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# Effects of Complexation with Sulfuric Acid on the Photodissociation of Protonated Cinchona Alkaloids in the Gas Phase

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## *Supplementary Information*

## 1. *Nomenclature describing the cinchona alkaloid geometry*

The most important dihedral angles for describing the geometry of these flexible species are labeled $\boldsymbol{\tau_1}$($C_{3'}$, $C_{4'}$, $C_9$, $C_8$), $\boldsymbol{\tau_2}$($C_{4'}$, $C_9$, $C_8$, N), $\boldsymbol{\tau_3}$(N, $C_8$, $C_9$, O) and $\mathbf{T_3}$($C_8$, $C_9$, O, H) (see **Figure 1** for the atom numbering). The value of $\boldsymbol{\tau_2}$ defines two classes of structures, Closed and Open that correspond to $\boldsymbol{\tau_2} < 120°$ and $120 < \boldsymbol{\tau_2} < 240°$, respectively. In the Open geometries, the alkaloid extends outside the molecule, while in the Closed forms, it slightly interacts with the aromatic ring. The relative abundance of these two forms depends on solvation or complex formation[1-3] and is also impacted by protonation of the molecule,[4, 5] or its substituents.[6] The value of $\boldsymbol{\tau_1}$ define Syn or Anti conformations.[7] Syn geometries correspond to $\boldsymbol{\tau_1} <0$, which corresponds to the $C_{3'}$ atom and hydroxyl group located on $C_9$ on opposite sides relative to the $C_9$-$C_{4'}$ bond. Anti corresponds to $\boldsymbol{\tau_1} >0$ with $C_{3'}$ and the hydroxyl of $C_9$ on same side relative to the $C_9$-$C_{4'}$ bond. Combination of the $\mathbf{T_3}$ and $\boldsymbol{\tau_3}$ dihedral angles defines the existence of an internal hydrogen bond or not.[7] In particular, $\mathbf{T_3}$ defines **α**, **β** or **γ** conformations of the hydroxyl geometry. For cinchonidine and quinine, $-120° < \mathbf{T_3} < 0°$ corresponds to **α** (hydroxyl hydrogen is localized between $C_8$ and $C_{4'}$). $\mathbf{T_3}$ between 0° and 120° corresponds to β (hydroxyl hydrogen is localized between $C_8$ and $C_9$). Last, for $\mathbf{T_3}$ around ± 180°, the conformation is called γ (hydroxyl hydrogen is localized between $C_{4'}$ and $C_9$).

## 2. *Analysis of the NBO charges and orbital populations*

### a) *Anti γ-open $CdH^+H_2SO_4$ complex*

The NBO charges are 0.49 (+δq) and -0.96 (-δq') on the hydrogen of the $N_{alk}H^+$ group and the oxygen atom of the SO group, respectively, as compared to 0.48 and -0.90 in the bare molecules. There is negligible increase in population in the $\sigma^*_{NalkH+}$ orbital, from 0.022 in the bare molecule to 0.033 in the complex. Interestingly, the population of the lone pair located on the oxygen of $H_2SO_4$ interacting with the $N_{alk}H^+$ group increases by ~0.030 relative to bare $H_2SO_4$. Moreover, the lone pair of the oxygen of the other SO group and that of the two SOH groups show a decrease in population of similar magnitude, from 0.005 to 0.010 relative to bare $H_2SO_4$. Therefore, the population changes in $H_2SO_4$ mostly result from the polarization of the molecule, due to the electrostatic interaction, rather than intermolecular population transfer due to hydrogen-bond formation. The population of the $\sigma^*_{OH}$ of $H_2SO_4$ is the same (0.006) as in the isolated molecule.

### b) *Anti γ-open' $CdH^+H_2SO_4$ complex*

The weak interaction between the $H_2SO_4$ OH is reflected in the population transfer to the the $\sigma^*_{OH}$ of $H_2SO_4$, from 0.006 in the bare molecule to 0.020 in the complex.

*c) Anti γ-closed $CdH^+H_2SO_4$ complex*

The OH…$\pi_{aromC}$ interaction observed in Anti-γ-closed and Anti-γ-closed' is stronger than that observed in Anti γ-open'. It manifests itself by a larger increase in population from 0.006 to 0.034 in the $\sigma^*_{OH}$ orbital. In Anti-γ-closed', the strong OH…$N_{arom}$ hydrogen bond results to a noticeable population transfer (0.078) from the $N_{arom}$ lone pair (1.839 in the complex *vs.* 1.917 in the bare molecule) to the $\sigma^*_{OH}$ of $H_2SO_4$ (0.119 in the complex *vs.* 0.006 in the bare molecule).

*d) Anti-β-open $CdH_2^{2+}HSO_4^-$ complex*

The NBO charge is 0.51 (+δq) and -1.01 (-δq') on the hydrogen of the $N_{alk}H^+$ group and the oxygen atom of the SO group, respectively and there is no modification of the population of the $\sigma^*_{NalkH}$ orbital.

### *3. Description of the quinine and quinidine complexes with $HSO_4^-$*

The geometries obtained for $QnH_2^{2+}$:$HSO_4^-$ are shown in **Figure S1** and those for $QdH_2^{2+}$:$HSO_4^-$ in **Figure S2**. The dihedral angles of the calculated complexes are listed in **Table S1** and their energetics in **Table S2** for $QnH_2^{2+}$:$HSO_4^-$ and in **Tables S3** and **S4** for $QdH_2^{2+}$:$HSO_4$.

The calculated complexes are similar for the cis and trans structures and resemble those obtained for $CdH_2^{2+}$:$HSO_4^-$. The presence of the $OCH_3$ substituent slightly modifies the energetic order between the different geometries and complexes with Open forms become energetically competitive with the complexes with Closed forms. The complexes built from the Closed cis conformers resemble those obtained for $CdH_2^{2+}$:$HSO_4^-$, with $HSO_4^-$ bridging the two protonated sites of the molecule and showing no interaction with the OH or the $OCH_3$ groups of Qn. Cis and Trans syn-γ-Open show no difference relative to the $CdH_2^{2+}$:$HSO_4^-$ system. In contrast, the Cis-anti-β-Open structure slightly differs from its counterpart in $CdH_2^{2+}$:$HSO_4^-$ because $HSO_4^-$ interacts not only with the $N_{alk}H^+$ group but also with the $OCH_3$ group (distance of 2 Å) and the OH group of $QnH_2^{2+}$. These additional hydrogen bonds contribute to the stability to the complex. In Trans-syn-β-open, only the additional interaction between $HSO_4^-$ and OH is observed.

The IR spectra of all these complexes, in the 3μ region and the fingerprint region, are presented in **Figures S3** to **S6**. In the 3 μm region, the spectra of the cis/trans $QnH_2^{2+}$:$HSO_4^-$ complexes parallel those of the $CdH_2^{2+}$:$HSO_4^-$ complex. In the fingerprint region, the calculated spectra of cis/trans $QnH_2^{2+}$:$HSO_4^-$ have some transitions in common with $CdH_2^{2+}$:$HSO_4^-$. Most of the differences

between $QnH_2^{2+}$:$HSO_4^-$ and $CdH_2^{2+}$:$HSO_4^-$ are due to modes localized on the methoxy substituent. The ν(CO) stretch of the $OCH_3$ is calculated between ~ 1110 $cm^{-1}$ and ~ 1220 $cm^{-1}$, with a weak intensity. It is higher in energy and has larger intensity in the trans forms. No particularly intense band stands out in the cis conformers. A very intense β($C_{arom}H$) bend is calculated at ~ 1300 $cm^{-1}$ - 1330 $cm^{-1}$ for all the trans conformers of $QnH_2^{2+}$, becoming the most intense in the fingerprint region. The absence of intense transition in the ~ 1400 $cm^{-1}$ region of the experimental spectrum and the presence of bands above 1650 $cm^{-1}$ allows discarding the trans conformers.

As observed for cinchonidine, the spectrum of the Closed cis geometries shows better correspondence with the experimental data than those of the Open cis geometries. Moreover, for a given geometry, the cis conformers are more stable than the trans. Cis-Syn-γ-closed, Cis-Syn-γ-closed' and Cis-Anti-γ-closed show good correspondence with the experiment. It is therefore likely that the observed spectrum contains contributions of these three cis Closed forms, whose relative Gibbs energy (1.0-1.5 kcal/mol) is of the order of the expected calculation error. [8]

**Table S1:** Significant calculated dihedral angles (°) and distances (Å) of the most stable conformers of the Cis and Trans $QnH_2^{2+}HSO_4^-$ complex optimized at the B3LYP-D3/6-31++G(d,p) level of theory**.**

| **Dihedral angles (°) and distances (Å)** | **Cis-Anti-β-open** | **Cis-Syn-γ-open** | **Cis-Syn-γ-closed** | **Cis-Syn-γ-closed'** | **Cis-Anti-γ-closed** |
|---|---|---|---|---|---|
| $\tau_1$ ($C_3$, $C_4$, $C_9$ $C_8$) | 98 | -85 | -110 | -107 | 74 |
| $\tau_2$ ($C_4$, $C_9C_8N_{alk}$) | 162 | 160 | 59 | 47 | 60 |
| $\tau_3$ (N $C_8$ $C_9$ O) | -74 | -73 | -178 | 171 | -180 |
| $T_3$ ($C_8$ $C_9$ O H) | 111 | 151 | 171 | 165 | 170 |
| $d_{N_{alk}H}{}^{+\delta}\ldots{}^{-\delta}{}_{OS}$ | 1.6 | 1.58 | 1.62 | 1.62 | 1.64 |
| $d_{N_{arom}H}{}^{+\delta}\ldots{}^{-\delta}{}_{OS}$ | 7.17 | 6.19 | 2.51 | 2.34 | 2.51 |
| | | | | | |
| | **Trans-Anti-β-open** | **Trans-Syn-γ-open** | **Trans-Syn-γ-closed** | **Trans-Syn-γ-closed'** | **Trans-Anti-γ-closed** |
| $\tau_1$ ($C_3$, $C_4$, $C_9$ $C_8$) | 103 | -87 | -109 | -108 | 76 |
| $\tau_2$ ($C_4$, $C_9$ $C_8N_{alk}$) | 166 | 160 | 57 | 46 | 60 |
| $\tau_3$ (N $C_8$ $C_9$ O) | -71 | -74 | -180 | 170 | 180 |
| $T_3$ ($C_8$ $C_9$ O H) | 106 | 153 | 171 | 166 | 169 |
| $d_{N_{alk}H}{}^{+\delta}\ldots{}^{-\delta}{}_{OS}$ | 1.57 | 1.58 | 1.62 | 1.63 | 1.67 |
| $d_{N_{arom}H}{}^{+\delta}\ldots{}^{-\delta}{}_{OS}$ | 7.08 | 6.16 | 2.49 | 2.34 | 2.5 |

**Table S2:** Calculated relative electronic energy **ΔE** and Gibbs free energy **ΔG** including counterpoise correction, for the most stable conformers of $QnH_2^{2+}HSO_4^-$ at the B3LYP-D3/ 6-31++G (d,p) level of theory. Counterpoise correction to the energy **BSSE**.

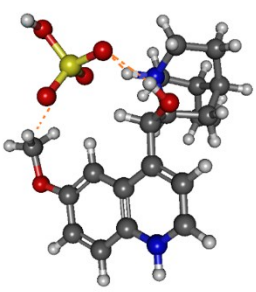
| **Complex [$QnH_2^+HSO_4^-$]** | **ΔE (kcal/mol)** with counterpoise correction | **ΔG (kcal/mol)** with counterpoise correction |
|---|---|---|
| **Cis-Anti-β-open** | 0.4 | 0.0 |
| **Cis-Syn-γ-open** | 5.9 | 5.0 |
| **Cis-Syn-γ-closed** | 0.0 | 0.6 |
| **Cis-Syn-γ-closed'** | 1.1 | 0.8 |
| **Cis-Anti-γ-closed** | 1.5 | 0.9 |
| | | |
| **Trans-Anti-β-open** | 5.4 | 4 |
| **Trans-Syn-γ-open** | 7.1 | 5.9 |
| **Trans-Syn-γ-closed** | 1.2 | 1.7 |
| **Trans-Syn-γ-closed'** | 1.9 | 1.5 |
| **Trans-Anti-γ-closed** | 1.4 | 1.2 |

**Table S3**: Significant calculated dihedral angles (°) and distances (Å) of the most stable Cis and Trans $QdH_2^+HSO_4^-$ complexes optimized at the B3LYP-D3/6-31++G(d,p) level of theory.

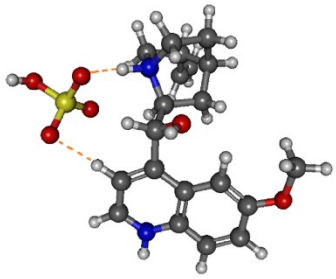
| **Dihedral angles (°) and distances (Å)** | **Cis-Syn-γ-closed** | **Cis-Anti-γ-closed** | **Cis-Anti-α-closed** | **Cis-Syn-β-closed** | **Cis-Anti-α-closed'** |
|---|---|---|---|---|---|
| $\tau_1$ ($C_3$, $C_4$, $C_9$ $C_8$) | 108 | -73 | -54 | 87 | -95 |
| $\tau_2$ ($C_4$, $C_9$ $C_8$ $N_{alk}$) | -49 | -56 | -52 | 68 | 73 |
| $\tau_3$ ($N_{alk}$ $C_8$ $C_9$ O) | -173 | -176 | -178 | -60 | -60 |
| $T_3$ ($C_8$ $C_9$ O H) | -162 | -169 | 74 | -23 | 80 |
| $d_{N_{alk}H^{\delta+}\ldots^{\delta-}OS}$ | 1.59 | 1.64 | 1.59 | 1.58 | 1.61 |
| $d_{N_{arom}H^{+\delta}\ldots^{-\delta}OS}$ | 2.33 | 2.46 | 2.41 | 7.53 | 5.91 |
| | | | | | |
| | **Trans-Anti-γ-closed** | **Trans-Syn-γ-closed** | **Trans-Anti-α-closed** | **Trans-Anti-α-closed'** | **Trans-Syn-γ-closed'** |
| $\tau_1$ ($C_3$, $C_4$, $C_9$ $C_8$) | -73 | 109 | -60.5 | -96 | 88 |
| $\tau_2$ ($C_4$, $C_9$ $C_8$ $N_{alk}$) | -56 | -49 | -51 | 73 | 70 |
| $\tau_3$ ($N_{alk}$ $C_8$ $C_9$ O) | -176 | -172 | -177 | -60 | -58 |
| $T_3$ ($C_8$ $C_9$ O H) | -168 | -163 | 69 | 80 | -153 |
| $d_{N_{alk}H^{\delta+}\ldots^{\delta-}OS}$ | 1.65 | 1.6 | 1.6 | 1.62 | 1.47 |
| $d_{N_{arom}H^{+\delta}\ldots^{-\delta}OS}$ | 2.43 | 2.34 | 2.41 | 5.8 | 7.35 |

**Table S4:** Calculated relative electronic energy **ΔE** and Gibbs free energy **ΔG** of Cis and Trans $QdH_2^+HSO_4^-$ complexes at the B3LYP/ 6-31++G (d,p) level of theory.

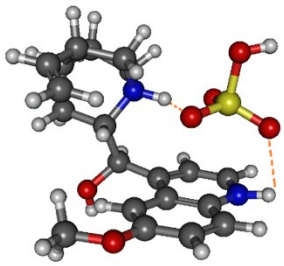
| **Complex** | **ΔE (kcal/mol)** | **ΔG (kcal/mol)** |
|---|---|---|
| **Cis-Syn-γ-closed** | 1 | 0.4 |
| **Cis-Anti-γ-closed** | 1.4 | 0.7 |
| **Cis-Anti-α-closed** | 4.8 | 4.1 |
| **Cis-Syn-β-closed** | 6.7 | 6.7 |
| **Cis-Anti-α-closed'** | 13.1 | 12 |
| | | |
| **Trans-Anti-γ-closed** | 1.4 | 0.8 |
| **Trans-Syn-γ-closed** | 1.9 | 1 |
| **Trans-Anti-α-closed** | 4.5 | 4.2 |
| **Trans-Anti-α-closed'** | 13.9 | 13 |
| **Trans-Syn-γ-closed'** | 21.1 | 19.8 |



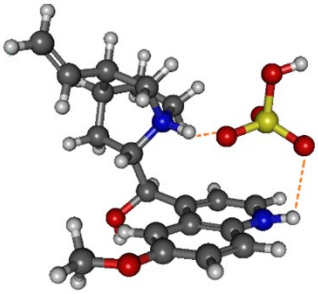
**Cis-Anti-β-open (0.0)**



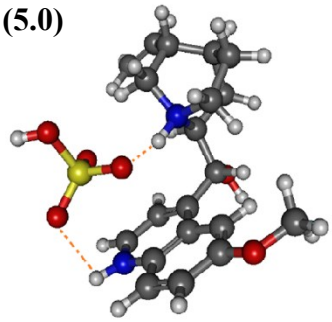
**Cis-Syn-γ-open (5.0)**



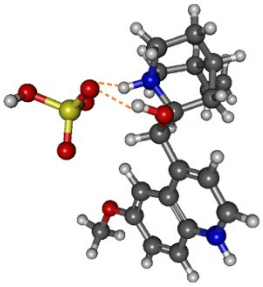
**Cis-Syn-γ-closed (0.6)**



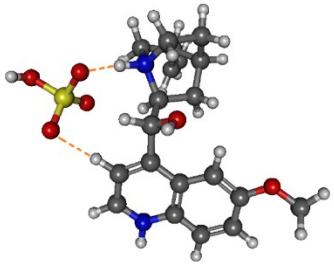
**Cis-Syn-γ-closed' (0.8)**



**Cis-Anti-γ-closed (0.9)**



**Trans-Anti-β-open (4.0)**



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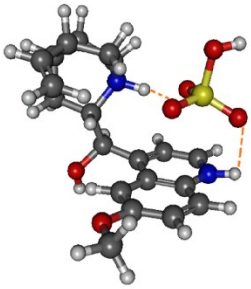

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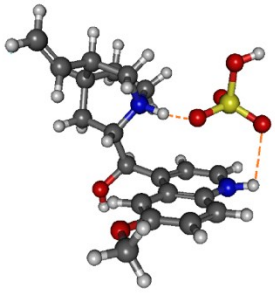

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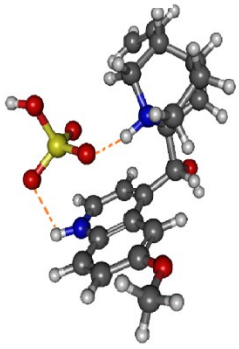
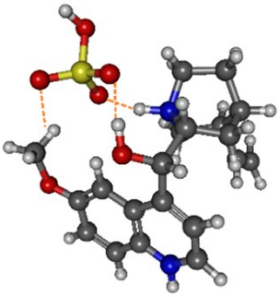
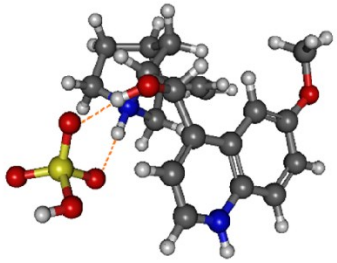


**Trans-Anti-γ-closed (1.2)**

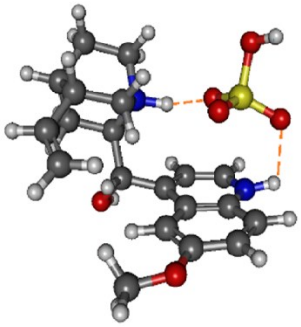
**Figure S1:** ***Structure of the five most stable conformers of the cis $QnH_2^{2+}HSO_4^-$ and trans $QnH_2^{2+}HSO_4^-$ system optimized at the B3LYP/6-31++G(d,p) level of theory. The Gibbs free energy relative to the most stable calculated complex is given in parentheses in kcal/mol***



**Cis-Syn-β-closed (6.7)**



**Cis-Anti-α-closed' (12)**



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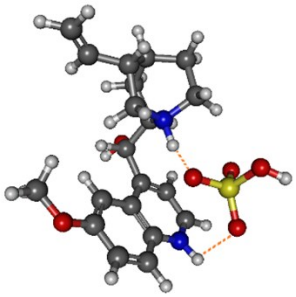
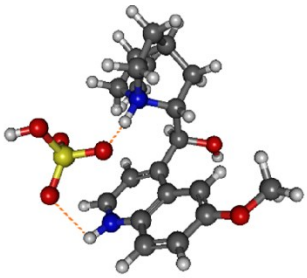
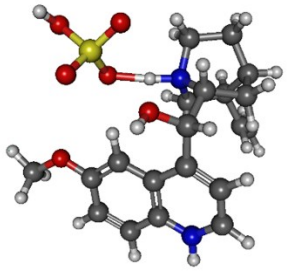


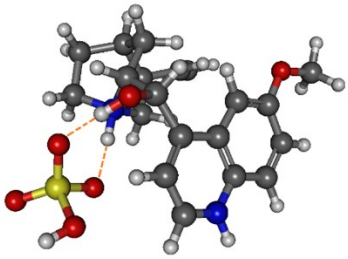
**Cis-Anti-γ-closed (0.7)**



**Cis-Syn-γ-closed (0.4)**



**Trans-Syn-γ-closed' (19.8)**



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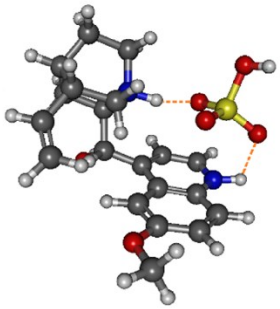
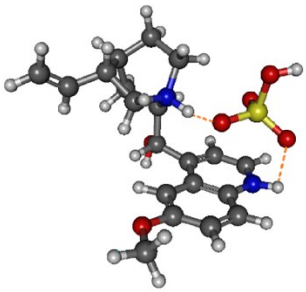
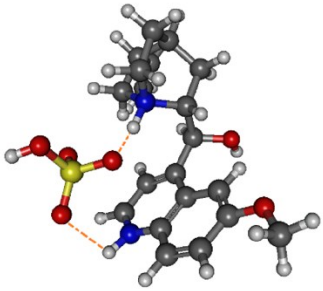


**Trans-Anti-α-closed (4.2)**



**Trans-Anti-γ-closed (1)**



**Trans-Syn-γ-closed (0.8)**

***Figure S2: Structure of the four most stable Cis $QdH^+H_2SO_4$ and Trans $QdH^+H_2SO_4$ complexes calculated at the B3LYP-D3/6-31++G (d,p) level of theory. The Gibbs free energy relative to the most stable calculated complex is given in parentheses in kcal/mol***

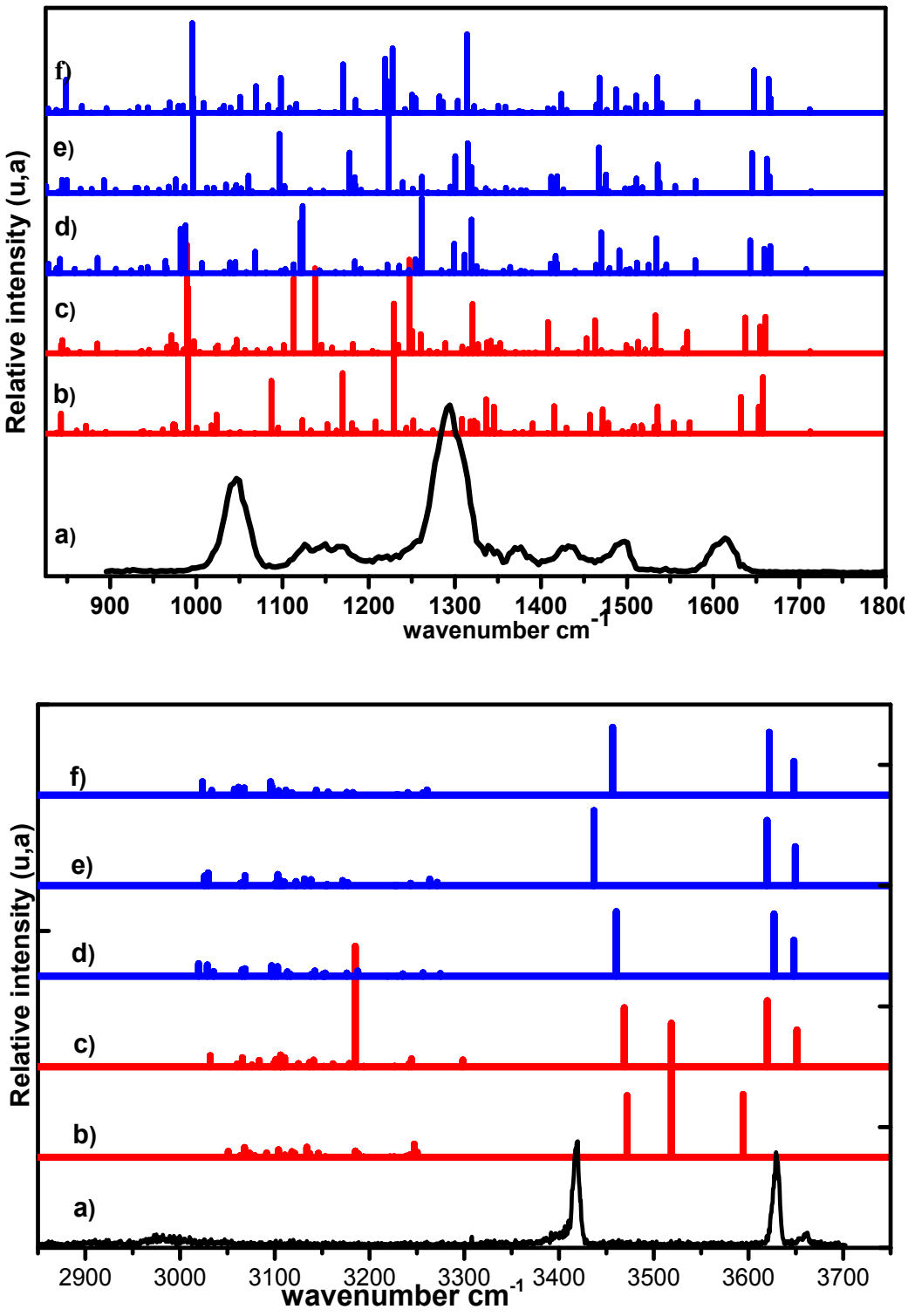



**Figure S3:** ***Comparison between the IR experimental spectrum of $QnH^+H_2SO_4$ (a) and the IR simulated spectra of the most stable Cis conformers: b) Cis-Anti-β-open, c) Cis-Syn-γ-open, d) Cis-Syn-γ-closed, e) Cis-Syn-γ-closed', f) Cis-Anti-γ-closed.***
***Fingerprint region (Top) and high frequencies region (Bottom)***

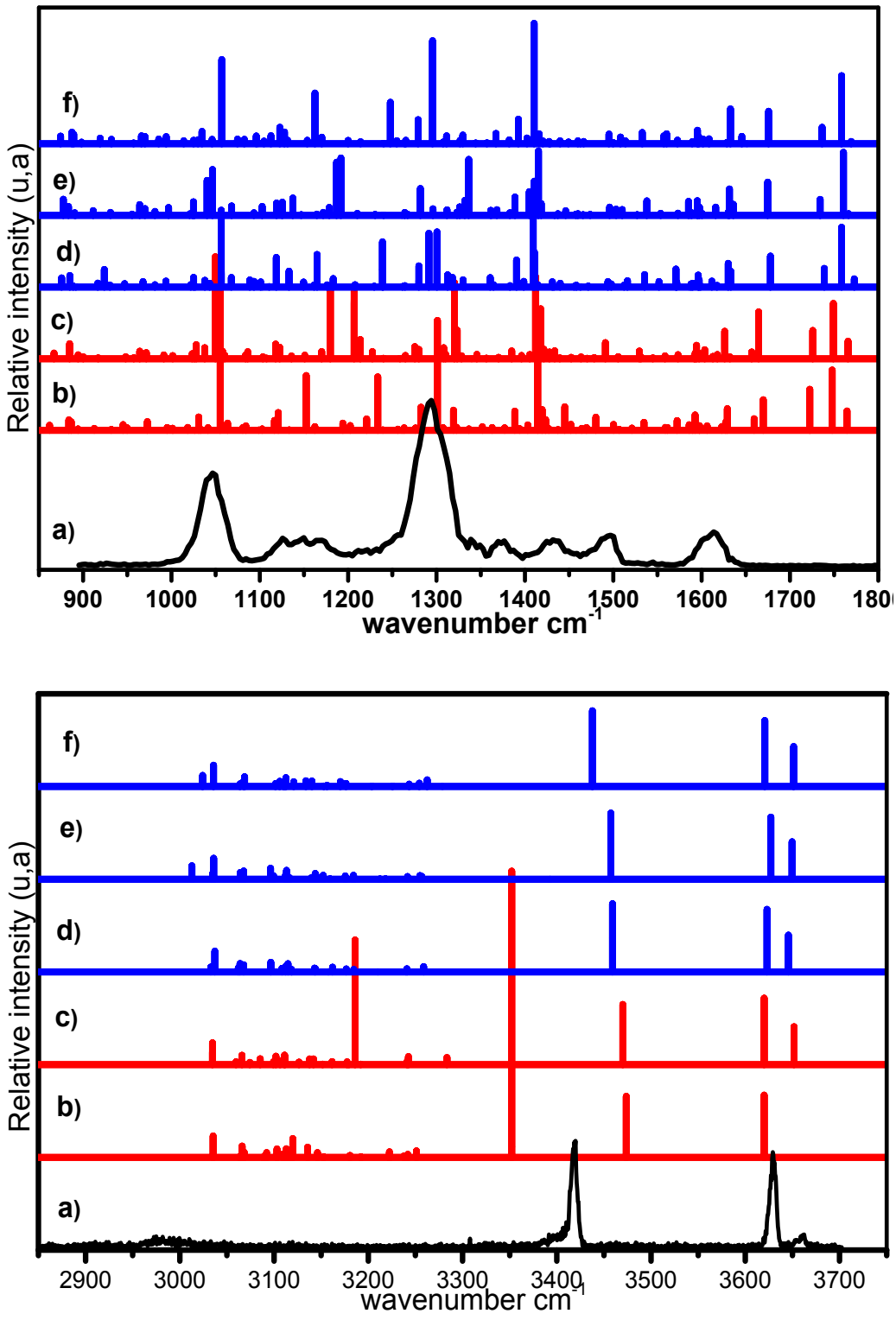



**Figure S4:** ***Comparison between the IR experimental spectrum of $QnH^+H_2SO_4$ (a) and the IR simulated spectra of the most stable Trans conformers: b) Trans-Anti-β-open, c) Trans-Syn-γ-open, d) Trans-Anti-γ-closed, e) Trans-Syn-γ-closed, f) Trans-Syn-γ-closed'***
***Fingerprint region (Top) and high frequencies region (Bottom)***

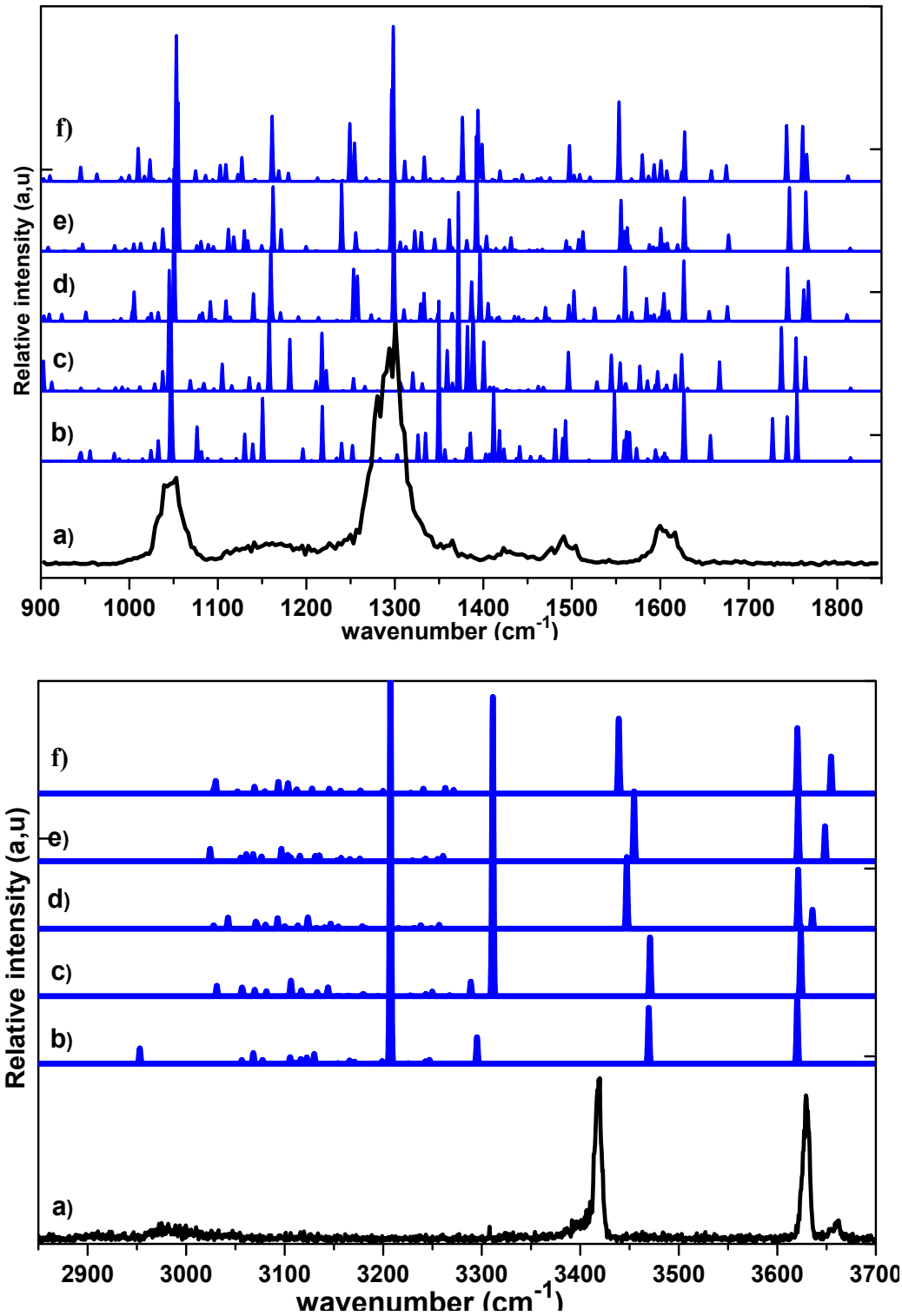



*Figure S5: Comparison between the IR experimental spectrum of $QdH^+H_2SO_4$ (a) and the IR simulated spectra of: b) Cis-Syn-β-closed, c) Cis-Anti-α-closed', d) Cis-Anti-α-closed, e) Cis-Anti-γ-closed', f) Cis-Syn-γ-closed in fingerprint region (Top) and in high frequency region (Bottom)*

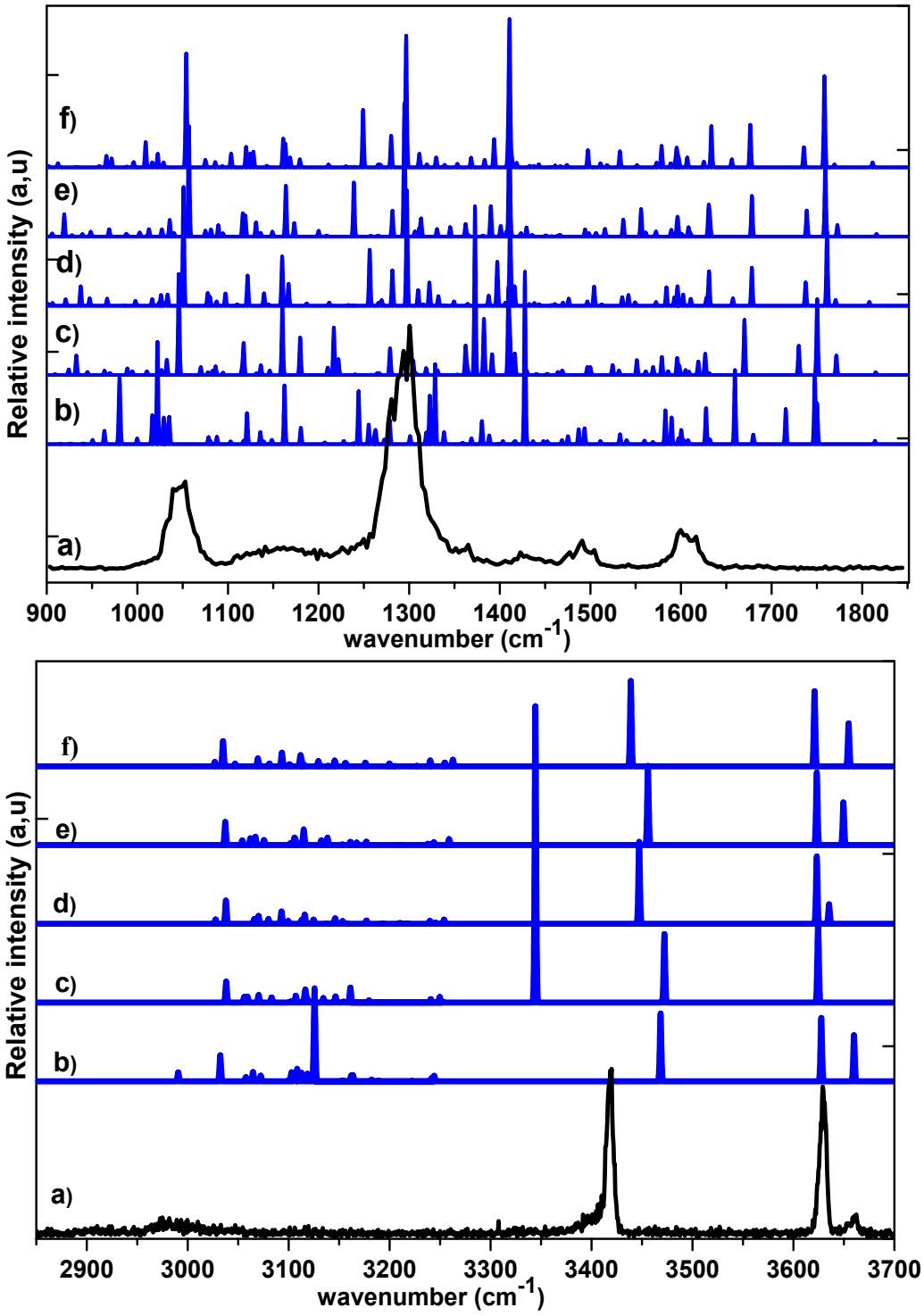



*Figure S6: Comparison between a) the IR experimental spectrum of $QdH^+H_2SO_4$ and the IR simulated spectra of: b) Trans-Syn-γ-closed', c) Trans-Anti-α-closed', d) Trans-Anti-α-closed, e) Trans-Anti-γ-closed, f) Trans-Syn-γ-closed in low frequencies region (Top) and in high frequencies region (Bottom)*

Coordinates of the most stable geometry of the $CdH_2^{2+}HSO_4^-$ complex.

XYZ file for syn γ closed (coordinates in Å)

| | | | |
|---|---|---|---|
| N | 0.1135340000 | 0.6332160000 | -1.9086190000 |
| C | 0.0590710000 | 1.9784290000 | -1.2124880000 |
| C | -1.3861490000 | 2.5495680000 | -1.2543590000 |
| C | -2.2348260000 | 1.5930310000 | -2.1366990000 |
| C | -2.2930440000 | 0.1862090000 | -1.5105640000 |
| C | -0.8515470000 | -0.3117280000 | -1.2323750000 |
| C | -0.1867640000 | 0.8109900000 | -3.3771220000 |
| C | -1.5697740000 | 1.4884720000 | -3.5243210000 |
| H | 0.4243510000 | 1.8167380000 | -0.1962960000 |
| H | 0.7858140000 | 2.6125520000 | -1.7229710000 |
| H | -1.3594340000 | 3.5220390000 | -1.7579230000 |
| H | -3.2462020000 | 1.9955740000 | -2.2327680000 |
| H | -2.8687840000 | 0.1799630000 | -0.5839150000 |
| H | -2.8021830000 | -0.4994940000 | -2.1958630000 |
| H | -0.6137200000 | -0.2400070000 | -0.1686420000 |
| H | 0.6421340000 | 1.3842170000 | -3.7926750000 |
| H | -0.1429240000 | -0.1743990000 | -3.8401960000 |
| H | -1.4590770000 | 2.4841140000 | -3.9639230000 |
| H | -2.2021800000 | 0.9073590000 | -4.2020700000 |
| C | -2.4492650000 | 3.9093330000 | 0.5751200000 |
| C | -1.9502790000 | 2.7545080000 | 0.1289100000 |
| H | -2.8500140000 | 4.0051500000 | 1.5792820000 |
| H | -1.9376490000 | 1.8909040000 | 0.7955290000 |
| H | -2.4727210000 | 4.7999360000 | -0.0488780000 |
| O | -1.5030220000 | -2.4967260000 | -0.7299750000 |
| H | -1.6500790000 | -3.4006390000 | -1.0404310000 |
| C | -0.6614310000 | -1.7977630000 | -1.6379390000 |
| H | -1.0282030000 | -1.9270190000 | -2.6650660000 |
| N | 3.5222470000 | -2.6053250000 | -1.7737360000 |
| C | 2.8073930000 | -2.6007950000 | -2.8943660000 |
| C | 1.4216210000 | -2.4492070000 | -2.8282850000 |
| C | 0.7943080000 | -2.2482740000 | -1.6081520000 |
| C | 1.5573860000 | -2.3383350000 | -0.4027900000 |
| C | 2.9739470000 | -2.4939290000 | -0.5186960000 |
| H | 3.3529080000 | -2.6383140000 | -3.8282610000 |
| H | 0.8721660000 | -2.4028240000 | -3.7606680000 |
| C | 3.8156300000 | -2.4833730000 | 0.6089410000 |
| H | 3.8921020000 | -2.3307190000 | 2.7380870000 |
| C | 3.2542300000 | -2.3433980000 | 1.8605990000 |
| H | 4.8900000000 | -2.5714840000 | 0.4811940000 |
| C | 1.0206180000 | -2.2175910000 | 0.9085430000 |
| C | 1.8520170000 | -2.2215400000 | 2.0088590000 |
| H | 1.4268990000 | -2.1341750000 | 3.0033220000 |
| H | -0.0518860000 | -2.1562830000 | 1.0348960000 |
| H | 1.1224550000 | 0.3315180000 | -1.7777670000 |
| O | 2.9126320000 | 0.2619860000 | -3.7908000000 |
| O | 3.9534420000 | 2.1079350000 | -2.4209300000 |
| O | 2.6836690000 | 0.3294060000 | -1.3410000000 |
| S | 3.6171800000 | 0.4999800000 | -2.5077100000 |
| O | 4.8965190000 | -0.2240670000 | -2.3534450000 |
| H | 4.7237180000 | 2.2909650000 | -2.9861180000 |
| H | 4.5319670000 | -2.4971860000 | -1.8593840000 |

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