁻ > KAN1⁻, consistent with the theoretical predictions for the deprotonated cytosine anions both from the current study (Table S1) and the previous calculation by Vázquez et al.^[22] It is interesting that the three observed anions could all stem from direct deprotonation of the KAN3H tautomer (Scheme S2), which is the second most stable tautomer in solution. The tKAN3H8band cKAN3H8a⁻ anions can also stem from direct deprotonation of the rare trans- and cis-keto-imino tautomers, respectively. Only the KAN1⁻ anion can stem from direct deprotonation of the most stable KAN1H canonical cytosine in solution. Direct deprotonation of the KAN1H canonical cytosine would also produce the cKAN1H8a⁻ and tKAN1H8b⁻ anions, which are higher-energy species.

In summary, two tautomeric deprotonated cytosine anions, tKAN3H8b⁻ and cKAN3H8a⁻, have been identified by high-resolution PEI, photodetachment spectroscopy, and resonant PEI. The EAs of tKAN3H8b and cKAN3H8a are measured accurately to be 3.0870(5) eV and 3.0471(5) eV, respectively. Excited dipole-bound states are observed for tKAN3H8b⁻ and cKAN3H8a⁻ and their vibrational ground states are found to be bound by 577 cm^{-1} and 325 cm^{-1} below the respective detachment thresholds. Tautomer-specific photoelectron spectra are obtained for tKAN3H8b⁻ and cKAN3H8a⁻ using resonant PEI via vibrational autodetachment from specific vibrational resonances of the DBSs. Photodetachment spectroscopy also reveals weak DBS resonances assigned to a third tautomer, KAN1-, which is relatively high in energy. The ion abundances revealed in the relative intensities in the PEI and photodetachment spectra indicate the order of stability for the three anions as $tKAN3H8b^- > cKAN3H8a^- > KAN1^-$. The current study suggests that photodetachment spectroscopy and resonant PEI, coupled with cryogenic ion cooling, are powerful techniques to investigate the structures and stability of the nucleic-acid-base anions and to obtain tautomer-specific spectroscopic information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anions · cytosine · dipole-bound states · photoelectron spectroscopy · tautomerism

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