SUPPLEMENTARY INFORMATION

"On the character of the cyclic ionic H-bond in cryogenically cooled deprotonated cysteine"

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I. Comparison of the vibrational predissociation spectrum of the $(\text{Cys-H}^{+})^{-}$ isotopologue to the calculated harmonic spectra of different isomers

Figure S1 compares the vibrational predissociation spectrum of $(\text{Cys-H}^{+})^{-}\cdot D_2$ to the calculated harmonic spectra of six low energy isomers that were also considered in the IRMPD study of Oomens *et. al.*[1] As discussed in the manuscript, the broadening of the carbonyl and CIHB regions as well as the presence of extra bands in the NH stretching region makes it difficult to compare the experimental spectrum with harmonic level calculations for a definitive structural assignment. Nevertheless, we include a comparison for the interested reader. To the right of each structure, its zero-point corrected relative energy is also given.

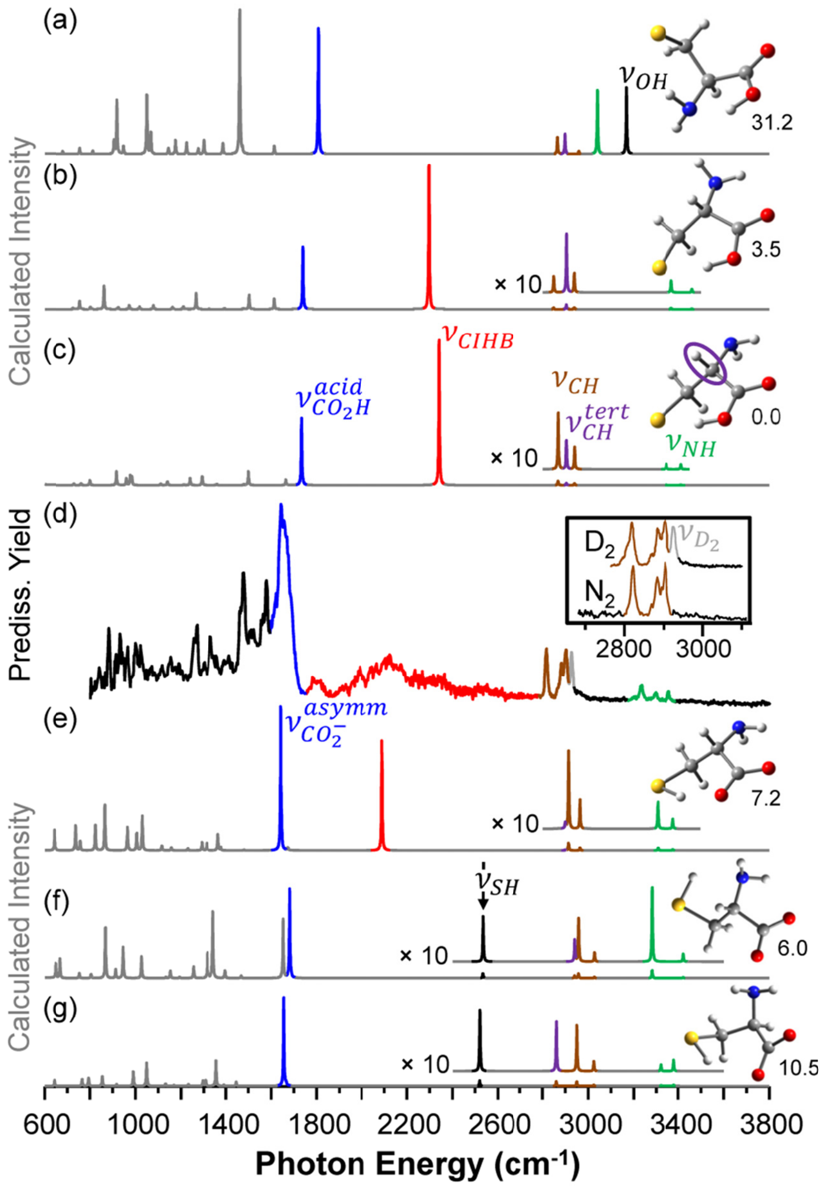

Fig. S1. Comparison between the calculated spectra of various thiolate (a-c) and carboxylate (e-g) isomers and the D_2 vibrational predissociation spectrum (d) of $(\mathrm{Cys}\text{-}\mathrm{H}^+)^-$ taken over the 800-3800 cm^{-1} range. Minimum energy structures of each isomer are given on the right with their respective energies in kJ·mol^{-1}. Colour coding of bands is consistent with Fig. 2 and 3 of the manuscript text. For the structure in (c), the unique tertiary CH stretch (ν_{CH}^{tert}) is indicated in purple and involves the circled CH group. In trace (d), the scale is expanded in the CH stretching region (box) to highlight the comparison between the spectrum of the D_2-tagged all D isotopologue and the N_2-tagged all H isotopologue (same as Fig. 2a) to identify the D_2 stretch (ν_{D_2}, grey).

II. Comparison of the vibrational predissociation spectrum of the $(Cys\text{-}D^+)^-$ isotopologue to the calculated harmonic spectra of additional isomers

Figure S2 gives the vibrational predissociation spectrum of the $(Cys\text{-}D^+)^-\cdot D_2$ isotopologue (with D in all exchangeable sites) and the calculated harmonic spectra of six low energy isomers that were also considered in the IRMPD study of Oomens *et. al.*[1] Traces (a)-(c) are the thiolate structures while (e)-(g) correspond to carboxylate structures. In trace (a), the structure has the highest relative energy and an OD stretch is expected, which is clearly absent from the experimental spectrum. The strucutres in traces (b) and (c) are very similar, differing by a rotation of the NH_2 group about the C-N bond.

We also have included zero-point corrected energies of this heavy isotopologue to assess weather any of the isomers change in relative energy upon deuteration, modulating their population in the experimental spectrum. Upon comparing Figures S1 and S2, it can be seen that the ordering in energy between the isomers is unchanged and the relative energies vary by about 1-2 $kJ\cdot mol^{-1}$. This may explain why the spectrum of $(Cys\text{-}D^+)^-$ has two rather than four dominant peaks, as the weaker bands associated with the less dominant isomer would become less apparent. Another possibility is that the extra bands in the all H isomer results from Fermi resonances between two quanta in the NH bending and one quantum in the NH stretching fundamentals. For example, at the harmonic level, the NH_2 bending overtone is as 3329 cm^{-1}, which is 300 cm^{-1} lower in energy than the symmetric stretching fundamental at 3459cm^{-1}. It is common for such anharmonic coupling to decrease in the heavier isomer.[2,3] The presence of a minor isomer would not explain, however, the blue shift of the carbonyl, which becomes significantly sharper upon deuteration. If the complexity of the carbonyl region in the all H isotopologue was only attributed to the presence of multiple isomers, there would be a major band at the same position as the all D isotopologue (1710 cm^{-1}) unless completely different isomers were present in the two isotopologues. This is unlikely based on the comparison of the experimental and calculated spectra. However, to avoid possible ambiguities, we have focused on the deuterated species rather than the protonated one in which these extra bands are not significantly present.

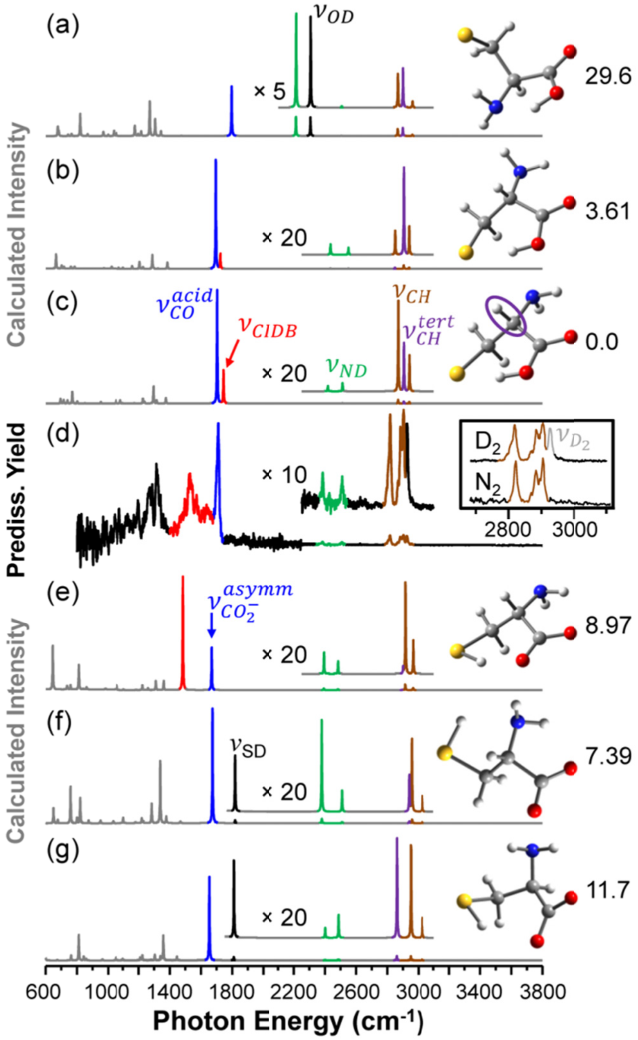

Fig. S2. Comparison between the calculated spectra of various thiolate (a-c) and carboxylate (e-g) isomers and the D_2 vibrational predissociation spectrum (d) of $(\text{Cys-D}^+)^-$ taken over the 800-3800 cm^{-1} range. Minimum energy structures of each isomer are given on the right with their respective energies in kJ·mol^{-1}. Colour coding of bands is consistent with Fig. 2 and 3 of the manuscript text. For the structure in (c), the unique tertiary CH stretch (ν_{CH}^{tert}) is indicated in purple and involves the circled CH group. In trace (d), the scale is expanded in the CH stretching region (box) to highlight the comparison between the spectrum of the D_2-tagged all D isotopologue and the N_2-tagged all H isotopologue (same as Fig. 2a) to identify the D_2 stretch (ν_{D_2}, grey). Note that the CH features are not isotope dependent.

III. Effect of the Tag on the Spectrum of (Cys-H$^+$)$^-$

One might expect the soft potential associated with proton transfer between the two competitive bases (thiolate and carboxylate) to be easily susceptible to perturbations from the solvation environment. Thus, we have obtained spectra tagged with 1-2D_2 and N_2 (Fig. S3) to assess whether the strength and/or number of tags imparts a solvatochromic effect on the cyclic ionic hydrogen bonded stretching transition (ν_{CIHB}) and the carbonyl region (ν_{CO}). We have previously observed[4] a tag-dependent solvatochromic shift for the C_5- hydrogen bonded NH stretch of GlyGlyH$^+$ because the binding of the tag to the free NH_2 hydrogen atoms increases the proton affinity of the amine. In the case of (Cys-H$^+$)$^-$, the binding location of the tag is less apparent because the charge center is not expected to occur on the amine as it did in the cation example. Thus, a future ab initio study using a method that includes dispersion interactions is warranted in order to identify likely binding cites of the tags and the consequence of these interactions on the Born Oppenheimer surface. However, because the C-O bond lengths change according to Fig. 5 along the proton transfer coordinate, it is feasible that a solvation effect that impacts the shared proton may also lead to complication of the carbonyl region that should be manifested in the experimental spectrum. It can be seen from Fig. S3 that the overall band structure in the ν_{CIHB} and ν_{CO} regions of the spectra are relatively unaffected by the addition of a second D_2 tag, but change substantially when the species is tagged with N_2. It appears that the addition of N_2 red-shifts the ν_{CIHB} transition, which is evidence for a shallower potential curve connecting the thiolate and carboxylate structures. This is consistent with the simultaneous broadening of the ν_{CO} transition in the spectrum of the N_2-tagged adduct as discussed in the "Low-Barrier Proton Transfer and Implications on the Vibrational Spectra of Cold (Cys-H$^+$)$^-$ and (Cys-D$^+$)$^-$ Ions" section of the manuscript. Furthermore, the N_2-taggeed species were generated by increasing the temperature of the trap to 25 K, which is greater than the temperature at which the D_2 adducts are formed (10 K). If the ground state wavefunction of the proton can sample motion of the C-O bonds, then it stands to reason that this effect would be exacerbated with an increase in temperature. Thus, one can fully appreciate why structural elucidation of (Cys-H$^+$)$^-$ by IRMPD spectroscopy of room temperature ions is a very difficult task.

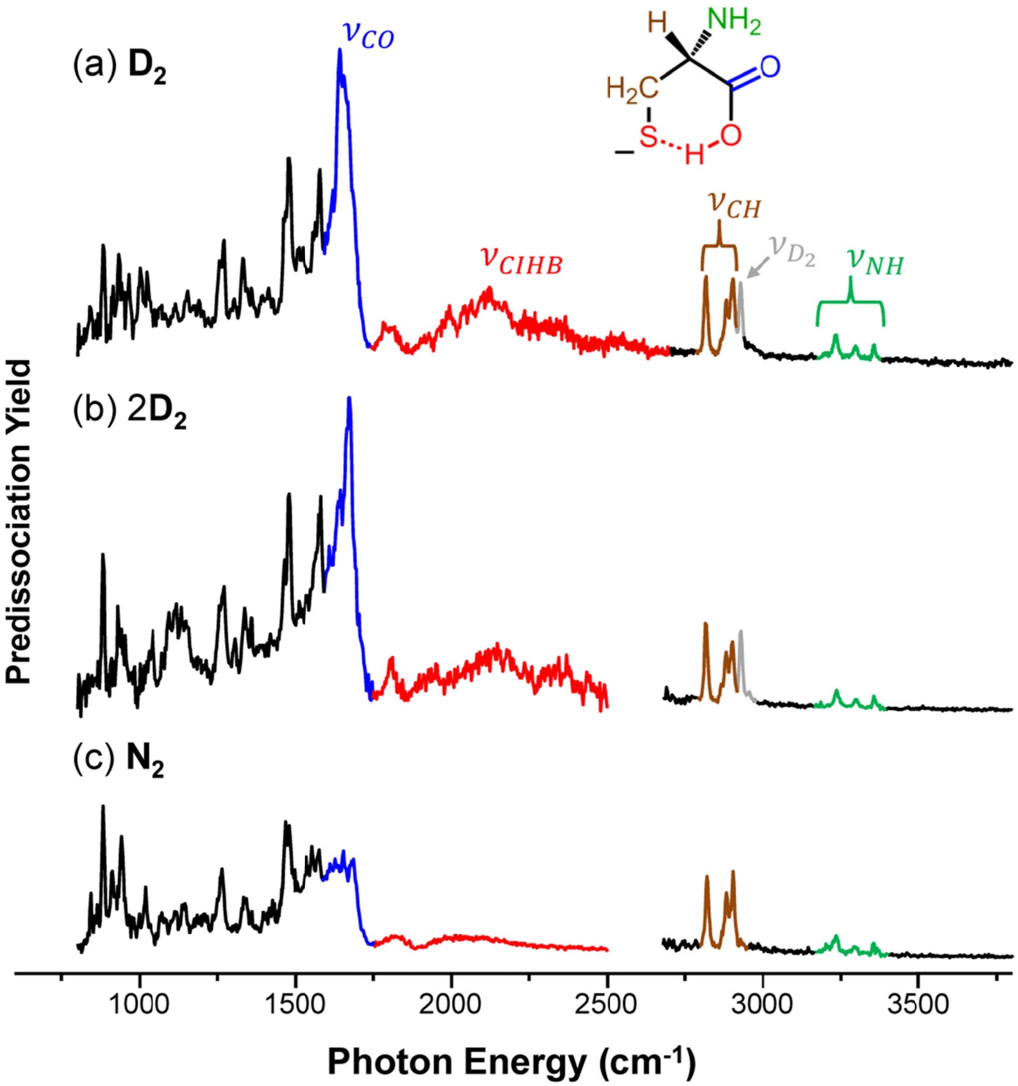

Fig. S3. The vibrational predissociation spectrum of (Cys-H$^+$)$^-$ tagged with D_2 (a), $2D_2$ (b), and N_2 (c). All spectra were obtained by monitoring photodissociation of all tag molecules. Bonds are coloured in the chemical structure to correspond to the stretching vibrations that are labelled in the spectrum. It can be seen that while most of the bands remain unaffected, the ν_{CIHB} feature is red-shifted and the ν_{CO} transition becomes broader when the ions are tagged with N_2.

References

1. J. Oomens, J. D. Steill and B. Redlich, *J. Am. Chem. Soc.*, 2009, **131**, 4310-4319.
2. H. K. Gerardi, A. F. DeBlase, C. M. Leavitt, X. G. Su, K. D. Jordan, A. B. McCoy and M. A. Johnson, *Journal of Chemical Physics*, 2012, **136**.
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4. C. M. Leavitt, A. F. DeBlase, M. van Stipdonk, A. B. McCoy and M. A. Johnson, *J. Phys. Chem. Lett.*, 2013, **4**, 3450-3457.