Electronic Supplementary Material†:

Derivation of the Auger decay rate for the $2p^{-1}\sigma^*$ state of HCl molecule

The Auger transition $\mathrm{HCl}(\Psi_i) \rightarrow \mathrm{HCl}^+(\Psi_f) + e^-(\psi_\epsilon)$ occurs with a decay rate

$$A_{i\rightarrow f} = 2\pi\Big|\Big\langle \Psi_f\psi_\epsilon\Big|\sum_{i<j}\frac{1}{r_{ij}}\Big|\Psi_i\Big\rangle\Big|^2\delta(E_i - E_f - \epsilon), \tag{1}$$

where Ψ_i and E_i are the initial state and energy of the HCl molecule and Ψ_f and E_f are the final state and energy of the HCl^+ molecular ion. The free Auger electron with kinetic energy ϵ and spin-projection $m_{s\epsilon}$ is described by a continuum state ψ_ϵ, which is approximated by the sum of partial waves

$$\psi_\epsilon = |m_{s\epsilon}\rangle\sum_{l_\epsilon,m_\epsilon}|l_\epsilon m_\epsilon\rangle, \tag{2}$$

centered on the Cl atom.

Specifically, we are interested in the initial state with one unpaired electron in the $|2p;m\frac{1}{2}m_s\rangle$ spin-orbital and one unpaired electron in the $|\sigma^*;0\frac{1}{2}m_{\sigma'}\rangle$ molecular orbital. The state has to be antisymmetric with respect to exchange of any two electrons (denoted by $\{\}$) and has a total spin S', spin projection M'_S and the projection of the total orbital angular momentum m. We decouple the state to the sum of products of spin-orbitals as

$$\Psi_i = \Big\{|2p\sigma^*;m,S',M'_S\rangle\Big\} = \Big\{\sum_{m_s,m_{\sigma'}}\langle\frac{1}{2}m_s\frac{1}{2}m_{\sigma'}|S'M'_S\rangle|2p;m\frac{1}{2}m_s\rangle|\sigma^*;0\frac{1}{2}m_{\sigma'}\rangle\Big\}. \tag{3}$$

The final state of the molecular ion consists of three unpaired electrons in spin-orbitals v and v' and σ^*. Namely, the σ^* electron remains spectator in the Auger transition. The spins of the three electrons are coupled into the S, M_S state with Λ projection of the total orbital angular momentum. The unpaired vv' electrons are spin-coupled to the $S_{vv'}, M_{S_{vv'}}$ state with the same Λ projection of the orbital angular momentum because the projection of the spectator electron is zero:

$$\Psi_f = \Big\{\Big|(vv';\Lambda S_{vv'}M_{S_{vv'}})\sigma^*;\Lambda SM_S\Big\rangle\Big\}. \tag{4}$$

We represent the final state by the sum of uncoupled products of spin-coupled vv' states and σ^* electron as

$$\Psi_f = \Big\{\sum_{m_{sv},m_{sv'}}\sum_{M_{S_{vv'}},m_\sigma}\langle\frac{1}{2}m_{sv}\frac{1}{2}m_{sv'}|S_{vv'}M_{S_{vv'}}\rangle\langle S_{vv'}M_{S_{vv'}}\frac{1}{2}m_\sigma|SM_S\rangle|v;m_v\frac{1}{2}m_{sv}\rangle|v';m_{v'}\frac{1}{2}m_{sv'}\rangle|\sigma^*;0\frac{1}{2}m_\sigma\rangle\Big\}. \tag{5}$$

The indices $m_{sv}, m_{sv'}$ and m_σ run over the spin projections of the electrons in the v, v' and σ^* orbitals, respectively.

The Auger rate is then written as

$$\begin{aligned} A_{i\rightarrow f} = 2\pi\Big|\Big\{&\sum_{m_{sv},m_{sv'}}\sum_{M_{S_{vv'}},m_\sigma}\sum_{l_\epsilon,m_\epsilon}\langle\frac{1}{2}m_{sv}\frac{1}{2}m_{sv'}|S_{vv'}M_{S_{vv'}}\rangle\langle S_{vv'}M_{S_{vv'}}\frac{1}{2}m_\sigma|SM_S\rangle \\ &\times\langle v;m_v\frac{1}{2}m_{sv}|\langle v';m_{v'}\frac{1}{2}m_{sv'}|\langle\sigma^*;0\frac{1}{2}m_\sigma|\langle l_\epsilon m_\epsilon\frac{1}{2}m_{s\epsilon}|\Big\} \\ &\times\sum_{i<j}\frac{1}{r_{ij}}\Big\{\sum_{m_s,m_{\sigma'}}\langle\frac{1}{2}m_s\frac{1}{2}m_{\sigma'}|S'M'_S\rangle|2p;m\frac{1}{2}m_s\rangle|\sigma^*;0\frac{1}{2}m_{\sigma'}\rangle\Big\}\Big|^2. \end{aligned} \tag{6}$$

This expression can be simplified using rules for Slater determinants that apply for orthogonal spin-orbitals. The two electrons, that are missing to pair the unpaired vv' electrons, are the only ones that change their spin-orbitals in the transition to the final state: one is ejected as Auger electron and the other fills the singly occupied $2p_m$ orbital. Thus the only surviving terms are the direct and exchange two-electron matrix elements between these spin-orbitals.

The spin of the third unpaired electron must not change for the Coulomb matrix element to be non-zero, so we have $m_\sigma = m_{\sigma'}$. When we contract the sums over $m_{sv}, m_{sv'}$ back to $S_{vv'}M_{S'}$ states we obtain

$$A_{i\to f} = 2\pi\Big(\sum_{M_{S_{vv'}},m_\sigma,m_s} \langle S_{vv'}M_{S_{vv'}}\frac{1}{2}m_\sigma|SM_S\rangle\langle\frac{1}{2}m_s\frac{1}{2}m_\sigma|S'M'_S\rangle\Big)^2$$
$$\times\Big|\sum_{l_\epsilon,m_\epsilon}\Big(\langle(2p;m\frac{1}{2}m_s)(l_\epsilon m_\epsilon\frac{1}{2}m_{s\epsilon})|\frac{1}{r_{12}}|vv';\Lambda S_{vv'}M_{S_{vv'}}\rangle + (-1)^{S_{vv'}}\langle(2p;m\frac{1}{2}m_s)(l_\epsilon m_\epsilon\frac{1}{2}m_{s\epsilon})|\frac{1}{r_{12}}|v'v;\Lambda S_{vv'}M_{S_{vv'}}\rangle\Big)\Big|^2.$$

The Auger transition conserves the total spin and projection of the total spin, as well as the projection of the total orbital angular momentum. To use these selection rules, it is convenient to represent the product of the $2p$ and the continuum spin-orbitals with a linear combination of terms having exactly these good quantum numbers:

$$\sum_{l_\epsilon,m_\epsilon}|2p;m\frac{1}{2}m_s\rangle|l_\epsilon m_\epsilon\frac{1}{2}m_{s\epsilon}\rangle = \sum_{l_\epsilon m_\epsilon}\sum_{S'',M''_S}\langle\frac{1}{2}m_s\frac{1}{2}m_{s\epsilon}|S''M''_S\rangle|2pl_\epsilon;m+m_\epsilon,S'',M''_S\rangle \tag{7}$$

The rate can be nonzero only if $S''=S_{vv'}$, $M''_S = M_{S_{vv'}}$, and $\Lambda = m+m_\epsilon$ so that

$$A_{i\to f} = 2\pi\Big(\sum_{M_{S_{vv'}},m_\sigma,m_s}\langle S_{vv'}M_{S_{vv'}}\frac{1}{2}m_\sigma|SM_S\rangle\langle\frac{1}{2}m_s\frac{1}{2}m_\sigma|S'M'_S\rangle\langle\frac{1}{2}m_s\frac{1}{2}m_{s\epsilon}|S_{vv'}M_{S_{vv'}}\rangle\Big)^2$$
$$\times\Big|\sum_{l_\epsilon,m_\epsilon}\Big(\langle 2pl_\epsilon;m+m_\epsilon S_{vv'}M_{S_{vv'}}|\frac{1}{r_{12}}|vv';\Lambda S_{vv'}M_{S_{vv'}}\rangle + (-1)^{S_{vv'}}\langle 2pl_\epsilon;m+m_\epsilon S_{vv'}M_{S_{vv'}}|\frac{1}{r_{12}}|v'v;\Lambda S_{vv'}M_{S_{vv'}}\rangle\Big)\Big|^2.$$

To compare to experiment, the rates have to be averaged over the initial spin projection M'_S and summed over both final spin projections M_S and $m_{s\epsilon}$. Note, that two-electron Auger matrix elements do not depend on a particular value of $M_{S_{vv'}}$ and not at all on any other spin projection, so that the averaged rate $\tilde{A}_{i\to f}$ can be factored as follows

$$\begin{aligned}
\tilde{A}_{i\to f} &= \frac{1}{2S'+1}\sum_{M'_S,M_S,m_{s\epsilon}} A_{i\to f}(m_{s\epsilon},M_S,M'_S)\\
&= \pi\Big|\sum_{l_\epsilon,m_\epsilon}\Big(\langle 2p_m l_\epsilon m_\epsilon|r_{12}^{-1}|vv';\Lambda S_{vv'}\rangle + (-1)^{S_{vv'}}\langle 2p_m l_\epsilon m_\epsilon|r_{12}^{-1}|v'v;\Lambda S_{vv'}\rangle\Big)\Big|^2\\
&\times\frac{2}{2S'+1}\sum_{M'_S,M_S,m_{s\epsilon}}\Big(\sum_{m_s,M_{S_{vv'}},m_\sigma}\langle\frac{1}{2}m_s\frac{1}{2}m_\sigma|S'M'_S\rangle\langle S_{vv'}M_{S_{vv'}}\frac{1}{2}m_\sigma|SM_S\rangle\langle\frac{1}{2}m_s\frac{1}{2}m_{s\epsilon}|S_{vv'}M_{S_{vv'}}\rangle\Big)^2\\
&\equiv \pi\Big|\sum_{l_\epsilon,m_\epsilon}\Big(J_{vv'}(\Lambda,S_{vv'},l_\epsilon,m_\epsilon,m) + (-1)^{S_{vv'}}K_{v'v}(\Lambda,S_{vv'},l_\epsilon,m_\epsilon,m)\Big)\Big|^2\mathcal{S}(S',S_{vv'},S).
\end{aligned}$$

Above we have denoted the direct and exchange matrix elements as $J_{vv'}$ and $K_{vv'}$ and defined a new spin factor $\mathcal{S}$, which depends on the spin of the initial state ($S'=0,1$), on the spin of the vv' holes ($S_{vv'}=0,1$) and on the spin of the final state ($S=1/2,3/2$). Altogether this gives 8 possible combinations that evaluate to:

$$\begin{aligned}
&\mathcal{S}(0,0,1/2)=1, \quad \mathcal{S}(0,0,3/2)=0, \quad \mathcal{S}(0,1,1/2)=3, \quad \mathcal{S}(0,1,3/2)=0,\\
&\mathcal{S}(1,0,1/2)=1, \quad \mathcal{S}(1,0,3/2)=0, \quad \mathcal{S}(1,1,1/2)=\frac{1}{3}, \quad \mathcal{S}(1,1,3/2)=\frac{8}{3}.
\end{aligned} \tag{8}$$

Integrating the rate over the Auger electron emission angles allows us to place the sum over the partial waves out of the absolute value bars because the cross terms cancel out. Considering rates, averaged also over the projection of the orbital angular momentum ($m=-1,0,1$) of the initial $2p$ hole, we finally have

$$\tilde{A}_{i\to f} = \frac{\pi}{3}\mathcal{S}(S',S_{vv'},S)\sum_{l_\epsilon,m_\epsilon,m}\Big|\Big(J_{vv'}(\Lambda,S_{vv'},l_\epsilon,m_\epsilon,m) + (-1)^{S_{vv'}}K_{v'v}(\Lambda,S_{vv'},l_\epsilon,m_\epsilon,m)\Big)\Big|^2. \tag{9}$$

If we also want to average the rate over spin $S'=0,1$ of the initial state, we replace the spin factor above with the average spin-factor

$$\tilde{\mathcal{S}}(S_{vv'},S) = \frac{1}{4}\mathcal{S}(0,S_{vv'},S) + \frac{3}{4}\mathcal{S}(1,S_{vv'},S), \tag{10}$$

which evaluates to

$$\tilde{\mathbb{S}}(0,1/2)=1,\quad \tilde{\mathbb{S}}(0,3/2)=0,\quad \tilde{\mathbb{S}}(1,1/2)=1,\quad \tilde{\mathbb{S}}(1,3/2)=2. \tag{11}$$