

Spin-orbit-resolved resonant Auger spectrum of a dissociating HCl molecule

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The photodissociation of HCl via the antibonding $2p^{-1}\sigma^*$ resonance occurs on the same 10-fs timescale as the Auger decay of the $2p$ vacancy. This means that the v , v' , and σ^* valence molecular orbitals involved in the electronic transition can significantly differ from the orbitals at the ground state equilibrium internuclear position. The nonrelativistic $L - vv'$ resonant Auger (RA) spectrum based on the stationary Green's function approach gives a good estimate of relative intensities of the three main spectral features in the 173–182 eV emission energy range, but fails to reproduce highly resolved experimental data. We show that addition of the spin-orbit interaction of the $2\pi^{-2}\sigma^*$ and $5\sigma^{-1}2\pi^{-1}\sigma^*$ final states significantly improves the agreement for the spectral feature arising from the $^4\Pi, ^2\Sigma$, and $^4\Sigma$ states that converge to the $\text{H} + \text{Cl}^+(^3P)$ dissociation limit. Somewhat surprisingly, we found that the ^3P nonrelativistic limit splits to five instead of three $3p^{-2}(^3P_{0,1,2})$ dissociation limits of the Cl^+ fragment at large internuclear distances. The similarity with the atomic case is broken because of a different nature of the $^2\Pi$ molecular state, which is populated by a weak participator Auger decay and converges to a different, significantly higher $\text{H}^+ + \text{Cl}(^2P)$ dissociation limit. Our analysis shows that the remaining differences with an angle-integrated experimental spectrum are caused primarily by inaccuracies of the nonrelativistic final state potentials and not by the one-center approximation of the spectator Auger transition rates. The potential slope differences are imprinted on the RA spectrum with a sensitivity and range depending on the duration of molecular dissociation with respect to the core-hole lifetime.

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I. INTRODUCTION

In the pioneering work of Morin and Nenner on HBr, sharp lines in the $M_{4,5} - vv'$ resonant Auger spectrum were explained by introducing the concept of ultrafast dissociation (UFD) [1]. Upon absorbing a photon, the molecule is excited to a state with a strongly repulsive potential energy curve (PEC) and dissociates so quickly that the Auger decay of the Br $3d$ hole to the vv' valence holes occurs with a high probability in the so-called atomic limit (i.e., at large internuclear distances, where the Br atom is practically free). Since then, many other molecules were found to exhibit atomic sharp features in the resonant Auger (RA) and resonant inelastic x-ray scattering (RIXS) spectra [2–5]. A simultaneous presence of electronic decay and dissociation results in a nontrivial excitation energy sharing between the electronic and nuclear degrees of freedom, which is reflected in the nonlinear Raman shift and photon energy dependent modulation of the emission spectra [6–9]. However, a dissociation timescale is already encoded in the core-hole spectrum acquired at a single (zero) photon energy detuning because the dissociation dynamics govern a relative share of the sharp atomic signal with respect to the broad spectral background, signaling electronic decay in the molecular environment [10,11].

Although dissociation of polyatomic molecules often evolves along complicated trajectories on multidimensional potential energy surfaces, the initial movement is likely approximated by a simple distancing of the core-hole excited atom and its atomic neighbor, which is governed by the reduced mass m_r of the pair and the local slope $\mathcal{F}$ of the potential [12]. It is therefore not surprising that dissociation of $1s^{-1}\sigma^*$ state makes a similar spectral imprint on the Cl $K - L$ RIXS spectra for a number of chlorinated hydrocarbons, because in all of them, chlorine atoms are bound to carbon atoms and the lifetime of the Cl $1s$ hole (1 fs) is much shorter than the time needed for the dissociation. However, the Cl $2p$ hole features an eight times longer lifetime [13], and the corresponding RA spectra in chloromethanes show a gradual loss of the atomic component with an increasing number of Cl atoms [14]. To understand the trend, one would need to propagate the $2p^{-1}\sigma^*$ molecular state along its potential energy surface and calculate kinetic energy distribution of Auger electrons emitted during a transition to various final molecular states. In fact, even for the simplest version of this problem, the resonant Auger decay of the $2p^{-1}\sigma^*$ antibonding state in HCl, the *ab initio* RA spectrum has only recently been constructed [15], despite a number of previous experimental and theoretical studies of this diatomic molecule [13,16–24]. Below we summarize the methodology that goes beyond well-established approximations of the Kramers-Heisenberg formula [25] and discuss a role of the spin-orbit interaction of final states in obtaining tighter agreement of the calculated resonant $L - vv'$ spectrum with the state-of-art experimental data for HCl.

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While both radiative and nonradiative electronic decays occur within the same core-hole lifetime, there is an important difference between the two regarding the PEC slope of the final dissociative state with respect to the slope of the dissociative core-hole state. When the transition substitutes a single $1s$ hole by a relaxed but still localized hole, PECs of both states remain approximately parallel. The corresponding RIXS spectrum is not sensitive to the dissociation dynamics and depends only on the ratio of the electronic decay rate Γ_i and the bound-continuum Franck-Condon factor F_{bc} that connects an initial bound state of the nuclei with an excited dissociative core-hole state [6]. On the other hand, Auger electron emission leads to a pair of holes in the final dissociative state of the molecular ion, and the corresponding PEC slope $\mathcal{F}_f$ may differ significantly from the PEC slope $\mathcal{F}_i$ of the upper core-hole state for a range of molecular geometries visited during the dissociation. The Auger electron emission therefore induces a considerable change of the continuum wave function describing the nuclear motion, which boosts the effect of the continuum-continuum Franck-Condon factor F_{cc} on the RA spectrum. Such a situation occurs in RIXS, too, when the final hole is delocalized in the valence shell and the corresponding PEC is not parallel anymore to the core-hole potential [26].

The effects of dissociation dynamics are more pronounced at longer core-hole lifetimes when a significant part of electronic transitions occurs outside the Franck-Condon region prompting for an accurate description of PECs and of the corresponding nuclear wave functions also far from the equilibrium position. The Kramers-Heisenberg formula can be efficiently simplified only if Γ_i is *much larger or much smaller* than the PEC slope difference parameter

$$\gamma_{fi} = [(\mathcal{F}_f - \mathcal{F}_i)\sqrt{\mathcal{F}_f\mathcal{F}_i}/(2m_r)]^{1/3} \quad (1)$$

at any internuclear distance visited during the decay [6]. While the first condition ultimately holds for any value of Γ_i at large enough internuclear distances, where the PECs of the intermediate and final states necessarily become parallel (making $\mathcal{F}_i$ and $\mathcal{F}_f$ zero), it may not be fulfilled at small internuclear distances close to the equilibrium if the lifetime is long. In such cases, a simplified lineshape calculation over *the whole spectral range* is not possible, and often time-dependent wavepacket evolution is performed to generate the spectrum [22,27]. In Ref. [15] an alternative stationary approach has been employed recently to calculate the line shapes of $L - vv'$ RA transitions in HCl over their entire spectral range. The implementation of this methodology leads to good agreement with the experimental data and answers a key question: at which internuclear distance is an Auger electron with a given kinetic energy emitted. Indeed, relying on a classical description of molecular dynamics, the answer clearly points to the molecular geometry in which the PEC difference equals the electron kinetic energy [19]. We show that a fully quantum description of the RA process and simultaneous molecular dissociation unavoidably deals with delocalized photon absorption and electron emission events.

This work focuses on the spin-orbit (SO) interaction of the HCl^+ states populated by Auger decay of the antibonding $2p^{-1}\sigma^*$ HCl state and represents an upgrade of work presented in Ref. [15]. The SO interaction heavily affects the

$v^{-1}v'^{-1}\sigma^*(^4\Pi, ^2\Sigma, ^4\Sigma)$ spectral lines that otherwise converge to the same $3p^{-2}(^3P) \text{Cl}^+ + \text{H}(1s)$ dissociation limit, and its inclusion promises to reduce the remaining differences with the highly resolved experimental data. Our modeling is based on the published nonrelativistic final state potentials [28] too, but to build up the spectral profiles corresponding to SO-mixed final states, the R -dependent Auger transition amplitudes to the nonrelativistic parent states must be fully reconstructed. Throughout this work we also rely on one-center approximation and the data tables from Ref. [29] and use previously published R -dependent decomposition of the 5σ molecular orbital to Cl-centered atomic orbitals [15] as an input.

II. THEORY

A. RA amplitude

We first describe essentials of recently published theoretical description of RA spectrum emitted by a dissociating diatomic molecule [15]. The corresponding cross section describes the yield of emitted Auger electrons with energy ϵ at photon energy ω and is given by [30]

$$\sigma(\omega, \epsilon) = 4\pi^2\alpha\omega \sum_f |F_f(\omega, \epsilon)|^2 \mathcal{L}(E_0 + \omega - E_f - \epsilon, \Gamma_f). \quad (2)$$

The RA amplitudes to different final states f are expressed in the frame of the second-order perturbation theory [6] as

$$F_f(\omega, \epsilon) = \sum_i \frac{\langle \Phi_f | \hat{V} | \Phi_i \rangle \langle \Phi_i | \hat{D} | \Phi_0 \rangle}{E_0 + \omega - E_i + i\Gamma_i/2}. \quad (3)$$

The dipole interaction D drives electronic transitions from the molecular ground state Φ_0 with energy E_0 to the core-hole excited state Φ_i with energy E_i . The Coulomb interaction V causes the molecule to transit within the lifetime Γ_i^{-1} to the final molecular state Φ_f with energy $E_f + \epsilon$ where ϵ is the kinetic energy of the Auger electron. In our case the decay width Γ_f of the $v^{-1}v'^{-1}\sigma^*$ final state is negligibly small relative to the experimental spectral broadening, and the Lorentzian $\mathcal{L}(a, b) \equiv (b/2\pi)(a^2 + b^2/4)^{-1}$ in (2) can be approximated by the Dirac's delta $\delta(E_0 + \omega - E_f - \epsilon)$. In the Born-Oppenheimer approximation, the molecular states are described by the product, $\Phi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}; \mathbf{R})\varphi(\mathbf{R})$, where ψ describes the electronic and φ the nuclear part, and $\mathbf{r}$ and $\mathbf{R}$ denote the coordinates of the electrons and the nuclei. The electronic transitions are assumed vertical, meaning that the molecule jumps from the ground state potential U_0 to the intermediate state potential U_i , and then to the potential U_f of the final molecular ion in two frozen, but generally different, molecular geometries defined by internuclear distances R and R' , respectively.

Formally, $F_f(\omega, \epsilon)$ can be expressed by a double integral:

$$F_f = \int_0^\infty dR \int_R^\infty dR' \varphi_f^*(R') V_{fi}(R') G_{i,\omega}^+(R', R) D_{i0}(R) \varphi_0(R), \quad (4)$$

TABLE I. PEC numbering (U_f , column 1) associated with the HCl^+ electronic states (column 5) that are populated by $L - vv'$ Auger decay of the dissociative $2p^{-1}\sigma^*$ state of HCl by emission of electrons in the 173–181 eV kinetic energy range. The states are build by coupling the σ^* electron to the $v^{-1}v'^{-1} \text{HCl}^{2+}$ states (column 3). The scaling factor S [column 4; see Eq. (25) for the definition] converts the spectator-less $2p^{-1}\text{HCl}^+ \rightarrow v^{-1}v'^{-1}\text{HCl}^{2+}$ Auger decay rate to the corresponding RA rate (see text for details). At large R , the molecular states converge to the $^1S, ^1D$, or ^3P state of the $3p^{-2} \text{Cl}^+$ ion plus the hydrogen atom $\text{H}(1s)$ (column 6), except for the $A(^2\Sigma)$ bound electronic state and a pair of degenerate $f_{10x,y}$ dissociative states that converge to the $\text{Cl}(3p^{-1}^2P) + \text{H}^+$ dissociation limit. The asymptotic Auger electron kinetic energies (column 7) are obtained from the experimental data [13,28]. The f_i notation of final nonrelativistic states follows the Ref. [15]. The calculated partial Auger rates Γ_{fi} at HCl equilibrium internuclear distance R_0 (column 8) and at infinite separation (column 9) are about 20% lower than the corresponding rates reported in Ref. [15] (see the comparison in Fig. 8 in Appendix D).

U_f	State	$vv'(^{2S}v'^{-1}\Lambda)$	$S(S_{vv'}, S)$	$vv'(^{2S}v'^{-1}\Lambda)\sigma^* ^{2S+1}\Lambda$	Atomic limit $R \rightarrow \infty$	$\epsilon(\infty)$ (eV)	$\Gamma_{fi}(R_0)$ ($\times 10^{-4}$ a.u.)	$\Gamma_{fi}(\infty)$ ($\times 10^{-4}$ a.u.)
1	f_2	$5\sigma^{-2}(^1\Sigma^+)$	1	$5\sigma^{-2}(^1\Sigma^+)\sigma^*(^2\Sigma^+)$	$\text{Cl}^+(3p^{-2}^1S) + \text{H}(1s)$	176.99	1.21	3.51
2	f_9	$5\sigma^{-1}2\pi_{x,y}^{-1}(^1\Pi)$	1	$5\sigma^{-1}2\pi_{x,y}^{-1}(^1\Pi)\sigma^*(^2\Pi)$	$\text{Cl}^+(3p^{-2}^1D) + \text{H}(1s)$	179.00	3.52	5.99
3	f_{12}	$2\pi^{-2}(^1\Sigma^+)$	1	$2\pi^{-2}(^1\Sigma^+)\sigma^*(^2\Sigma^+)$	$\text{Cl}^+(3p^{-2}^1D) + \text{H}(1s)$	179.00	4.02	4.02
4	f_{14}	$2\pi^{-2}(^1\Delta)$	1	$2\pi^{-2}(^1\Delta)\sigma^*(^2\Delta)$	$\text{Cl}^+(3p^{-2}^1D) + \text{H}(1s)$	179.00	5.84	5.84
8	f_{10}	$5\sigma^{-1}2\pi_{x,y}^{-1}(^3\Pi)$	1	$5\sigma^{-1}2\pi_{x,y}^{-1}(^3\Pi)\sigma^*(^2\Pi)$	$\text{Cl}(3p^{-1}^2P) + \text{H}^+$	179.87	1.30	0
9	f_A			$5\sigma^{-1}(^2\Sigma^+)$	$\text{Cl}(3p^{-1}^2P) + \text{H}^+$	179.87	0	0
5	f_{11}	$5\sigma^{-1}2\pi_{x,y}^{-1}(^3\Pi)$	2	$5\sigma^{-1}2\pi_{x,y}^{-1}(^3\Pi)\sigma^*(^4\Pi)$	$\text{Cl}^+(3p^{-2}^3P) + \text{H}(1s)$	180.45	5.04	8.58
6	f_{13}	$2\pi^{-2}(^3\Sigma^-)$	1	$2\pi^{-2}(^3\Sigma^-)\sigma^*(^2\Sigma^-)$	$\text{Cl}^+(3p^{-2}^3P) + \text{H}(1s)$	180.45	2.15	2.15
7	f_{15}	$2\pi^{-2}(^3\Sigma^-)$	2	$2\pi^{-2}(^3\Sigma^-)\sigma^*(^4\Sigma^-)$	$\text{Cl}^+(3p^{-2}^3P) + \text{H}(1s)$	180.45	4.30	4.30

where the propagation between the absorption point R and emission point R' is governed by the Green's function

$$G_{i,\omega}^+(R', R) = \int dE_i \frac{\varphi_{E_i}(R')\varphi_{E_i}^*(R)}{E_0 + \omega - E_i + i\Gamma_i/2}. \quad (5)$$

Note that here the integration over the continuum of dissociative molecular states replaces the summation over intermediate states in (3). The dipole and Coulomb transition integrals are evaluated by integrating over the coordinates of all electrons $\mathbf{r}$:

$$D_{i0}(R) = \int d\mathbf{r} \psi_i^*(\mathbf{r}; R) D(\mathbf{r}) \psi_0(\mathbf{r}; R), \quad (6)$$

$$V_{fi}(R') = \int d\mathbf{r} \psi_f^*(\mathbf{r}; R') V(\mathbf{r}) \psi_i(\mathbf{r}; R'). \quad (7)$$

In Ref. [30] the Green's function was calculated using a semiclassical approximation for the nuclear wave function,

$$\varphi_i^{\text{cl}}(R) = A \frac{\exp\left[-i \int_{R_{E_i}}^R k_i(R'') dR''\right]}{\sqrt{k_i(R)}}, \quad (8)$$

where

$$k_i = m_r v_i = \sqrt{2m_r[E_i - U_i(R)]} \quad (9)$$

is the momentum of the particle with a reduced molecular mass m_r and R_{E_i} is the classical turning point on the potential curve U_i for the energy of the molecule equal to E_i . By replacing φ_{E_i} with φ_i^{cl} in Eq. (5) we get

$$G_{i,\omega}^+ \approx -2i\pi A^2 \frac{\exp\left[-i \int_R^{R'} k_i(R'') dR''\right]}{\sqrt{k_i(R')k_i(R)}} \exp\left[-\frac{\Gamma_i \tau_i(R', R)}{2}\right], \quad (10)$$

where the time needed to increase the internuclear distance from R to R' is given by

$$\tau_i(R', R) = \int_R^{R'} \frac{dR''}{v_i(R'')}. \quad (11)$$

The approximation applies at internuclear distances for which the kinetic energy $E_i - U_i(R) \approx E_0 + \omega - U_i(R)$ of the nuclei is larger than Γ_i . For steep U_i and small Γ_i , this is practically the entire classically accessible region ($R \geq R_{E_i}$). The Green's function is thus suppressed exponentially when the point R' of the Auger emission is distancing from the photon absorption point R ; clearly there can be no significant contribution to the RA cross section when the time to travel from R to R' is much longer than Γ_i^{-1} because the intermediate state population has been already exhausted. In the derivation of Eq. (10) in Ref. [30], Γ_i is assumed constant. However, if the intermediate state lifetime is long, so that important contributions to the Auger electron yield come from internuclear distances with significantly different active electronic orbitals, Γ_i depends on the internuclear distance too. As shown in Ref. [15] and in Fig. 1(b), the $2p^{-1}\sigma^* - 2\pi^{-1}5\sigma^{-1}\sigma^*$ RA decay rates in HCl may increase by a factor of two when R' increases from the ground state equilibrium internuclear distance ($R_0 = 2.408$ a.u.) to infinity. This happens because the 5σ molecular orbital gradually loses its $\text{Cl}(3s)$ and $\text{H}(1s)$ character and becomes a pure $\text{Cl}(3p_z)$ orbital. The variability of Γ_i can be accounted for by placing it under the integral (11):

$$\exp\left[-\frac{\Gamma_i}{2} \int_R^{R'} \frac{dR''}{v_i(R'')}\right] \rightarrow \exp\left(-\frac{1}{2} \int_R^{R'} dR'' \frac{\Gamma_i(R'')}{v_i(R'')}\right) \equiv e^{-\eta(R,R')}. \quad (12)$$

The approximation (10) implies the proportionality of the Green's function with $\varphi_i^{\text{cl}}(R')\varphi_i^{\text{cl}*}(R)$. This suggests that one substitute the product of semiclassical nuclear wave

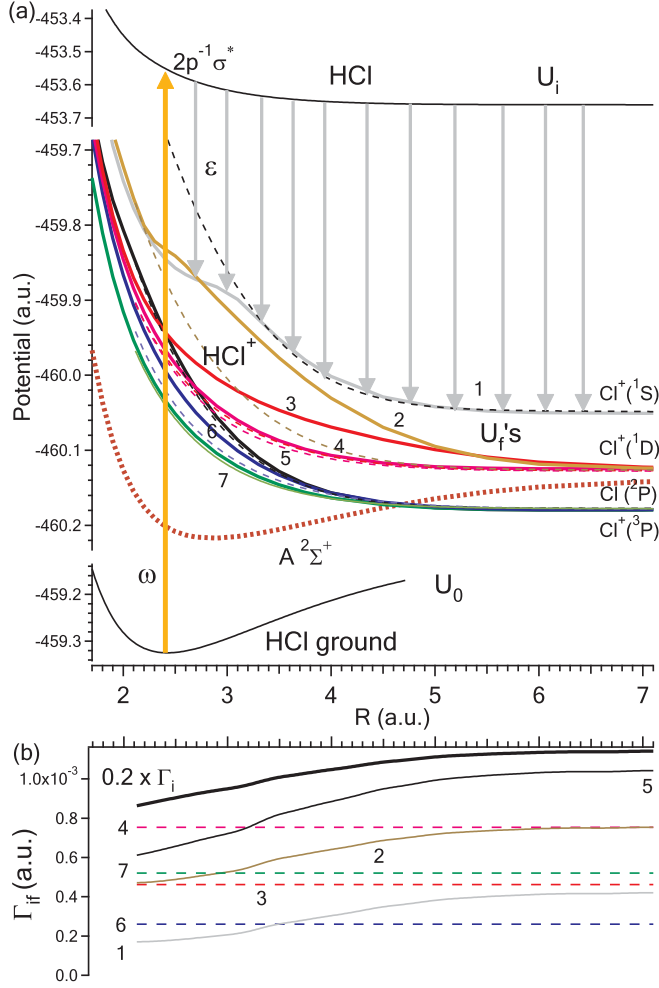


FIG. 1. (a) Scheme of the RA process in the presence of UFD initiated by absorption of a photon with energy ω . PEC of the HCl ground state (U_0) and the $2p^{-1}\sigma^*$ state (U_i) are from [15]. PECs of $\text{HCl}^+ v^{-1}v'^{-1}\sigma^*$ final states (U_f) are from [28]. Dotted (red) line denotes bound state potential of the $5\sigma^{-1}A^2\Sigma^+$ state in HCl^+ [28]. PECs from a single-configuration calculation [31] are plotted by the black dashed curves. See Table I for the final state description and the corresponding potential numbering. (b) The calculated Γ_{fi} (thin numbered curves) and Γ_i (bold curve) dependence on the internuclear distance (from [15]).

functions with $\varphi_i(R')\varphi_i^*(R)$, the product of properly normalized incoming-wave quantum nuclear wave functions to extend the functionality of approximation to the $R \approx R_0$ region.

Finally, the RA amplitude [Eq. (4)] is given by

$$F_f \approx \int_0^\infty dR \int_R^\infty dR' (\varphi_f^*(R') V_{fi}(R') \varphi_i(R')) \times e^{-\eta(R,R')} \varphi_i^*(R) D_{i0}(R) \varphi_0(R). \quad (13)$$

B. Nuclear wave functions

The HCl molecule is initially in the $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 2\pi^4 \ ^1\Sigma^+$ electronic state and occupies the lowest vibrational state φ_0 in the ground state

potential U_0 ,

$$\varphi_0(R) = \left(\frac{m_r \omega_0}{\pi} \right)^{1/4} \exp \left[-\frac{m_r \omega_0}{2} (R - R_0)^2 \right], \quad (14)$$

with half a quantum of vibrational energy $\omega_0 = 1.362 \times 10^{-2}$ a.u. and $m_r = 1723$ a.u. The ground state is thus taken equal to the lowest eigenstate of the harmonic oscillator arising from the harmonic approximation to the U_0 potential.

The nuclear wave functions $\varphi_i(R)$ and $\varphi_f(R)$ take part in description of molecular states with eigenenergy E_i and E_f on dissociative potentials $U_i(R)$ and $U_f(R)$, respectively (see Fig. 1). In the studied case, $\Gamma_i \approx 0.1$ eV is relatively small, and E_i can be taken equal to the resonant photon energy $\omega = U_i(R_0) - E_0$. In a vertical transition, the kinetic energy ϵ of the emitted Auger electron may take any value between the minimum and maximum PEC difference $U_{if}(R) = U_i(R) - U_f(R)$ in the range of internuclear distances R traversed during the dissociation (Fig. 1). The Auger decay populates state of the molecular ion with energy $E_f = E_0 + \omega - \epsilon$. Both nuclear wave functions thus have well-defined asymptotic kinetic energies:

$$\epsilon_{i,\infty} = E_0 + \omega - U_i(R \rightarrow \infty) \equiv k_{i,\infty}^2 / (2m_r), \quad (15)$$

$$\epsilon_{f,\infty} = E_0 + \omega - \epsilon - U_f(R \rightarrow \infty) \equiv k_{f,\infty}^2 / (2m_r). \quad (16)$$

Each of the two nuclear wave functions is expressed by a linear combination of two independent standing-wave solutions φ^a and φ^b of the corresponding radial Schrödinger equation,

$$\frac{1}{2m_r} \frac{d^2 \varphi_i^{a,b}}{dR^2} + [U_i(R_0) - U_i(R)] \varphi_i^{a,b} = 0, \quad (17)$$

$$\frac{1}{2m_r} \frac{d^2 \varphi_f^{a,b}}{dR^2} + [U_f(R_f) - U_f(R)] \varphi_f^{a,b} = 0. \quad (18)$$

When R changes from R_0 or R_f towards smaller internuclear distances, φ^a and φ^b take exponentially vanishing and exponentially increasing values, respectively. As dissociation is a half-scattering process, at large R the nuclear wave functions on the U_i and U_f potentials must be proportional to $\exp(-ik_{i,\infty}R)$ and $\exp(-ik_{f,\infty}R)$ waves, respectively, so that

$$\varphi_i(R) = \sqrt{\frac{2\sqrt{m_r}}{\pi k_{i,\infty}}} (\varphi_i^a(R) + i\varphi_i^b(R)), \quad (19)$$

$$\varphi_f(R) = \sqrt{\frac{2\sqrt{m_r}}{\pi k_{f,\infty}}} (\varphi_f^a(R) + i\varphi_f^b(R)). \quad (20)$$

Note that R_f , the position of the classical turning point of the U_f potential, depends on the kinetic energy of Auger electron via the ϵ dependence of the final molecular ion state energy E_f . Consequently, the continuum-continuum Franck-Condon factor $F_{cc} = \langle \varphi_f | \varphi_i \rangle$ also depends on the Auger kinetic energy ϵ . If the amplitudes of the $\varphi^{a,b}$ asymptotically approach one, the nuclear wave functions (19) and (20) are energy-normalized:

$$\langle \varphi_i | \varphi_i' \rangle = \delta(\epsilon_{E_i} - \epsilon_{E_i'}), \quad \langle \varphi_f | \varphi_f' \rangle = \delta(\epsilon_{E_f} - \epsilon_{E_f'}), \quad (21)$$

as anticipated by expression (2).

C. Potential energy curves and Auger transition rates to nonrelativistic states

In Ref. [15] the dissociative potential energy curves U_i and U_f were initially calculated with the single-configuration nonrelativistic approximation. While for U_i the perfect overlap was found with previously published $2p^{-1}\sigma^*$ potential in HCl [3], significant differences were seen for U_f potentials with respect to the multiconfiguration results of Pradhan *et al.* [28]. Indeed, the φ_f nuclear wave functions generated by these more accurate potential energy curves lead to better agreement with the experimental RA spectrum, so these PECs are selected as the starting point of our spin-orbit study.

While the dipole transition amplitude (13) can be fixed to $D_{0i}(R_0)$ because of the strong localization of the bound-continuum Franck-Condon factor $F_{bc} = \langle \varphi_i | \varphi_0 \rangle$, a relatively long core-hole lifetime prevents selection of any particular molecular geometry when calculating the Auger rate. Each final molecular state features a characteristic Coulomb transition integral (7) with the intermediate state that may change with the internuclear distance R . In fact, to reproduce an angle-integrated RA spectrum, the *effective* partial Auger amplitudes may be generated back from the partial decay rates Γ_{fi} if these are known. Since the rate never falls to zero, the corresponding amplitude retains the same sign for all R and $+\sqrt{\Gamma_{fi}(R)/(2\pi)}$ can be inserted into Eq. (13) instead of $V_{fi}(R)$ to calculate the corresponding spectral distribution. Reference [15] reports the nonrelativistic rates Γ_{fi} for the spectator RA decays of the $2p$ hole in HCl that constitute a major part of the total decay rate $\Gamma_i(R) \approx \sum_f \Gamma_{fi}(R)$. These partial rates were calculated in the frame of one-center approximation [32,33], where the contributions of electronic orbitals *not centered* on the Cl atom to the Coulomb transition integrals (7) are neglected because of a strong localization of the $2p$ hole on the Cl site. The electron orbitals were allowed to change with R , but were assumed to remain frozen upon a vertical Auger transition at any R . However, our spin-orbit calculation requires a complete determination of complex partial Auger amplitudes to nonrelativistic states, because it is their superposition that defines the amplitude and consequently the corresponding partial Auger decay rate to the spin-orbit coupled state.

Each nonrelativistic final state is characterized by a dominant configuration of molecular orbitals with respect to the ground state configuration, the absolute value Λ of the projection of the orbital momentum on the internuclear axis, the total spin S , and the state character ($\pm$, only for Σ states). As the dissociation unfolds, the molecular orbital σ^* occupied by the spectator electron transforms to the $1s$ orbital centered on the H atom. It therefore makes sense to represent these final molecular states by coupling the σ^* electron to two vacancies vv' that end up localized on the Cl atom (see Table I and Fig. 1). Moreover, the angular momentum recoupling in such a framework shows that the $L - vv'$ partial RA decay rates, averaged over the spin and orbital angular momentum projection of the $2p^{-1}\sigma^*$ state, are proportional to the $L - vv'$ partial Auger rates of the $2p$ hole in the HCl^+ molecular ion where the missing σ^* spectator electron still drives the dissociation. The scaling factor S depends only on the spin $S_{vv'}$ of the vv' valence holes and the spin S of the final molecular

state $v^{-1}v'^{-1}(2S_{vv'}+1)\Lambda\sigma^* 2S+1\Lambda$ [31]. Thus, the partial Auger rates for reaction $\text{HCl}^+ 2p^{-1} \rightarrow \text{HCl}^{2+} v^{-1}v'^{-1}(S_{vv'}\Lambda) + e^-(\epsilon)$ were calculated first, following the procedure and data tables of Chelkowska and Larkins [29], along with using the R -dependent decomposition of the 5σ orbital to the Cl^+ -centered $3s$ and $3p_z$ orbitals as an input. These spectator-less Auger rates were then multiplied by the corresponding scaling factors S (see Table I) to obtain the partial rates Γ_{fi} for Auger decay of the $\text{HCl} 2p^{-1}\sigma^*$ state and calculate back the effective R -dependent Coulomb transition integrals that are needed to construct the spectrum via Eq. (13).

The Auger decay imprints PEC modulations on the kinetic-energy-dependent yield of emitted electrons. In the classical description of dissociation dynamics this mapping is exact, i.e., an Auger electron with kinetic energy ϵ is emitted exactly at the internuclear distance $R'(\epsilon)$ where $\epsilon = U_i(R) - U_f(R)$. To model the RA spectrum, the classical electron yield is broadened with the Lorentzian $\mathcal{L}(\Delta\epsilon, \Gamma_i)$ to correctly reproduce the yield at large R , in the region of the so-called atomic peak. In quantum mechanics it is in principle impossible to determine from a RA spectrum at which R the photon with energy ω was absorbed and at which R' the Auger electron with a given kinetic energy was emitted because, for each ϵ , the amplitudes of all absorption-emission paths interfere, as clearly indicated by the form of Eq. (4). Still the mapping is robust enough to withstand the broadening due to the quantum description of the nuclear movement. A delocalization of Auger emission populating the $5\sigma^{-2}\sigma^*$ state is illustrated in Fig. 2. For each ϵ , the map reports an absolute square of the RA amplitude obtained by integration (4), where an increasingly higher cutoff distance R_{max} is used instead of infinity in the upper integration limits. It is evident that the tail of the spectral line, usually associated with emission in the “molecular regime,” receives its most significant contribution at internuclear distances smaller than 5 a.u. The atomic peak starts to build up only at higher R' and acquires its final shape and intensity only when the emission events in the 15–28 a.u. range are also included. Between these two regimes, signal oscillations appear that smooth out (receiving positive, as well as negative contributions) only after considering emission events up to a large enough R' . However, it remains true that the spectral yield in the tail region reflects the PEC behavior at small internuclear distances. The spectral yield in this region can be estimated simply by the $|F_{cc}|^2$ dependence on the electron energy ϵ , which itself diverges in the atomic limit (Fig. 2). In the present case, the configuration-interaction (CI) mixing of the $^2\Sigma^+$ states $5\sigma^{-2}\sigma^*$ and $2\pi^{-2}\sigma^*$ modulates both PEC for $2.5 < R < 5$ a.u., which is reflected in the appearance of the secondary maximum in the RA spectral contribution. This maximum is offset by -2.6 eV and -1.4 eV, respectively, from the corresponding “atomic” peak $\text{Cl}^+(^1S)$ and $\text{Cl}^+(^1D)$ [see profiles (14) and (11) in Fig. 5(a)].

In the following, we focus on the SO coupling of the $5\sigma^{-1}2\pi^{-1}\sigma^*$ and $2\pi^{-2}\sigma^*$ states in HCl^+ that are populated from the $\text{HCl } 2p^{-1}\sigma^*$ state by emission of the spectator electron in the 173–182 eV kinetic energy range. Besides the HCl^+ final states dissociating to the $\text{H} + \text{Cl}^+$ limits, Table I lists the $5\sigma^{-1}2\pi^{-1}\sigma^* {}^2\Pi$ and $5\sigma^{-1} {}^2\Sigma^+$ states that converge to a different dissociation channel, $\text{H}^+ + \text{Cl}(^2P)$. While the

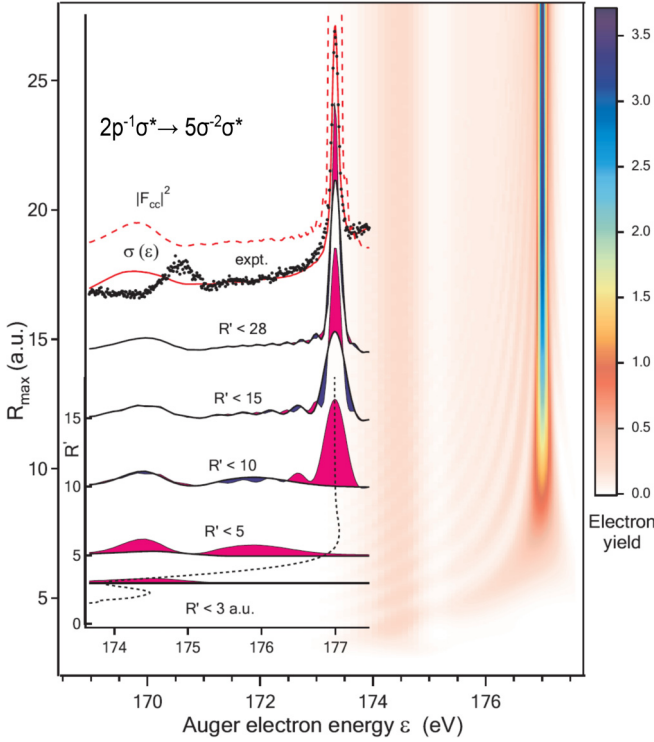


FIG. 2. Buildup of the $2p^{-1}\sigma^* \rightarrow 5\sigma^{-2}\sigma^*$ Auger spectral line in HCl by increasing the cutoff internuclear distance $R_{\max}$ of the Auger emission. The inset shows projections of the calculated electron yield on the ϵ axis at five different values of $R_{\max}$. The difference with the lower curve is either positive (marked red) or negative (marked blue). The theoretical spectrum $\sigma(\epsilon)$ (red curve) is compared to the experimental spectrum (black dots) and with a modulus square of the F_{cc} factor (red dashed curve with an offset). The dotted black curve is used for the classical $R'(\epsilon)$ mapping.

probability for Auger emission to the $5\sigma^{-1}2\Sigma^+$ bound state is zero in single-configuration picture, the population of the $5\sigma^{-1}2\pi^{-1}\sigma^*2\Pi$ dissociative state from the $2p^{-1}\sigma^*$ resonance is strongly suppressed at large internuclear distances because it is driven by the Coulomb interaction of electrons localized at different nuclei. Despite the negligible Auger yields, these states are added to our research framework because they exhibit SO interaction with other states in Table I that are populated by the spectator Auger transition.

III. SPIN-ORBIT MIXING OF FINAL STATES

Before dealing with the SO interaction of the $v^{-1}v'^{-1}\sigma^*$ states in a dissociating HCl^+ molecular ion, it is useful to discuss a close analogy with the $3p^{-2}ns$ states in the Cl atom. Here an ns electron features zero SO interaction and, if $n \gg 3$, the spatial overlap of the ns orbital with the $3p$ orbital becomes vanishingly small. This is mimicking the role of the σ^* electron in the $\text{Cl}^+ + \text{H}(1s)$ dissociation limit, where the electron settles in the $1s$ orbital of the receding H atom and becomes completely separated from the $v^{-1}v'^{-1}$ vacancy pair on the Cl^+ fragment. We may therefore expect the same SO splitting in both situations: the atomic case at large n and the molecular case at large R .

A. The atomic analogy

In Cl^+ , the energy splitting of the $3p^{-2}(^1S, ^1D, ^3P)$ states due to the Coulomb interaction is much larger than SO splitting of the $3p^{-2}(^3P)$ multiplet. While the former is of the order of eV, the energy shifts of $^{2S+1}L_J$ states with respect to the ^{2S+1}L are at least an order of magnitude smaller. The shifts are estimated from the matrix elements of the SO interaction, $\hat{H}_{so} = -\sum_i \xi_i \mathbf{l}_i \cdot \mathbf{s}_i$ where the sum runs over the open subshells and ξ_i denotes the corresponding SO parameter. For the $3p^{-2}3P_{0,1,2}$ multiplets, the SO energy shifts are simply given by the diagonal matrix elements of the $\hat{H}_{so}$ operator; they are equal to ξ , $\xi/2$, $-\xi/2$ for the total angular momentum $J = 0, 1, 2$, respectively. This agrees very well with the measured splittings of the lowest three ionization thresholds of the Cl atom for the SO parameter of the $3p$ electron set to $\xi = 84$ meV [34]. The SO splitting of the Cl^+ ground state was also calculated by the multiconfiguration Dirac-Fock code *grasp2K* [35]. The $^3P_2$ state energy was found 89 meV and 128 meV below the $^3P_1$ and $^3P_0$ state energies, respectively, resulting in a similar ξ value (87 meV).

Adding an ns electron to the $\text{Cl}^+3p^{-2}(^3P)$ state generates an LS -splitting of the $3p^{-2}(^3P)ns$ configuration in the Cl atom into doublet (^2P) and quartet (^4P) states. For $n = 4$, the $^2P - ^4P$ energy splitting ΔE due to the Coulomb interaction is the largest, and the J -dependent atomic levels are expected to form two groups corresponding to the $^2P_{1/2,3/2}$ and $^4P_{1/2,3/2,5/2}$ multiplets. To obtain the splitting for higher n , where ΔE becomes comparable to ξ , $\hat{H}_{so}$ was represented in the basis of 18 atomic states $|LSM_L M_S\rangle$ where $L = 1$ and $S = 1/2$ or $3/2$. The basis states are constructed by coupling orbital angular momenta and spins of the three $|lsm_l m_s\rangle$ single-electron atomic orbitals entering the $|3p^{-2}(^3P)ns LSM_L M_S\rangle$ configuration states (see Appendix A). Since $\hat{H}_{so}$ is written as a sum of one-electron operators and the electron orbitals are orthogonal, its matrix representation ($\mathbf{H}_{so}$) is expressed by matrix elements of $\hat{H}_{so}$ in the $\{p_1 \bar{p}_1, p_{-1}, \bar{p}_{-1}, p_0, \bar{p}_0\}$ single-electron basis:

$$\mathbf{H}_{so}^{(1)} = -\frac{\xi}{2} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & -1 & 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{2} & 0 & 0 & 0 \end{bmatrix}. \quad (22)$$

Above, p_{m_l} and $\bar{p}_{m_l}$ denote spin projection $m_s = 1/2$ and $-1/2$ of an electron in the $3p_{m_l}$ orbital, respectively. For zero $^2P - ^4P$ energy splitting, the diagonalization results in three distinct energy levels featuring 2, 6, and 10 degenerate eigenstates shifted by ξ , $\xi/2$ and $-\xi/2$, respectively, from the nonrelativistic limit. This corresponds exactly to the splitting of the $3p^{-2}(^3P_{0,1,2})$ multiplet in Cl^+ with doubled degeneracies because at high n , the Coulomb interaction of a pair of $3p$ holes with an electron in the ns or $n\bar{s}$ orbital becomes negligible.

The calculated splittings are compared with the experimental energy splitting of the Cl $3p^{-2}(^3P)ns$ atomic states [36]. For the ^2P basis states, the diagonal matrix elements of $\mathbf{H}_{so}$ were shifted for ΔE to account for the effect of the $^2P - ^4P$ Coulomb splitting. The resulting $\mathbf{H}_{so}(\Delta E)$ matrix

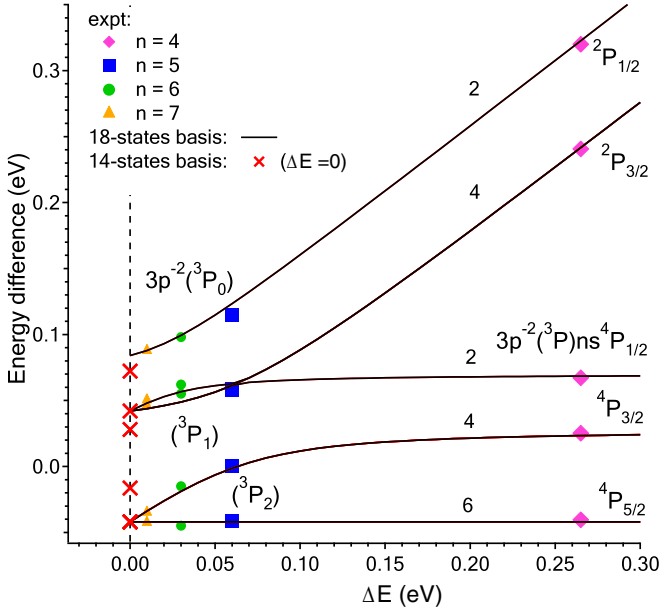


FIG. 3. Calculated SO splittings of the $3p^{-2}(^3P)ns$ configuration in Cl^+ as a function of ΔE , a difference in the Coulomb interaction energy of the ^2P and ^4P multiplets. The SO parameter is fixed to $\xi = 84$ meV. The data points represent measured energy splittings of $n = 4, \dots, 7$ multiplets [34]. They are shifted horizontally to obtain the best match to the calculated splitting. At $\Delta E > \xi$, the 18 $LSM_L M_S$ states of a given n manifold split to five different energies, reducing to three when $\Delta E = 0$. Crosses indicate the splitting at $\Delta E = 0$ when four states are removed from the basis (see the text).

[explicitly given as $\mathbf{H}_{\text{so}}^{18m}(\Delta E)$ by Eq. (A2) in Appendix A] was diagonalized for $0 \leq \Delta E \leq 0.3$ eV. Figure 3 shows good agreement of our model result with the experimental splittings for $n = 4, \dots, 7$ after independently adjusting ΔE for each experimental n manifold of states. Note that at higher n , the atomic manifolds start to overlap and our single-manifold basis becomes too small to properly describe the SO mixing.

B. The asymptotic HCl^+ case

In a molecule, the situation with a negligible Coulomb interaction may be approached not only by promoting an electron to a higher Rydberg state, but also by molecular dissociation. When the distance between molecular fragments increases, the occupied molecular orbitals undergo significant modifications and the electronic state experiences an energy shift, which is described by the potential energy curve. A HCl^+ equivalent of the above Cl^+ manifold of states are the molecular states that converge to the same $\text{Cl}^+ 3p^{-2}(^3P) + \text{H}(1s)$ dissociation limit, i.e., the three quartet states $5\sigma^{-1}2\pi_x^{-1}(^3\Pi)\sigma^* ^4\Pi$, $5\sigma^{-1}2\pi_y^{-1}(^3\Pi)\sigma^* ^4\Pi$, and $2\pi^{-2}(^3\Sigma^-)\sigma^* ^4\Sigma^-$, and a doublet state $2\pi^{-2}(^4\Sigma^-)\sigma^* ^2\Sigma^-$ (see Table I). At large internuclear distances, where the $v^{-1}v'^{-1}\sigma^*$ states attain stable energies, it is therefore sufficient to consider the mixing of these 14 molecular states to calculate the actual SO splitting (see Appendix A for the list of states). However, the splitting in the molecular case now differs from the atomic case because there are four states fewer in the asymptotic molecular manifold. Although the remaining

$5\sigma^{-1}2\pi_x^{-1}(^3\Pi)\sigma^* ^2\Pi$ and $5\sigma^{-1}2\pi_y^{-1}(^3\Pi)\sigma^* ^2\Pi$ states are also built on the triplet $v^{-1}v'^{-1}(^3\Lambda)$ state, they propagate to a 0.6 eV higher $\text{Cl} 3p^{-1}(^2P) + \text{H}^+$ dissociation limit (see Fig. 1) and therefore do not mix significantly with the other 14 states at large internuclear distances. The difference becomes evident as soon as the $\mathbf{H}_{\text{so}}$ matrix is diagonalized in the 14-state Cl^+ atomic basis obtained from the old basis by removing the four $3p^{-2}(^3P)ns^2P M_L = \pm 1, M_S = \pm 1/2$ states. Indeed, instead of three one obtains five distinct eigenvalues in the truncated basis: $-\xi/2$, $-\xi(\sqrt{10}-2)/6$, $\xi/3$, $\xi/2$ and $\xi(\sqrt{10}+2)/6$ with respective six-, two-, two-, two-, and two-fold degeneracies (Fig. 2).

By using a molecular basis which asymptotically corresponds to the atomic basis, the same result is obtained since the two bases are connected by a unitary transform. Note that at large R , $\sigma^* \rightarrow 1s(\text{H})$, and at the same time $5\sigma \rightarrow 3p_z(\text{Cl})$ and $2\pi_{x,y} = 3p_{x,y}(\text{Cl})$ (see Appendix B).

C. The HCl^+ case

The $\text{Cl}^+ 3p^{-2}(^3P) + \text{H}(1s)$ dissociation channel of HCl^+ splits into five instead of the three dissociation limits. Below we investigate how the 14 nonrelativistic states which propagate on three PECs ($U_{5,6,7}$ in Table I) towards a single dissociation limit couple to form seven different PECs that converge to the five SO-split limits. Note that the number of different PECs equals one-half of the number of basis states because of the $\pm M_S$ state degeneracy in diatomic molecules. However, to construct the SO-resolved RA spectrum over the whole electron energy range (173–181 eV), the 14-state basis must be expanded to include all 32 states from Table I (see Appendix C). This is required also to capture the effects of anticrossings these states may have at finite R with PECs converging to other, energetically distant, dissociation limits. For example, the U_3 and U_4 final state potentials, both converging to the $\text{Cl}^+ 3p^{-2}(^1D) + \text{H}(1s)$ dissociation limit, are calculated to cross the U_5 potential at $R = 2.4$ and 2.7 a.u., respectively (see Fig. 1). At $R \approx 4.6$ a.u., the $U_{5,6,7}$ dissociative PECs are crossed by the U_A binding potential of the first excited HCl^+ electronic state $\text{A}^2\Sigma^-$: the absence of spectral features corresponding to $n > 7$ vibrational modes in U_A points to a predissociation mostly driven by the SO interaction with the $5\sigma^{-1}2\pi^{-1}\sigma^* ^4\Pi$ dissociative state in the vicinity of the crossing point [37]. On the other hand, the electronic states on the U_1 dissociative potential exhibit nonzero SO coupling with states on the $U_{5,6,7}$ potential too [see (C8) in Appendix C], but since the energy difference between the two groups of PECs remains large at all R , the U_1 potential is primarily modulated by the Coulomb mixing with states on the U_3 potential. This effect is already included in the nonrelativistic model [28]. The SO mixing of electronic states therefore varies during the dissociation, and leads to an R -dependent redistribution of the RA decay rates and potential slope modulations which both affect the formation of RA spectral lines.

The complete set of basis states $\mathcal{B}_{\text{mol}}^{32}(R)$ thus consists of 32 HCl^+ states from Table I, which are the eigenstates of the nonrelativistic Hamiltonian $\hat{H}_0(R)$ with $U_f(R)$ eigenvalues. The SO matrix elements are calculated using a single-configuration representation of the basis states, as listed explicitly in Appendixes B and C. To describe the SO mixing and determine the new final state potentials $\bar{U}_f(R)$, the

Hamiltonian operator $\hat{H}(R) = \hat{H}_0(R) + \hat{H}_{\text{so}}(R)$ was diagonalized in the $\mathcal{B}_{\text{mol}}^{32}(R)$ basis for a number of internuclear distances covering the $1.5 \leq R \leq 28$ a.u. range. Since all the diagonal matrix elements of the $\mathbf{H}_{\text{so}}(R)$ matrix are zero, the $\mathbf{H}(R)$ matrix is obtained from $\mathbf{H}_{\text{so}}(R)$ simply by setting its diagonal matrix elements to $U_f(R)$. To improve the accuracy of the calculation, the multiconfiguration (but still nonrelativistic) PECs of Pradhan *et al.* [28] were used for $U_f(R)$. Some of the matrix elements of $\mathbf{H}_{\text{so}}(R)$ scale with $a(R)$, the R -dependent weight of the $p_z(\text{Cl})$ atomic orbital in the expansion of the 5σ molecular orbital, which converges to unity in the dissociation limit [15]. The SO interaction of the $A^2\Sigma^+$ bound electronic state at the intersection of U_A with $U_{5,6,7}$ is fixed to the previously published value of 32 meV [37], while the SO coupling of U_A with U_6 and U_7 was neglected because it is equal to zero in the single-configuration representation. Prior to diagonalization, the diagonal of $\mathbf{H}(R)$ was offset by $-U_5(R)$ so that all the potentials, including the newly calculated eigenvalues $\bar{U}_f(R)$, referred to the $U_5(R)$ nonrelativistic potential of Pradhan *et al.* [28]. The diagonalization of $\mathbf{H}(R)$ results in 16 different pairs of degenerate eigenvalues at each R , which define 16 different new final state potentials $\bar{U}_f(R)$ and 32 new final electronic eigenstates $\bar{\mathcal{B}}_{\text{mol}}^{32}(R) = \mathbf{C}(R)\mathcal{B}_{\text{mol}}^{32}(R)$, where $\mathbf{C}(R)$ is the 32×32 unitary transformation matrix. Auger transitions from the upper state potential U_i to 16 different final state potentials generate 16 different spectral lines. As before, to calculate the contribution of a given new final state to an angle-integrated Auger spectrum, the Coulomb transition integral in (13) is replaced by $+\sqrt{\Gamma_{fi}(R)}/(2\pi)$, where $\Gamma_{fi}(R)$ denotes the partial Auger decay rate to the new electronic state on the $\bar{U}_f$ potential. In principle, both the transformation matrix $\mathbf{C}$ and the Auger transition amplitudes to all nonrelativistic basis states are now required to construct the partial rate to any of the SO-coupled states because, at each R , the new state is a different superposition of nonrelativistic states. However, as argued below, the neglect of the cross-term contributions results in less than 1% error in $\Gamma_{fi}(R)$. The partial Auger decay rates to SO-mixed states are thus well approximated already by a linear combination of the nonrelativistic rates $\Gamma_{ji}(R)$ weighted by $|C_{fj}|^2$, where C_{fj} is matrix element of the transformation matrix $\mathbf{C}$, i.e., equal to the expansion coefficient of the j th nonrelativistic state in the f th SO-coupled eigenstate.

D. Auger decay rates to SO-coupled states

To obtain partial Auger transition rates $\bar{\Gamma}_{fi}$ to the SO-coupled states, we start by expressing partial Auger decay rates Γ_{fi} to the nonrelativistic basis states $\mathcal{B}_{\text{mol}}^{32}(R)$ by averaging the incoherent sum of amplitudes to unresolved final degrees of freedom over the unresolved intermediate states. Approximating the states by a single set of orthogonal molecular orbitals at each R , Γ_{fi} factorizes to a product of two sums [31],

$$\Gamma_{fi}(R) = \frac{\pi}{2l_c + 1} \left(\sum_{l_\epsilon, m_\epsilon, m_c} |A_{vv'}(S_{vv'}, \Lambda, l_\epsilon, m_\epsilon, m_c; R)|^2 \right) \times \frac{1}{2} \sum_{S'} \sum_{M_S, M_S'} S^2(S', M_S', m_{S\epsilon}, S_{vv'}, S, M_S). \quad (23)$$

The former is the sum over the spectator-less partial rates describing Auger decay without any coupling with the spectator electron,

$$\text{HCl}^+ 2p^{-1}(l_c, m_c) \rightarrow \text{HCl}^{2+} v^{-1}v'^{-1}(\Lambda, S_{vv'}, M_{S_{vv'}}) + e^-(l_\epsilon, m_\epsilon, m_{S\epsilon}), \quad (24)$$

and the latter the sum over the spin factors that accounts for the coupling of the spectator electron in the σ^* orbital with the $2p$ and vv' holes [15]. The spin factors are calculated by summing the products of Clebsch-Gordan coefficients,

$$S = \sum_{m_S, m_{S'}, M_{S_{vv'}}} \left\langle S_{vv'} M_{S_{vv'}} \frac{1}{2} m_\sigma \middle| S M_S \right\rangle \times \left\langle \frac{1}{2} m_S \frac{1}{2} m_\sigma \middle| S' M_{S'} \right\rangle \left\langle \frac{1}{2} m_S, \frac{1}{2} m_{S\epsilon} \middle| S_{vv'} M_{S_{vv'}} \right\rangle. \quad (25)$$

For a given final state, the sum of spin factors reduces to $\bar{S}(S_{vv'}, S)$ from Ref. [31] (see also Table I). Previous calculations have shown that only the p wave of the continuum wave function of the Auger electron ($l_\epsilon = 1$) significantly contributes to the Auger decay rate. This limits the corresponding projection to $m_\epsilon = \pm 1, 0$ and the same range applies for m_c , the projection of the orbital angular momentum $l_c = 1$ of the initial $2p$ -hole Cl atom. Since in our framework, there are eight different sets of final state quantum numbers ($S_{vv'} = 0, 1; S = 1/2, 3/2; M_S$), and for each of them there are eight possible spin functions differing by ($S' = 0, 1; M_{S'}; m_{S\epsilon} = \pm 1/2$) quantum numbers, the spin functions are packed into an 8×8 spin matrix $\mathbf{S}$ [see (D3) in Appendix D].

For the spectator-less decay (24), each partial Auger amplitude is expressed by a linear combination of a direct and exchange two-electron integral

$$A_{vv'} = J_{vv'}(S_{vv'}, \Lambda, l_\epsilon, m_\epsilon, m_c; R) + (-1)^{S_{vv'}} K_{vv'}(S_{vv'}, \Lambda, l_\epsilon, m_\epsilon, m_c; R), \quad (26)$$

where

$$J_{vv'} = \langle \phi_v(1) \phi_{v'}(2) | r_{12}^{-1} | \phi_c(1) \phi_\epsilon(2) \rangle, \quad (27)$$

$$K_{vv'} = \langle \phi_{v'}(1) \phi_v(2) | r_{12}^{-1} | \phi_c(1) \phi_\epsilon(2) \rangle, \quad (28)$$

and ϕ denotes either a bound or a continuum electronic orbital. Applying the one-center approximation, Auger amplitudes (D1) are constructed for each final state using the tables from Ref. [29] and the calculated weights of Cl-centered orbitals in the expansion of v and v^{-1} molecular orbitals [15]. In our case each of the nine $A(m_\epsilon, m_c)$ partial amplitudes for a given final state $|vv^{-1} 2S_{vv'} + 1 \Lambda\rangle$ is expressed by a specific linear combination of $R_0(2p, \epsilon; 3p, 3p)$ and $R_2(2p, \epsilon; 3p, 3p)$ Slater integrals (see Table VIII in Appendix D). Note that for $5\sigma 2\pi$ combination of holes, the partial amplitudes depend on R via the $a(R)$ weight of the $\text{Cl} 3p_z$ orbital in the molecular 5σ orbital. The spectator-less partial Auger amplitudes are evaluated using the tabulated values of Slater integrals from Ref. [29]: the $2p$ and $3p$ atomic orbitals alongside the continuum ϵp wave were calculated in the $\text{Cl}^+ 2p^{-1}$ potential. The nine partial spectator-less amplitudes $A(m_\epsilon, m_c; R)$ for each of the 32 nonrelativistic final states $\mathcal{B}_{\text{mol}}^{32}$ are stacked in the 9×32 $\mathbf{A}(R)$ matrix (see Appendix D).

At each R , the 32 partial Auger rates $\bar{\Gamma}_{fi}$ to SO-coupled states $\bar{B}_{\text{mol}}^{32}(R)$ are calculated by combining the $\mathbf{A}(R)$, $\mathbf{S}$ and $\mathbf{C}(R)$ matrices as follows:

$$\bar{\Gamma}_{fi}(R) = \frac{\pi}{6} \sum_{m=1}^9 \sum_{p=1}^8 \left| \sum_{j=1}^{32} C_{fj}(R) (A_{mj}(R) S_{j \rightarrow q})_{jp} \right|^2. \quad (29)$$

The $S_{j \rightarrow q}$ notation means that the eight-component vector of the S_{qp} spin matrix (the q th row of the matrix) is selected in such a way that its $(S_{vv'}, S, M_S)$ quantum numbers match quantum numbers of the j th nonrelativistic basis state (see Appendix D for the $q = T_j$ correspondence vector). Note that the nonrelativistic partial Auger rates Γ_{fi} are recovered if a diagonal unit matrix $\mathbf{I}$ is inserted instead of the transformation matrix $\mathbf{C}$ in Eq. (29).

It is interesting to see the difference in the calculated rates if in Eq. (29) the cross-terms containing the $C_{fj}^* C_{fj'}$ products with $j \neq j'$ are set to zero. In such a case, the partial Auger rates to the SO-coupled states simplify to become equal to the weighted sum of the nonrelativistic rates Γ_{fi} ,

$$\tilde{\Gamma}_{fi}(R) = \sum_{j=1}^{32} |C_{fj}(R)|^2 \Gamma_{ji}(R). \quad (30)$$

It turns out that the calculated relative difference $\Delta_{fi} = (\tilde{\Gamma}_{fi} - \bar{\Gamma}_{fi})/\bar{\Gamma}_{fi}$ is not larger than 1% for any studied final state at any internuclear distance R (see Appendix D), so that Eq. (30) already gives an excellent approximation to $\bar{\Gamma}_{fi}$. Note that Auger amplitudes to different single-configuration states in the mixture must contribute to the same (m_c, m_e) channel for cross-terms to have any effect on the angle-integrated spectrum. This is possible only for configurations with the same Λ value (Table VII) and was already accounted for partially by replacing the nonrelativistic single-configuration potentials U_f by the multiconfiguration PECs of Pradhan *et al.* [28] on the diagonal of the $\mathbf{H}_0$ matrix.

By inspecting the $\mathbf{H}_{\text{so}}$ matrix before the diagonalization (see Appendix C), one notices the nonzero matrix elements between the nonrelativistic $vv'(^3\Sigma, ^3\Pi)\sigma^*$ “triplet” states. The corresponding potentials merge only at large R where the diagonalization leads to seven different final state potentials $\bar{U}_f$ and splitting of the $\text{Cl}^+(^3P) + \text{H}$ channel into five different dissociation limits. However, since at large R the Auger decay rates Γ_{fi} to all 14 nonrelativistic “triplet” states are equal and the cross-terms contributions are negligible, the Auger decay rate $\bar{\Gamma}_{fi}$ to any of the 14 SO-coupled states acquires the same asymptotic value [Fig. 4(b)]. The SO coupling between the nonrelativistic $vv'(^1\Sigma^+, ^1\Pi, ^1\Delta)\sigma^*$ “singlet” states is zero in our model, but there is nonzero coupling between the blocks: the effect of SO interaction is evident in the vicinity of the crossing points of “singlet” and “triplet” U_f potentials, where a significant redistribution of $\bar{\Gamma}_{fi}$ occurs [Fig. 4(b)]. Note that the sum of the Auger rates populating the SO-mixed states remains equal to the sum of the nonrelativistic decay rates at every R . Except for the splitting of the $\text{Cl}^+(^3P)$ dissociation limit at large R , the spectral changes thus originate only from localized anticrossing regions. However, the Auger emissions happening in the vicinity of the anticrossing are contributing a relatively small part to the total number of decays to the same final state, which is receiving contributions

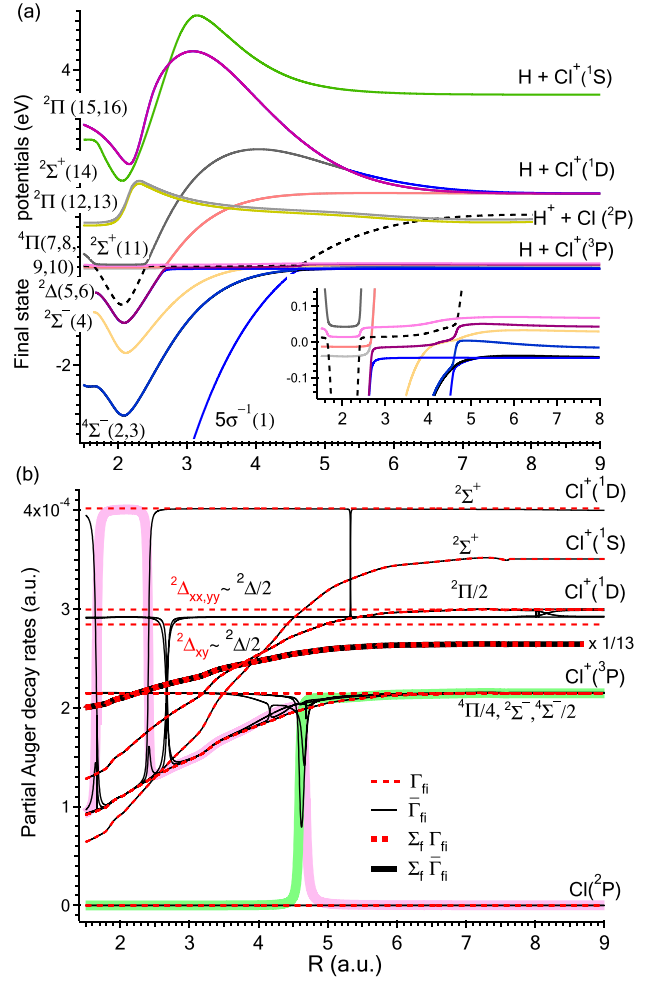


FIG. 4. (a) Sixteen $\bar{U}_f$ potentials relative to the U_5 nonrelativistic potential of Pradhan *et al.* [28], each plotted by a different color. The nine nonrelativistic U_f potentials from Fig. 1 can be traced out by neglecting the anticrossings of $\bar{U}_f$ potentials. The groups of new potentials are marked by their $^{2S+1}\Lambda$ character at $R = 1.5$ a.u. and a (number), starting from the lowest value of the potential. The inset magnifies energy region around zero where several anticrossings are located. (b) 16 Auger decay rates $\bar{\Gamma}_{fi}$ to the SO-coupled states (black curves) are compared to Γ_{fi} , the rates to the nonrelativistic final states (red dashed curves). Each $\bar{\Gamma}_{fi}$ rate is the sum of two equal rates populating two degenerate final states. The sum of the nonrelativistic partial Auger decay rates (thick red dashed curve) equals the sum of partial rates to SO-coupled states (thick black curve) at every R . The rates are associated with the corresponding nonrelativistic dissociation limits, and their asymptotic values are marked by $\Gamma_{fi}(\infty)$ of the nonrelativistic $^{2S+1}\Lambda$ states in Table I. As an example, the propagation of $\bar{\Gamma}_{fi}$ with R is shown for the SO-coupled final states (9) (pink trace) and (1) (green trace).

at the same kinetic energy ϵ from an extended interval of internuclear distances. Finally, a negligible contribution of the cross-terms terms that leads to $\bar{\Gamma}_{fi} \approx \tilde{\Gamma}_{fi}$ is explained by the fact that PECs of the “triplet” and “singlet” states that have the same Λ value never cross, for example, the potentials of $5\sigma^{-1}2\pi^{-1}\sigma^*^4\Pi$ and $5\sigma^{-1}2\pi^{-1}\sigma^*^2\Pi$ states and the potentials of $2\pi^{-2}\sigma^*^2\Sigma^{-,4}\Sigma^{-}$ and $2\pi^{-2}\sigma^*^2\Sigma^{+}$ states (Fig. 1).

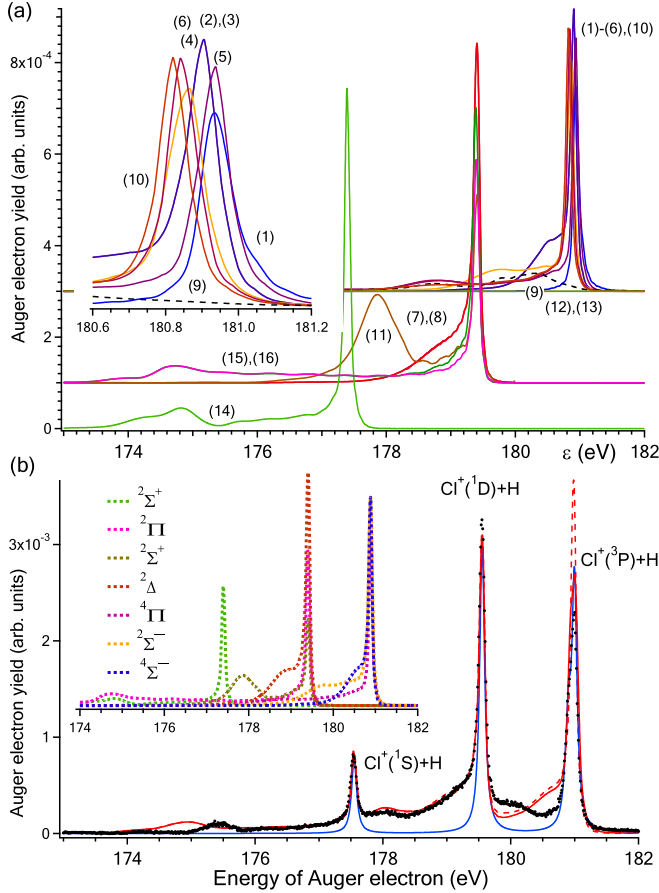


FIG. 5. (a) Sixteen components of the SO-resolved $2p^{-1}\sigma^* \rightarrow v^{-1}v'^{-1}\sigma^*$ RA spectrum of HCl. Each spectral profile is denoted by a number, in correspondence to the numbering of $\bar{U}_f$ potentials in Fig. 4(a). The inset magnifies the spectrum in the vicinity of the $\text{Cl}^+(^3P)$ “atomic” peak where the seven SO-coupled spectral components converge to five different dissociation limits. (b) Comparison of the SO-coupled molecular RA spectrum (red curve), the nonrelativistic molecular RA spectrum (red dashed curve), and the atomic RA spectrum (blue curve) with an angle-integrated experimental spectrum (black points). The inset shows seven line profiles of the nonrelativistic model.

IV. RESULTS

The 16 calculated $2p^{-1}\sigma^* \rightarrow v^{-1}v'^{-1}\sigma^* + e^-(\epsilon_f)$ components of the RA spectrum given by $|F_f|^2$ (13) are presented in Fig. 5(a). Each of them exhibits a tail on the low-energy side centered at the asymptotic Auger electron energy $U_i(\infty) - \bar{U}_f(\infty)$. The modulations reflect the slope changes of the corresponding final state potential with respect to the intermediate state potential U_i . For comparison, the spectral profiles of seven nonrelativistic final states are plotted in the inset of Fig. 5(b). One sees that no significantly different line shape is produced by the SO coupling except for the profile (9) that has the asymptotic peak missing (black dashed curve). This is a consequence of the anticrossing of the $5\sigma^{-1}2\Sigma^+$ bound state with the manifold of the $5\sigma^{-1}2\pi^{-1}\sigma^*4\Pi$ dissociative states at $R \approx 4.7$ a.u.: there is a significant probability of populating the profile (9) by the Auger decay at small R , but after the anticrossing, the final state acquires a bound

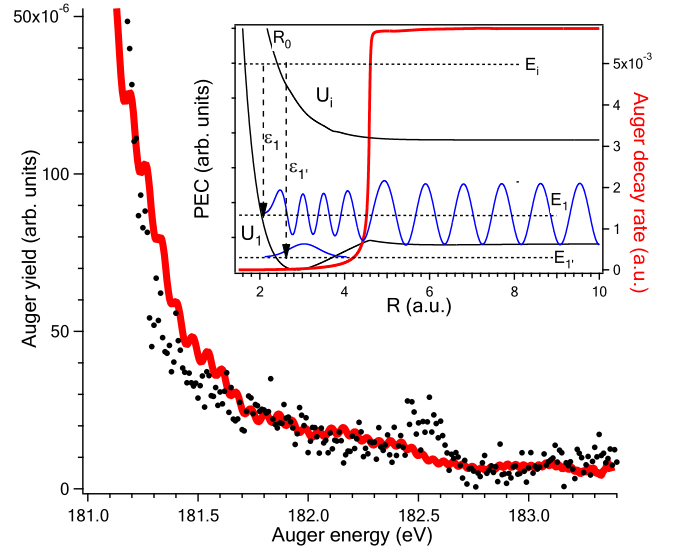


FIG. 6. A high-energy tail of the Auger line (1) signals the population of final state corresponding to the nonrelativistic $5\sigma^{-1}2\Sigma^+$ bound state at small R (red curve). The step in the Auger yield at 182.5 eV electron energy, in both the calculated and the experimental spectrum (points), is linked to the avoided crossing of $\bar{U}_1$ potential with the manifold of $5\sigma^{-1}2\pi^{-1}\sigma^*4\Pi$ potentials at $R \approx 4.7$ a.u. (see Fig. 4). As shown in the inset, the yield drops when the Auger electron energy ϵ_1 increases to ϵ_1' because the dissociation channel closes down and the molecule cannot reach large internuclear distances anymore to emit an Auger electron with a significant probability.

state character that prevents its further population by emission of more energetic Auger electrons. Instead, the Auger decay probability is switched to the final state with the profile (1) that has a bound state character at small R but turns to one of the $5\sigma^{-1}2\pi^{-1}\sigma^*4\Pi$ dissociative states after the anticrossing. In Fig. 6 the effect of same anticrossing is seen from a different angle: the calculated high-energy tail of the Auger line (1) indicates a drop of the electron yield for kinetic energies larger than 182.5 eV, which is clearly observable in the experimental data. This subtle feature can be explained by looking at the difference between the intermediate state potential U_i and final state potential $\bar{U}_1$. It is clear that the emission of the Auger electrons with lower energies populates a dissociative state with a substantial probability (blue oscillatory curve in Fig. 6), while the emission at higher energies would necessarily lead to a localized electronic state in the potential U_A , to which the Auger decay rate is zero.

In Fig. 5(b) the sum of the calculated line profiles is compared to the experimental $2p_{3/2}^{-1}\sigma^*$ RA spectrum of HCl in the 173–182 eV energy range. The experimental data were acquired on resonance at electron emission angles $\theta = 0^\circ$ and 90° with respect to the linear polarization of the incident light and also at 3 eV lower photon energy, so as to be able to subtract the nonresonant contributions to the $v^{-1}v'^{-1}\sigma^*$ population coming directly from photoionization of HCl in the ground state [13]. The angle-integrated spectrum in Fig. 5(b) is generated by adding the 0° spectrum to twice the 90° spectrum, as dictated by the general $1 + \beta P_2(\cos\theta)$ form of the RA angular distribution.

The agreement of the model spectrum with the experimental one is good, provided Γ_i is set to the measured value of 96 ± 5 meV [13]. This value was extracted from the fit of the “atomic” peak and therefore refers to the large R situation. Our calculation estimates $\Gamma_i(\infty)$ to 125 meV by comparing the $\Gamma_{fi}(\infty)$ entries in Table I with systematically larger asymptotic partial Auger rates in Ref. [15], resulting in $\Gamma_i(\infty) = 155$ meV. In the same way, the total decay rate of the Cl^+2p^{-1} atomic state is estimated to $\Gamma_i = 133$ meV from our GRASP calculation [35]. By using a single scaling factor, the calculated spectrum captures correctly the $\text{Cl}^+(^1S)$ and $\text{Cl}^+(^1D)$ relative intensity, but to obtain an overall agreement, the calculated $\text{Cl}^+(^3P)$ components must be additionally multiplied by 0.85. This is attributed to the deficiency of atomic description, because our GRASP calculation overestimates the relative intensity of the $\text{Cl}^+(^3P)$ peak with respect to the singlet peaks by the same factor [see Fig. 5(b)]. However, as mentioned before, not all spectral components converging to the ^3P atomic peak are activated at all possible emission energies in the molecular case, so there is no precise analogy between the two cases.

A significant improvement of the SO modeling over the nonrelativistic calculation is evident in the region of the $\text{Cl}^+(^3P)$ peak, which is now split to five peaks with both of the highest energy peaks holding contributions of two instead of one final state [see the inset of Fig. 5(a)]. In Fig. 7(a), the experimental peak is compared to the peak from the atomic calculation and to the result of the molecular modeling with the SO coupling included. At first glance it may be surprising that at large internuclear distances the molecular calculation with five peaks describes the RA decay more precisely than the three-peak relativistic atomic model that is more accurate in the atomic limit by design. This result confirms a substantial difference that exists between the Auger decay of the $\text{HCl}^+2p^{-1}\sigma^*$ molecular system at large internuclear distances and Auger decay of the $2p$ hole in the Cl^+ . Although most of the $v^{-1}v'^{-1}(^3\Lambda)\sigma^*$ final states with triplet coupling of the valence holes converge to the same $\text{Cl}^+(^3P) + \text{H}$ nonrelativistic dissociation limit, one of these states, the $5\sigma^{-1}2\pi^{-1}(^3\Pi)\sigma^* {}^2\Pi$ state, converges to the energetically distant $\text{Cl}(^2P) + \text{H}^+$ limit. Due to the 0.6-eV difference in energy at large R [28], this state effectively does not mix with the other final states despite the nonzero $\mathbf{H}_{\text{so}}$ coupling matrix elements. As this state is resonantly populated by the participator RA decay only and the participator electron is quickly taken away from Cl nucleus by dissociation, it cannot contribute to the Auger yield at the asymptotic electron energy $\epsilon \approx 180.4$ eV [28] simply because the Coulomb interaction of the participator with any other electron, all centered on Cl nucleus, becomes vanishingly small as soon as the internuclear distance is increased. As indicated by the slope of the corresponding potential, the signal of the participator RA decay should appear at lower emission energies, but the yield is expected to be negligibly small because, due to the UFD, the excited molecule spends most of the time at large internuclear distances (see Fig. 2).

The remaining discrepancies with the experimental data are mostly attributed to inaccuracies of the final state PECs. The first indicative example is a mismatch of the secondary peak appearing at 175.3 eV in the experimental spectrum in

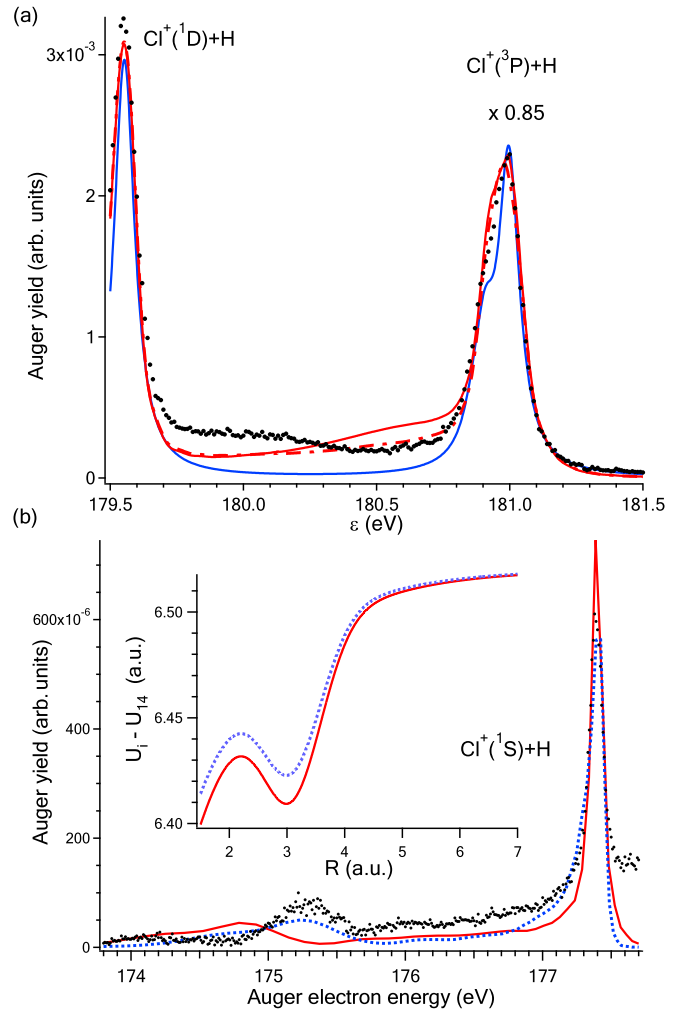


FIG. 7. (a) Zoom-in the region of the spectral lines contributing to the $\text{Cl}^+(^3P)$ asymptotic peak. The experimental data points are compared to the result of the molecular model with SO coupling (red curve) and the atomic calculation (blue curve). Also given is the result of the molecular model with secondary peak removed from the Auger lines (2) and (3) (dashed red line). (b) Auger line (14) calculated from $\bar{U}_{14}$ (red curve) and from the scaled version of $\bar{U}_{14}$ potential (blue dotted curve). The $\bar{U}_{14}$ potential practically equals the nonrelativistic potential of $5\sigma^{-2}\sigma^* {}^2\Sigma^+$ final state of Pradhan *et al.* [28], but its scaled version agrees better with the experimental Auger spectrum (points). The inset shows the difference of U_i with each of the two final state potentials. If this difference is zero at every R , the potentials are parallel and the corresponding spectral line is Lorentzian.

Fig. 5(b). While the corresponding main peak (the asymptotic $\text{Cl}^+(^1S)$ peak) is well reproduced, the model places secondary peak too low, at 174.8 eV [Fig. 7(b)]. This error, and also several deviations, are already present in the nonrelativistic model based on Ref. [28] and cannot be amended by consideration of the SO coupling. Although the more accurate calculation of the nonrelativistic final state potentials is out of the scope of this work, it is easy to demonstrate the sensitivity of the above mentioned secondary peak position with respect to the main peak on shape of $\bar{U}_{14}$ [Fig. 7(b)]. In this case, a simple scaling of the potential is sufficient to place

the secondary peak to the right position and no R shifting is needed [see the inset of Fig. 7(b)]. However, to properly capture the amplitude of this secondary peak, also $\bar{U}_{15}$ and $\bar{U}_{16}$ potentials [or rather the nonrelativistic $^2\Pi$ potential; see the inset of Fig. 5(b)] should be amended in a similar way. On the other hand, the secondary peak at 178.0 eV, attached to the $\text{Cl}^+(^1D)$ main peak, is already well reproduced by the line profile originating in the $\bar{U}_{11}$ potential (the nonrelativistic $^2\Sigma^+$ potential). A large discrepancy is remaining in the secondary peak, attached to the $\text{Cl}^+(^3P)$ main peak. This is attributed to the incorrect shapes of $\bar{U}_2$ and $\bar{U}_3$ potentials (the nonrelativistic $^4\Sigma^-$ potential), which results in the secondary peak placed too close to the main peak. The comparison with the experimental spectrum shows that the excess of the model yield at 180.5 eV could just compensate the missing yield at around 180.0 eV, and this change can be achieved by a suitable change of the corresponding PEC.

We have identified a few weak points of the nonrelativistic model above. In the future, one could imagine to use the power of Auger spectroscopy to look for a complete solution of the corresponding variational problem, i.e., to try to identify small adjustments of the final state potentials that result in the best overall agreement of the model spectrum with the experimental data.

V. CONCLUSIONS

The stationary Green's function approach was successfully employed to calculate the $L - vv'$ Auger spectrum of the $2p^{-1}\sigma^*$ resonance in HCl, which dissociates on the timescale of electronic decay. Despite a delocalized electron emission, the angle-integrated RA spectrum remains strongly affected by the potential slope changes induced by the molecular geometry-dependent final state interactions, which makes this case suitable for testing of the model. In this work the SO interaction has been considered in the final states description, which represents an upgrade of the recent nonrelativistic RA study [15]. The improved modeling leads to better description of the experimental spectrum primarily in the region of the “atomic” peaks, where the yield of Auger electrons emitted at the large separation between Cl^+ and H atomic fragments is concentrated. We show that even in this regime, one must be careful when using the atomic modeling: to obtain a reliable result, only those final states on the atom with the initial core

hole can be mixed that are connected with the same state on a distant atomic fragment and therefore converge to the same nonrelativistic dissociation limit. After accounting for SO-mixing effects, we realize that the one-center approximation of RA amplitudes is accurate enough to expose the primary cause of the remaining discrepancies with the experimental data: they are linked to the limited accuracy of the old nonrelativistic PECs calculations of $\text{HCl}^+v^{-1}v'^{-1}\sigma^*$ final states [28].

Finally, we note that the work of Chelkowska and Larkins [29] offers a straightforward path to the construction of partial-wave-dependent Auger amplitudes required to model angle-dependent Auger emission from a dissociating molecule. It has been shown recently that the $L - vv'$ angular emission pattern of Auger electrons in the “molecular” region of HCl differs from the pattern in the $3p^{-1}(^1D_2)$ atomic limit characterized by emission of electrons with the asymptotic kinetic energy [24]. As a complement to these ion-electron spectrally resolved coincidence measurements, where the yield still depends on the sum of angle-dependent resonant Auger amplitudes over a full range of internuclear distances, one could explicitly address the spectrum build up in Fig. 2 by a hypothetical XUV pump-visible light probe experiment. Here a short resonant pump pulse would initiate dissociation to be interrupted after a given time delay by a short VIS pulse. The probe pulse is going to transfer a substantial amount of HCl population, still in the $2p^{-1}\sigma^*$ state, to some higher Rydberg state or to the HCl^+2p^{-1} continuum, both of which decay by emission of Auger electrons at significantly lower kinetic energies.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

There are no publicly available research data or software supporting this paper. Requests for further information or data should be sent to the authors.

APPENDIX A: SO MATRIX IN THE BASIS OF $3p^{-2}(^3P)ns$ STATES

The 18 LSM_LM_S states of the $3p^{-2}(^3P)ns$ atomic configuration are constructed where L and S denote the total orbital angular momentum and spin of the electronic state, respectively, and M_L and M_S are the corresponding projections. The H_{so} matrix is calculated in this basis and reported below. In Table II single-electron orbitals $|nlm_l m_s\rangle$ are abbreviated by

$$\begin{aligned} p_1 &= |3p, 1, 1/2\rangle, & p_0 &= |3p, 0, 1/2\rangle, & p_{-1} &= |3p, -1, 1/2\rangle, & s &= |ns, 0, 1/2\rangle, \\ \bar{p}_1 &= |3p, 1, -1/2\rangle, & \bar{p}_0 &= |3p, 0, -1/2\rangle, & \bar{p}_{-1} &= |3p, -1, -1/2\rangle, & \bar{s} &= |ns, 0, -1/2\rangle, \end{aligned} \quad (\text{A1})$$

where l denotes the electron orbital momentum, $s = 1/2$ is the electron spin and m_l, m_s are the corresponding projections.

TABLE II. Ordered set of all $3p^{-2}ns |LSM_L M_S\rangle$ atomic states coupled to ^2P and ^4P forms the $\mathcal{B}_a^{18}$ basis.

No.	^{2S+1}L	M_L	M_S	State
1	^2P	1	1/2	$\sqrt{2/3}p_1p_0\bar{s} - (p_1\bar{p}_0s + \bar{p}_1p_0s)/\sqrt{6}$
2	^2P	1	-1/2	$(p_1\bar{p}_0\bar{s} + \bar{p}_1p_0\bar{s})/\sqrt{6} - \sqrt{2/3}\bar{p}_1\bar{p}_0s$
3	^2P	-1	1/2	$\sqrt{2/3}p_{-1}p_0\bar{s} - (p_{-1}\bar{p}_0s + \bar{p}_{-1}p_0s)/\sqrt{6}$
4	^2P	-1	-1/2	$(p_{-1}\bar{p}_0\bar{s} + \bar{p}_{-1}p_0\bar{s})/\sqrt{6} - \sqrt{2/3}\bar{p}_{-1}\bar{p}_0s$
5	^4P	1	3/2	p_1p_0s
6	^4P	1	1/2	$(p_1p_0\bar{s} + p_1\bar{p}_0s + \bar{p}_1p_0s)/\sqrt{3}$
7	^4P	1	-1/2	$(p_1\bar{p}_0\bar{s} + \bar{p}_1p_0\bar{s} + \bar{p}_1\bar{p}_0s)/\sqrt{3}$
8	^4P	1	-3/2	$\bar{p}_1\bar{p}_0\bar{s}$
9	^4P	-1	3/2	$p_{-1}p_0s$
10	^4P	-1	1/2	$(p_{-1}p_0\bar{s} + p_{-1}\bar{p}_0s + \bar{p}_{-1}p_0s)/\sqrt{3}$
11	^4P	-1	-1/2	$(p_{-1}\bar{p}_0\bar{s} + \bar{p}_{-1}p_0\bar{s} + \bar{p}_{-1}\bar{p}_0s)/\sqrt{3}$
12	^4P	-1	-3/2	$\bar{p}_{-1}\bar{p}_0\bar{s}$
13	^2P	0	1/2	$\sqrt{2/3}p_1p_{-1}\bar{s} - (p_1\bar{p}_{-1}s + \bar{p}_1p_{-1}s)/\sqrt{6}$
14	^2P	0	-1/2	$(p_1\bar{p}_{-1}\bar{s} + \bar{p}_1p_{-1}\bar{s})/\sqrt{6} - \sqrt{2/3}\bar{p}_1\bar{p}_{-1}s$
15	^4P	0	3/2	$p_1p_{-1}s$
16	^4P	0	1/2	$(p_1p_{-1}\bar{s} + p_1\bar{p}_{-1}s + \bar{p}_1p_{-1}s)/\sqrt{3}$
17	^4P	0	-1/2	$(p_1\bar{p}_{-1}\bar{s} + \bar{p}_1p_{-1}\bar{s} + \bar{p}_1\bar{p}_{-1}s)/\sqrt{3}$
18	^4P	0	-3/2	$\bar{p}_1\bar{p}_{-1}\bar{s}$

Below we give $\mathbf{H}_{so}^{18m}(\Delta E)$, the matrix of spin-orbit operator $\hat{H}_{so} = -\sum_i \xi_i \mathbf{l}_i \cdot \mathbf{s}_i \equiv \hat{h}_{so}^i$ in the $\mathcal{B}_a^{18}$ basis (see Table II). ξ is a shorthand notation for the ξ_{3p} SO parameter and $\xi_{ns} = 0$. The $\mathbf{H}_{so}^{18m}(\Delta E)$ matrix is

$$-\frac{\xi}{2} \begin{bmatrix} \frac{1}{3} + \Delta E & 0 & 0 & 0 & 0 & \frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & 0 \\ 0 & -\frac{1}{3} + \Delta E & 0 & 0 & 0 & 0 & \frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & \frac{a\sqrt{2}}{3} & 0 & 0 & -\frac{a}{6} & 0 & 0 \\ 0 & 0 & -\frac{1}{3} + \Delta E & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3\sqrt{2}} & 0 & 0 & 0 & \frac{a\sqrt{2}}{3} & 0 & 0 & \frac{a}{6} & 0 \\ 0 & 0 & 0 & \frac{1}{3} + \Delta E & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{2\sqrt{3}} \\ 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & 0 & 0 \\ 0 & \frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & \frac{a\sqrt{2}}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & \frac{a}{2\sqrt{3}} & 0 & 0 & \frac{a}{\sqrt{6}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & 0 \\ 0 & 0 & -\frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{6} & 0 & 0 & 0 & -\frac{a}{6} & 0 & 0 & \frac{a\sqrt{2}}{3} & 0 \\ 0 & 0 & 0 & -\frac{1}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{a\sqrt{2}}{3} & 0 & 0 & 0 & 0 & \frac{1}{6} & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & 0 & \Delta E & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{a\sqrt{2}}{3} & 0 & 0 & 0 & 0 & \frac{a}{2\sqrt{3}} & 0 & -\frac{a}{6} & 0 & 0 & 0 & \Delta E & 0 & 0 & 0 & 0 \\ -\frac{a}{2\sqrt{3}} & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{a}{6} & 0 & 0 & 0 & 0 & \frac{a\sqrt{2}}{3} & 0 & \frac{a}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{a}{6} & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & \frac{a\sqrt{2}}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{a}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}. \quad (\text{A2})$$

Note that to ^2P diagonal matrix elements at positions 1–4 and 13–14, an extra term ΔE term was added to mimic the $^2P - ^4P$ Coulomb splitting that can be evaluated by the nonrelativistic model (Hamiltonian $\hat{H}_0$ with Coulomb interaction only). At large n , when an s electron is far from the nucleus, $\Delta E = 0$. The eigenvalues of $\mathbf{H}_{so}^{18m}(0)$ matrix are ξ ($2\times$), $\xi/2$ ($6\times$), and $-\xi/2$ ($10\times$), where the eigenstate degeneracy is quoted in the parentheses. Factor a multiplies the nondiagonal matrix element whenever this

TABLE III. Ordered $\mathcal{B}_{\text{asy}}^{18}$ basis of $3p^{-2}ns |LS, |M_L|, M_S\rangle$ atomic states coupled to ^2P and ^4P , which is composed of oriented atomic p orbitals.

No.	$2S+1L$	$ M_L $	M_S	State
1	$^2P(xz)$	1	1/2	$\sqrt{2/3}p_x p_z \bar{s} - (p_x \bar{p}_z s + \bar{p}_x p_z s)/\sqrt{6}$
2	$^2P(xz)$	1	-1/2	$(p_x \bar{p}_z \bar{s} + \bar{p}_x p_z \bar{s})/\sqrt{6} - \sqrt{2/3} \bar{p}_x \bar{p}_z s$
3	$^2P(yz)$	1	1/2	$\sqrt{2/3}p_y p_z \bar{s} - (p_y \bar{p}_z s + \bar{p}_y p_z s)/\sqrt{6}$
4	$^2P(yz)$	1	-1/2	$(p_y \bar{p}_z \bar{s} + \bar{p}_y p_z \bar{s})/\sqrt{6} - \sqrt{2/3} \bar{p}_y \bar{p}_z s$
5	$^4P(xz)$	1	3/2	$p_x p_z s$
6	$^4P(xz)$	1	1/2	$(p_x p_z \bar{s} + p_x \bar{p}_z s + \bar{p}_x p_z s)/\sqrt{3}$
7	$^4P(xz)$	1	-1/2	$(p_x \bar{p}_z \bar{s} + \bar{p}_x p_z \bar{s} + \bar{p}_x \bar{p}_z s)/\sqrt{3}$
8	$^4P(xz)$	1	-3/2	$\bar{p}_x \bar{p}_z \bar{s}$
9	$^4P(yz)$	1	3/2	$p_y p_z s$
10	$^4P(yz)$	1	1/2	$(p_y p_z \bar{s} + p_y \bar{p}_z s + \bar{p}_y p_z s)/\sqrt{3}$
11	$^4P(yz)$	1	-1/2	$(p_y \bar{p}_z \bar{s} + \bar{p}_y p_z \bar{s} + \bar{p}_y \bar{p}_z s)/\sqrt{3}$
12	$^4P(yz)$	1	-3/2	$\bar{p}_y \bar{p}_z \bar{s}$
13	$^2P(xy)$	0	1/2	$\sqrt{2/3}p_x p_y \bar{s} - (p_x \bar{p}_y s + \bar{p}_x p_y s)/\sqrt{6}$
14	$^2P(xy)$	0	-1/2	$(p_x \bar{p}_y \bar{s} + \bar{p}_x p_y \bar{s})/\sqrt{6} - \sqrt{2/3} \bar{p}_x \bar{p}_y s$
15	$^4P(xy)$	0	3/2	$p_x p_y s$
16	$^4P(xy)$	0	1/2	$(p_x p_y \bar{s} + p_x \bar{p}_y s + \bar{p}_x p_y s)/\sqrt{3}$
17	$^4P(xy)$	0	-1/2	$(p_x \bar{p}_y \bar{s} + \bar{p}_x p_y \bar{s} + \bar{p}_x \bar{p}_y s)/\sqrt{3}$
18	$^4P(xy)$	0	-3/2	$\bar{p}_x \bar{p}_y \bar{s}$

is proportional to the single-electron SO matrix element with the p_0 orbital contribution, i.e. $\langle p_0 | \hat{h}_{\text{so}}^i | \bar{p}_1 \rangle$ and $\langle \bar{p}_0 | \hat{h}_{\text{so}}^i | p_{-1} \rangle$. While $a = 1$ in an isolated atom, it is important to keep track of the p_0 contribution for the molecular case where a will be replaced by an R -dependent weight $a(R)$ of the $3p_0 = 3p_z(\text{Cl})$ orbital in the expansion of $5\sigma(R) = a(R)3p_z(\text{Cl}) + b(R)3s(\text{Cl}) + c(R)1s(\text{H})$ molecular orbital. At large internuclear distances, $a \rightarrow 1$. An electron in the $3s(\text{Cl})$ atomic orbital does not contribute to the SO-mixing ($l = 0$) and SO interaction of an electron, localized in the $1s(\text{H})$ orbital, is neglected.

APPENDIX B: TRANSFORMATION FROM SPHERICAL ATOMIC TO ORIENTED MOLECULAR BASIS

In the next step, the SO matrix is transformed from $p_1 p_{-1} p_0$ to the $p_x p_y p_z$ atomic orbitals basis. Due to the rotational symmetry around the molecular axis, the degeneracy with respect to the atomic case is partially removed in HCl: the eigenstates differing in $|M_L| = \Lambda$ now have different energies but remain degenerate with respect to the total spin projection M_S . To accommodate this change, the atomic basis set $\mathcal{B}_a^{18}$ (Table II) is first transformed to the atomic basis set $\mathcal{B}_{\text{asy}}^{18}$ (Table III) by replacing the p_1 , p_{-1} and p_0 orbitals in $\mathcal{B}_a^{18}$ by p_x , p_y , and p_z orbitals, respectively. Since in each of the $\mathcal{B}_{\text{asy}}^{18}$ basis states the p_x and p_y orbital appear at most once and they are composed of equal shares of p_1 and p_{-1} orbitals,

$$\begin{aligned}
 p_x &= (p_1 - p_{-1})/\sqrt{2}, \\
 \bar{p}_x &= (\bar{p}_1 - \bar{p}_{-1})/\sqrt{2}, \\
 p_y &= i(p_1 + p_{-1})/\sqrt{2}, \\
 \bar{p}_y &= i(\bar{p}_1 + \bar{p}_{-1})/\sqrt{2}, \\
 p_z &= p_0, \\
 \bar{p}_z &= \bar{p}_0,
 \end{aligned} \tag{B1}$$

it is clear that each state has well-defined Λ . Thus, instead of having a specific M_L sign, the basis states in Table III are now composed of orbitals with well-defined directionality in space. The $\mathcal{B}_{\text{asy}}^{18}$ basis spans the same space as $\mathcal{B}_a^{18}$.

The SO matrix in the xyz -basis $\mathcal{B}_{\text{asy}}^{18}$ is given by

$$\mathbf{H}_{\text{so}}^{18xyz}(\Delta E) = \mathbf{T}_{18} \mathbf{H}_{\text{so}}^{18m}(\Delta E) \mathbf{T}_{18}^\dagger, \tag{B2}$$

where

$$\mathbf{T}_{18} = \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i \end{bmatrix} \quad (\text{B3})$$

is the transformation matrix from $\mathcal{B}_a^{18}$ to $\mathcal{B}_{\text{asy}}^{18}$ atomic basis:

$$\mathcal{B}_{\text{asy}}^{18} = \mathbf{T}_{18} \mathcal{B}_a^{18}. \quad (\text{B4})$$

In Eq. (B2), $\mathbf{T}_{18}^\dagger$ is an inverse of the unitary matrix $\mathbf{T}_{18}$, i.e., the transposed and complex-conjugated matrix $\mathbf{T}_{18}$. The SO matrix $\mathbf{H}_{\text{so}}^{18\text{xyz}}(\Delta E)$ in the new $\mathcal{B}_{\text{asy}}^{18}$ basis

$$-\frac{\xi}{2} \begin{bmatrix} \Delta E & 0 & \frac{i}{3} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i}{3\sqrt{2}} & 0 & 0 & 0 & \frac{ia}{3} & \frac{ia}{2\sqrt{6}} & 0 & \frac{ia}{6\sqrt{2}} & 0 \\ 0 & \Delta E & 0 & -\frac{i}{3} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i}{3\sqrt{2}} & 0 & -\frac{ia}{3} & 0 & 0 & \frac{ia}{6\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} \\ -\frac{i}{3} & 0 & \Delta E & 0 & 0 & -\frac{i}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{a}{3} & \frac{a}{2\sqrt{6}} & 0 & -\frac{a}{6\sqrt{2}} & 0 \\ 0 & \frac{i}{3} & 0 & \Delta E & 0 & 0 & -\frac{i}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & -\frac{a}{3} & 0 & 0 & \frac{a}{6\sqrt{2}} & 0 & -\frac{a}{2\sqrt{6}} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i}{2} & 0 & 0 & 0 & -\frac{ia}{2\sqrt{6}} & 0 & 0 & \frac{ia}{2\sqrt{3}} & 0 & 0 \\ 0 & 0 & \frac{i}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i}{6} & 0 & 0 & 0 & -\frac{ia}{6\sqrt{2}} & -\frac{ia}{2\sqrt{3}} & 0 & \frac{ia}{3} & 0 \\ 0 & 0 & 0 & \frac{i}{3\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{6} & 0 & -\frac{ia}{6\sqrt{2}} & 0 & 0 & -\frac{ia}{3} & 0 & \frac{ia}{2\sqrt{3}} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{2} & 0 & -\frac{ia}{2\sqrt{6}} & 0 & 0 & -\frac{ia}{2\sqrt{3}} & 0 \\ 0 & 0 & 0 & 0 & -\frac{i}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{2\sqrt{6}} & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 \\ -\frac{i}{3\sqrt{2}} & 0 & 0 & 0 & 0 & -\frac{i}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{6\sqrt{2}} & -\frac{ia}{2\sqrt{3}} & 0 & -\frac{a}{3} & 0 \\ 0 & -\frac{i}{3\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{i}{6} & 0 & 0 & 0 & 0 & 0 & -\frac{a}{6\sqrt{2}} & 0 & 0 & -\frac{a}{3} & 0 & -\frac{a}{2\sqrt{3}} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{i}{2} & 0 & 0 & 0 & 0 & -\frac{a}{2\sqrt{6}} & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 \\ 0 & \frac{ia}{3} & 0 & -\frac{a}{3} & \frac{ia}{2\sqrt{6}} & 0 & \frac{ia}{6\sqrt{2}} & 0 & \frac{a}{2\sqrt{6}} & 0 & -\frac{a}{6\sqrt{2}} & 0 & \Delta E & 0 & 0 & 0 & 0 & 0 \\ -\frac{ia}{3} & 0 & -\frac{a}{3} & 0 & 0 & \frac{ia}{6\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 & \frac{a}{6\sqrt{2}} & 0 & -\frac{a}{2\sqrt{6}} & 0 & \Delta E & 0 & 0 & 0 & 0 \\ -\frac{ia}{2\sqrt{6}} & 0 & \frac{a}{2\sqrt{6}} & 0 & 0 & \frac{ia}{2\sqrt{3}} & 0 & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{ia}{6\sqrt{2}} & 0 & \frac{a}{6\sqrt{2}} & -\frac{ia}{2\sqrt{3}} & 0 & \frac{ia}{3} & 0 & -\frac{a}{2\sqrt{3}} & 0 & -\frac{a}{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{ia}{6\sqrt{2}} & 0 & -\frac{a}{6\sqrt{2}} & 0 & 0 & -\frac{ia}{3} & 0 & \frac{ia}{2\sqrt{3}} & 0 & -\frac{a}{3} & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{ia}{2\sqrt{6}} & 0 & -\frac{a}{2\sqrt{6}} & 0 & 0 & -\frac{ia}{2\sqrt{3}} & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (\text{B5})$$

has exactly the same eigenvalues as $\mathbf{H}_{\text{so}}^{18m}(\Delta E)$.

TABLE IV. Ordered $\mathcal{B}_{\text{mol}}^{18}$ molecular basis obtained from $\mathcal{B}_{\text{asy}}^{18}$ by replacements $p_{x,y} \rightarrow \pi_{x,y}$, $p_z \rightarrow \sigma$ and $s \rightarrow \sigma^*$. The fifth column gives state notations consistent with Table I, and the last column gives the correspondence to the spectator-less Auger amplitudes in Table VII.

j	$(vv' {}^{2S_{vv'}+1} \Lambda) \sigma^* {}^{2S+1} \Lambda$	M_S	State	Notation	Spectator-less case
1	$(xz {}^3 \Pi) \sigma^* {}^2 \Pi$	1/2	$\sqrt{2/3} \pi_x \sigma \bar{\sigma}^* - (\pi_x \bar{\sigma} \sigma^* + \bar{\pi}_x \sigma \sigma^*)/\sqrt{6}$	f_{10x}	x
2	$(xz {}^3 \Pi) \sigma^* {}^2 \Pi$	-1/2	$(\pi_x \bar{\sigma} \bar{\sigma}^* + \bar{\pi}_x \sigma \bar{\sigma}^*)/\sqrt{6} - \sqrt{2/3} \bar{\pi}_x \bar{\sigma} \sigma^*$	f_{10x}	x
3	$(yz {}^3 \Pi) \sigma^* {}^2 \Pi$	1/2	$\sqrt{2/3} \pi_y \sigma \bar{\sigma}^* - (\pi_y \bar{\sigma} \sigma^* + \bar{\pi}_y \sigma \sigma^*)/\sqrt{6}$	f_{10y}	x
4	$(yz {}^3 \Pi) \sigma^* {}^2 \Pi$	-1/2	$(\pi_y \bar{\sigma} \bar{\sigma}^* + \bar{\pi}_y \sigma \bar{\sigma}^*)/\sqrt{6} - \sqrt{2/3} \bar{\pi}_y \bar{\sigma} \sigma^*$	f_{10y}	x
5	$(xz {}^3 \Pi) \sigma^* {}^4 \Pi$	3/2	$\pi_x \sigma \sigma^*$	f_{11x}	1a
6	$(xz {}^3 \Pi) \sigma^* {}^4 \Pi$	1/2	$(\pi_x \sigma \bar{\sigma}^* + \pi_x \bar{\sigma} \sigma^* + \bar{\pi}_x \sigma \sigma^*)/\sqrt{3}$	f_{11x}	1a
7	$(xz {}^3 \Pi) \sigma^* {}^4 \Pi$	-1/2	$(\pi_x \bar{\sigma} \bar{\sigma}^* + \bar{\pi}_x \sigma \bar{\sigma}^* + \bar{\pi}_x \bar{\sigma} \sigma^*)/\sqrt{3}$	f_{11x}	1a
8	$(xz {}^3 \Pi) \sigma^* {}^4 \Pi$	-3/2	$\bar{\pi}_x \bar{\sigma} \bar{\sigma}^*$	f_{11x}	1a
9	$(yz {}^3 \Pi) \sigma^* {}^4 \Pi$	3/2	$\pi_y \sigma \sigma^*$	f_{11y}	1b
10	$(yz {}^3 \Pi) \sigma^* {}^4 \Pi$	1/2	$(\pi_y \sigma \bar{\sigma}^* + \pi_y \bar{\sigma} \sigma^* + \bar{\pi}_y \sigma \sigma^*)/\sqrt{3}$	f_{11y}	1b
11	$(yz {}^3 \Pi) \sigma^* {}^4 \Pi$	-1/2	$(\pi_y \bar{\sigma} \bar{\sigma}^* + \bar{\pi}_y \sigma \bar{\sigma}^* + \bar{\pi}_y \bar{\sigma} \sigma^*)/\sqrt{3}$	f_{11y}	1b
12	$(yz {}^3 \Pi) \sigma^* {}^4 \Pi$	-3/2	$\bar{\pi}_y \bar{\sigma} \bar{\sigma}^*$	f_{11y}	1b
13	$(xy {}^3 \Sigma^-) \sigma^* {}^2 \Sigma^-$	1/2	$\sqrt{2/3} \pi_x \pi_y \bar{\sigma}^* - (\pi_x \bar{\pi}_y \sigma^* + \bar{\pi}_x \pi_y \sigma^*)/\sqrt{6}$	f_{13}	3
14	$(xy {}^3 \Sigma^-) \sigma^* {}^2 \Sigma^-$	-1/2	$(\pi_x \bar{\pi}_y \bar{\sigma}^* + \bar{\pi}_x \pi_y \bar{\sigma}^*)/\sqrt{6} - \sqrt{2/3} \bar{\pi}_x \bar{\pi}_y \sigma^*$	f_{13}	3
15	$(xy {}^3 \Sigma^-) \sigma^* {}^4 \Sigma^-$	3/2	$\pi_x \pi_y \sigma^*$	f_{15}	3
16	$(xy {}^3 \Sigma^-) \sigma^* {}^4 \Sigma^-$	1/2	$(\pi_x \pi_y \bar{\sigma}^* + \pi_x \bar{\pi}_y \sigma^* + \bar{\pi}_x \pi_y \sigma^*)/\sqrt{3}$	f_{15}	3
17	$(xy {}^3 \Sigma^-) \sigma^* {}^4 \Sigma^-$	-1/2	$(\pi_x \bar{\pi}_y \bar{\sigma}^* + \bar{\pi}_x \pi_y \bar{\sigma}^* + \bar{\pi}_x \bar{\pi}_y \sigma^*)/\sqrt{3}$	f_{15}	3
18	$(xy {}^3 \Sigma^-) \sigma^* {}^4 \Sigma^-$	-3/2	$\bar{\pi}_x \bar{\pi}_y \bar{\sigma}^*$	f_{15}	3

Next, the molecular basis states corresponding to $3p^{-2}(^3P)ns$ atomic states are constructed. In a diatomic heteronuclear molecule such as HCl, $|M_L| = \Lambda$ is a good quantum number, while the orbital angular momentum with respect to the nucleus is not: the molecular orbitals are often expressed as linear combinations of atomic orbitals with different orbital angular momenta. To Σ molecular states featuring $\Lambda = 0$, atomic orbitals with any value of orbital angular momentum l can contribute provided they have $m_l = 0$. On the other hand, contributions of s atomic electron orbitals are forbidden for Π molecular states that have $\Lambda = 1$, etc. In order to cast the xyz basis $\mathcal{B}_{\text{asy}}^{18}$ (Table III) to the molecular basis states having no specific assignment of orbital angular momentum, atomic orbitals s and p_z are replaced by σ^* and $p_z = \sigma$ molecular orbital, respectively, both having $\Lambda = \Sigma$. Next, p_x and p_y atomic orbitals are replaced by π_x and π_y molecular orbitals, respectively, that both have $\Lambda = \Pi$, etc. The molecular basis $\mathcal{B}_{\text{mol}}^{18}$ is shown in Table IV.

To each state in Table IV, an R -dependent nonrelativistic energy can be assigned according to the calculated PECs. The PECs from Ref. [28] are calculated in the higher-order approximation, while our estimate of the SO mixing is limited by a single configuration representation of molecular states. Note that in the large R limit, the molecular basis in Table IV becomes *almost* equal to the atomic basis in Table III, i.e., $\mathcal{B}_{\text{asy}}^{18} \rightarrow \mathcal{B}_{\text{mol}}^{18}$, because then the following replacements are valid: $\sigma \rightarrow p_z$, $\pi_x \rightarrow p_x$ and $\pi_y \rightarrow p_y$ [31]. In addition, $\sigma^* \rightarrow \text{H}(1s)$ at large R , and to mimic zero Coulomb interaction with the Cl^+ ion, $\sigma^* \rightarrow (n \gg 3)s$ atomic orbital in Cl atom without any change of the H_{s0} matrix elements. A single exception is the f_{10} molecular state $5\sigma^{-1}2\pi^{-1}(^3\Pi)\sigma^* {}^2\Pi$ that evolves to the Cl $3p^{-1}$ instead to the Cl^+3p^{-2} state.

APPENDIX C: ADDING THE STATES CORRESPONDING TO $3p^{-2}(^1S, ^1D)ns$

The molecular basis corresponding to $3p^{-2}(^1S, ^1D)ns$ atomic states is defined and the final 32×32 SO matrix $\mathbf{H}_{s0}$ is constructed.

To consider SO coupling of states at all R , the molecular basis in Table IV needs to be expanded to cover all the states in Table I. To do so, we first write the m -atomic basis $\mathcal{B}_a^{12}$ containing the rest of the atomic states build on the $3p^{-2}ns$ configuration. This basis set will be added to the m -basis $\mathcal{B}_a^{18}$ in Table II in order to construct the SO matrix $\mathbf{H}_{s0}^{30m}$ in the 30-state basis $\mathcal{B}_a^{30}$: A suitable molecular analog of the atomic basis set in Table V can not be obtained starting by simple replacement of the $p_{0,1,-1}$ orbitals with the $p_{x,y,z}$ orbitals (and their further substitution by π and σ orbitals) because this would end up in mixing the $M_L = 0$ states that belong to two energetically different $\sigma\sigma\sigma^*$ and $\pi\sigma\sigma^*$ molecular configurations. Therefore, an adequate atomic basis $\mathcal{B}_{\text{asy}}^{12}$ (i.e., the asymptotic molecular basis) must be partially recoupled with respect to $\mathcal{B}_a^{12}$ to form the set of pure single-configuration states but still covering the same space as $\mathcal{B}_a^{12}$. After the recoupling, the molecular basis $\mathcal{B}_{\text{mol}}^{12}$ is obtained from the asymptotic basis with the following replacements: $p_{x,y} \rightarrow \pi_{x,y}$, $p_z \rightarrow \sigma$ and $s \rightarrow \sigma^*$. The transformation matrix between the 12-state atomic m -base in Table V and 12-state asymptotic molecular base in Table VI,

$$\mathcal{B}_{\text{asy}}^{12} = \mathbf{T}_{12} \mathcal{B}_a^{12}, \quad (\text{C1})$$

TABLE V. Ordered set of all $3p^{-2}ns$ $|LSM_L M_S\rangle$ atomic states coupled to ^2S and ^2D to form the $\mathcal{B}_a^{12}$ basis.

No.	^{2S+1}L	M_L	M_S	State
1	^2D	2	1/2	$p_1\bar{p}_1s$
2	^2D	2	-1/2	$p_1\bar{p}_1\bar{s}$
3	^2D	1	1/2	$(p_0\bar{p}_1s - \bar{p}_0p_1s)/\sqrt{2}$
4	^2D	1	-1/2	$(p_0\bar{p}_1\bar{s} - \bar{p}_0p_1\bar{s})/\sqrt{2}$
5	^2D	0	1/2	$(p_1\bar{p}_{-1}s - \bar{p}_1p_{-1}s + 2p_0\bar{p}_0s)/\sqrt{6}$
6	^2D	0	-1/2	$(p_1\bar{p}_{-1}\bar{s} - \bar{p}_1p_{-1}\bar{s} + 2p_0\bar{p}_0\bar{s})/\sqrt{6}$
7	^2D	-1	1/2	$(p_0\bar{p}_{-1}s - \bar{p}_0p_{-1}s)/\sqrt{2}$
8	^2D	-1	-1/2	$(p_0\bar{p}_{-1}\bar{s} - \bar{p}_0p_{-1}\bar{s})/\sqrt{2}$
9	^2D	-2	1/2	$p_{-1}\bar{p}_{-1}s$
10	^2D	-2	-1/2	$p_{-1}\bar{p}_{-1}\bar{s}$
11	^2S	0	1/2	$(p_1\bar{p}_{-1}s - \bar{p}_1p_{-1}s - \bar{p}_0\bar{p}_0s)/\sqrt{3}$
12	^2S	0	-1/2	$(p_1\bar{p}_{-1}\bar{s} - \bar{p}_1p_{-1}\bar{s} - \bar{p}_0\bar{p}_0\bar{s})/\sqrt{3}$

is given by

$$\mathbf{T}_{12} = \begin{bmatrix} \frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{\sqrt{3}} & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{2}}{\sqrt{3}} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{3}} \end{bmatrix}. \quad (\text{C2})$$

TABLE VI. Ordered $\mathcal{B}_{\text{mol}}^{12}$ basis of molecular states and the correspondence to the no-spectator Auger amplitudes in Table VII.

No. (j)	$(vv' \ ^{2S_{vv'}+1} \Lambda) \sigma^* \ ^{2S+1} \Lambda$	M_S	State	Notation	No-spectator case
1(19)	$(xy \ ^1\Delta) \sigma^* \ ^2\Delta$	1/2	$(\pi_x\bar{\pi}_y\sigma^* - \bar{\pi}_x\pi_y\sigma^*)/\sqrt{2}$	$f_{14}(xy)$	5b
2(20)	$(xy \ ^1\Delta) \sigma^* \ ^2\Delta$	-1/2	$(\pi_x\bar{\pi}_y\bar{\sigma}^* - \bar{\pi}_x\pi_y\bar{\sigma}^*)/\sqrt{2}$	$f_{14}(xy)$	5b
3(21)	$(xx, yy \ ^1\Delta) \sigma^* \ ^2\Delta$	1/2	$(\pi_x\bar{\pi}_x\sigma^* - \pi_y\bar{\pi}_y\sigma^*)/\sqrt{2}$	$f_{14}(xx, yy)$	5a
4(22)	$(xx, yy \ ^1\Delta) \sigma^* \ ^2\Delta$	-1/2	$(\pi_x\bar{\pi}_x\bar{\sigma}^* - \pi_y\bar{\pi}_y\bar{\sigma}^*)/\sqrt{2}$	$f_{14}(xx, yy)$	5a
5(23)	$(xz \ ^1\Pi) \sigma^* \ ^2\Pi$	1/2	$(\pi_x\bar{\sigma}\sigma^* + \bar{\pi}_x\sigma\sigma^*)/\sqrt{2}$	$f_9(xz)$	2a
6(24)	$(xz \ ^1\Pi) \sigma^* \ ^2\Pi$	-1/2	$(\pi_x\bar{\sigma}\bar{\sigma}^* + \bar{\pi}_x\sigma\bar{\sigma}^*)/\sqrt{2}$	$f_9(xz)$	2a
7(25)	$(yz \ ^1\Pi) \sigma^* \ ^2\Pi$	1/2	$(\pi_y\bar{\sigma}\sigma^* + \bar{\pi}_y\sigma\sigma^*)/\sqrt{2}$	$f_9(yz)$	2b
8(26)	$(yz \ ^1\Pi) \sigma^* \ ^2\Pi$	-1/2	$(\pi_y\bar{\sigma}\bar{\sigma}^* + \bar{\pi}_y\sigma\bar{\sigma}^*)/\sqrt{2}$	$f_9(yz)$	2b
9(27)	$(xx, yy \ ^1\Sigma^+) \sigma^* \ ^2\Sigma^+$	1/2	$(\pi_x\bar{\pi}_x\sigma^* + \pi_y\bar{\pi}_y\sigma^*)/\sqrt{2}$	$f_{12}(xx, yy)$	4
10(28)	$(xx, yy \ ^1\Sigma^+) \sigma^* \ ^2\Sigma^+$	-1/2	$(\pi_x\bar{\pi}_x\bar{\sigma}^* + \pi_y\bar{\pi}_y\bar{\sigma}^*)/\sqrt{2}$	$f_{12}(xx, yy)$	4
11(29)	$(zz \ ^1\Sigma^+) \sigma^* \ ^2\Sigma^+$	1/2	$\sigma\bar{\sigma}\sigma^*$	$f_2(zz)$	6
12(30)	$(zz \ ^1\Sigma^+) \sigma^* \ ^2\Sigma^+$	-1/2	$\sigma\bar{\sigma}\bar{\sigma}^*$	$f_2(zz)$	6

In the next step we add the 12-dimensional atomic base states from Table V to 18-dimensional atomic base states in Table II to form the $\mathcal{B}_a^{30} = (\mathcal{B}_a^{18}, \mathcal{B}_a^{12})$ basis and calculate the corresponding 30×30 SO matrix $\mathbf{H}_{\text{so}}^{30m}$. This can be written in the block form

$$\mathbf{H}_{\text{so}}^{30m} = \begin{bmatrix} \mathbf{H}_{\text{so}}^{18m}(0) & \mathbf{H}_{12 \times 18}^{m\dagger} \\ \mathbf{H}_{12 \times 18}^m & 0 \end{bmatrix}, \quad (\text{C3})$$

where the $\mathbf{H}_{\text{so}}^{18m}(0)$ matrix is given above (A2). Note that all matrix elements of the $\hat{H}_{\text{so}}$ operator in the $\mathcal{B}_a^{12}$ basis (see Table V) are zero. There is, however, a nonzero SO coupling of the $\mathcal{B}_a^{12}$ basis states with the $\mathcal{B}_a^{18}$ basis states, which is described by the 12×18 matrix $\mathbf{H}_{12 \times 18}^m$,

$$\mathbf{H}_{12 \times 18}^m = -\frac{\xi}{2} \begin{bmatrix} 0 & 0 & 0 & 0 & \frac{a}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{a}{\sqrt{3}} & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{2\sqrt{3}} & 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{a}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2\sqrt{3}} & 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{\sqrt{6}} & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 \\ 0 & -\frac{a}{3\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{a}{6} & 0 & \frac{a}{2\sqrt{3}} & 0 & 0 & 0 & -\frac{1}{3} & 0 & 0 & \frac{\sqrt{2}}{3} & 0 & 0 \\ 0 & 0 & \frac{a}{3\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{a}{2\sqrt{3}} & 0 & \frac{a}{6} & 0 & 0 & 0 & \frac{1}{3} & 0 & 0 & \frac{\sqrt{2}}{3} & 0 \\ 0 & 0 & -\frac{1}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{6}} & 0 & 0 & 0 & -\frac{a}{\sqrt{6}} & 0 & 0 & \frac{a}{2\sqrt{3}} & 0 \\ 0 & 0 & 0 & \frac{1}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{2} \\ 0 & 0 & 0 & -\frac{a}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{a}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{2a}{3} & 0 & 0 & 0 & 0 & -\frac{a\sqrt{2}}{3} & 0 & -a\frac{\sqrt{2}}{\sqrt{3}} & 0 & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & \frac{2}{3} & 0 & 0 \\ 0 & 0 & -\frac{2a}{3} & 0 & 0 & 0 & 0 & -a\frac{\sqrt{2}}{\sqrt{3}} & 0 & -\frac{a\sqrt{2}}{3} & 0 & 0 & 0 & \frac{\sqrt{2}}{3} & 0 & 0 & \frac{2}{3} & 0 \end{bmatrix}. \quad (\text{C4})$$

The transformation matrix $\mathbf{T}_{30}$ from the atomic basis $\mathcal{B}_a^{30}$ to the asymptotic molecular basis, $\mathcal{B}_{\text{asy}}^{30} = \mathbf{T}_{30}\mathcal{B}_a^{30}$, is

$$\mathbf{T}_{30} = \begin{bmatrix} \mathbf{T}_{18} & 0 \\ 0 & \mathbf{T}_{12} \end{bmatrix}. \quad (\text{C5})$$

The SO matrix in the asymptotic molecular basis $\mathcal{B}_{\text{asy}}^{30}$ is then

$$\mathbf{H}_{\text{so}}^{30\text{xyz}} = \mathbf{T}_{30}\mathbf{H}_{\text{so}}^{30m}\mathbf{T}_{30}^\dagger, \quad (\text{C6})$$

where the result is conveniently expressed by

$$\mathbf{H}_{\text{so}}^{30\text{xyz}} = \begin{bmatrix} \mathbf{H}_{\text{so}}^{18\text{xyz}}(0) & \mathbf{H}_{12 \times 18}^{\text{xyz}\dagger} \\ \mathbf{H}_{12 \times 18}^{\text{xyz}} & 0 \end{bmatrix}. \quad (\text{C7})$$

While $\mathbf{H}_{\text{so}}^{18\text{xyz}}(0)$ is given by (B5), the 12×18 coupling matrix $\mathbf{H}_{12 \times 18}^{\text{xyz}}$ is

$$-\frac{\xi}{2} \begin{bmatrix} 0 & -\frac{ia}{2\sqrt{3}} & 0 & -\frac{a}{2\sqrt{3}} & \frac{ia}{2\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 & -\frac{a}{2\sqrt{2}} & 0 & \frac{a}{2\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{ia}{2\sqrt{3}} & 0 & -\frac{a}{2\sqrt{3}} & 0 & 0 & \frac{ia}{2\sqrt{6}} & 0 & \frac{ia}{2\sqrt{2}} & 0 & -\frac{a}{2\sqrt{6}} & 0 & \frac{a}{2\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{a}{2\sqrt{3}} & 0 & -\frac{ia}{2\sqrt{3}} & \frac{a}{2\sqrt{2}} & 0 & -\frac{a}{2\sqrt{6}} & 0 & \frac{ia}{2\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{a}{2\sqrt{3}} & 0 & \frac{ia}{2\sqrt{3}} & 0 & 0 & \frac{a}{2\sqrt{6}} & 0 & -\frac{a}{2\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 & \frac{ia}{2\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{i}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{6}} & 0 & 0 & 0 & -\frac{ia}{2\sqrt{3}} & \frac{ia}{2\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 \\ 0 & 0 & 0 & -\frac{i}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{6}} & 0 & \frac{i}{2\sqrt{3}} & 0 & 0 & \frac{ia}{2\sqrt{6}} & 0 & \frac{ia}{2\sqrt{2}} \\ \frac{i}{2\sqrt{3}} & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{a}{2\sqrt{3}} & -\frac{a}{2\sqrt{2}} & 0 & \frac{a}{2\sqrt{6}} & 0 \\ 0 & -\frac{i}{2\sqrt{3}} & 0 & 0 & 0 & 0 & -\frac{i}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2\sqrt{3}} & 0 & 0 & -\frac{a}{2\sqrt{6}} & 0 & \frac{a}{2\sqrt{2}} \\ 0 & -\frac{a}{2\sqrt{3}} & 0 & -\frac{ia}{2\sqrt{3}} & -\frac{a}{2\sqrt{2}} & 0 & \frac{a}{2\sqrt{6}} & 0 & \frac{ia}{2\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 & -\frac{i}{\sqrt{3}} & 0 & 0 & \frac{i\sqrt{2}}{\sqrt{3}} & 0 & 0 \\ -\frac{a}{2\sqrt{3}} & 0 & -\frac{ia}{2\sqrt{3}} & 0 & 0 & -\frac{a}{2\sqrt{6}} & 0 & \frac{a}{2\sqrt{2}} & 0 & \frac{ia}{2\sqrt{6}} & 0 & \frac{ia}{2\sqrt{2}} & 0 & \frac{i}{\sqrt{3}} & 0 & 0 & \frac{i\sqrt{2}}{\sqrt{3}} & 0 \\ 0 & -\frac{a}{\sqrt{6}} & 0 & -\frac{ia}{\sqrt{6}} & -\frac{a}{2} & 0 & \frac{a}{2\sqrt{3}} & 0 & \frac{ia}{2} & 0 & \frac{ia}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{a}{\sqrt{6}} & 0 & \frac{ia}{\sqrt{6}} & 0 & 0 & -\frac{a}{2\sqrt{3}} & 0 & \frac{a}{2} & 0 & \frac{ia}{2\sqrt{3}} & 0 & \frac{ia}{2} & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}. \quad (\text{C8})$$

TABLE VII. Spectator-less amplitudes $A(m_\epsilon, m_c; R)$ for Auger decay of the $\text{HCl}^+ 2p^{-1}$ core hole state to the nine final states of HCl^{2+} with $5\sigma 2\pi$ and $2\pi 2\pi$ combination of holes. The last column gives index m of the corresponding nonzero contributions to the Auger matrix A_{mj} [see Eq. (29)] quoted in column four. Index j marks the states in the nonrelativistic basis $\mathcal{B}_{\text{mol}}^{30}$ and is given in the first column of Tables IV and VI. The last column in the same two tables gives the reference to the corresponding spectator-less case, denoted in the first column of this table. The $j = 31, 32$ entries apply to the $A^2\Sigma^+$ bound states with $M_S = \pm 1/2$, for which all Auger amplitudes are zero.

No.	$vv' {}^{2S_{vv'}+1}\Lambda$	$J_{vv'} + (-1)^{S_{vv'}} K_{vv'}$	$A(m_\epsilon, m_c; R)$	m in A_{mj}
1a	$5\sigma 2\pi_x (^3\Pi)$	$J_{5\sigma 2\pi_x} - K_{2\pi_x 5\sigma}$	$a(R)(-w_1[-1, 0], -w_1[0, -1], w_1[0, 1], w_1[1, 0])$	2,4,6,8
1b	$5\sigma 2\pi_y (^3\Pi)$	$J_{5\sigma 2\pi_y} - K_{2\pi_y 5\sigma}$	$i a(R)(w_1[-1, 0], w_1[0, -1], w_1[0, 1], w_1[1, 0])$	2,4,6,8
2a	$5\sigma 2\pi_x (^1\Pi)$	$J_{5\sigma 2\pi_x} + K_{2\pi_x 5\sigma}$	$a(R)(-w_2[-1, 0], -w_2[0, -1], w_2[0, 1], w_2[1, 0])$	2,4,6,8
2b	$5\sigma 2\pi_y (^1\Pi)$	$J_{5\sigma 2\pi_y} + K_{2\pi_y 5\sigma}$	$i a(R)(w_2[-1, 0], w_2[0, -1], w_2[0, 1], w_2[1, 0])$	2,4,6,8
3	$2\pi_x 2\pi_y (^3\Sigma^-)$	$J_{2\pi_x 2\pi_y} - K_{2\pi_y 2\pi_x}$	$i (w_3[-1, 1], w_3[1, -1])$	3,7
4	$2\pi_{x,y} 2\pi_{x,y} (^1\Sigma^+)$	$(J_{2\pi_x 2\pi_x} + K_{2\pi_x 2\pi_x} + J_{2\pi_y 2\pi_y} + K_{2\pi_y 2\pi_y})/2$	$(w_{42}[-1, 1], w_{41}[0, 0], w_{42}[1, -1])/2$	3,5,7
5a	$2\pi_{x,y} 2\pi_{x,y} (^1\Delta)$	$(J_{2\pi_x 2\pi_x} + K_{2\pi_x 2\pi_x} - J_{2\pi_y 2\pi_y} - K_{2\pi_y 2\pi_y})/2$	$(w_{51}[-1, -1], w_{51}[1, 1])/2$	1,9
5b	$2\pi_x 2\pi_y (^1\Delta)$	$J_{2\pi_x 2\pi_y} + K_{2\pi_y 2\pi_x}$	$i (-w_{52}[-1, -1], w_{52}[1, 1])$	1,9
6	$5\sigma 5\sigma (^1\Sigma^+)$	$J_{5\sigma 5\sigma} + K_{5\sigma 5\sigma}$	$a^2(R)(w_{62}[-1, 1], w_{61}[0, 0], w_{62}[1, -1])/\sqrt{2}$	3,5,7

To obtain an R -dependent $\mathbf{H}^{30}$ matrix in the basis of molecular states $\mathcal{B}_{\text{mol}}^{30}$, the matrix H_{so}^{30xyz} is supplemented by adding the nonrelativistic potential energies $U_f(R)$ to the corresponding diagonal matrix elements, and at the same time, a is replaced an R -dependent weight $a(R)$ of $3p_z$ atomic orbital in the expansion of the 5σ molecular orbital [31].

Prior to the diagonalization, two more states,

$$1 : |^2\Sigma^+, M_S = 1/2\rangle = \sigma^{-1} \equiv \mathbf{f}_A(M_S = 1/2), \quad 2 : |^2\Sigma^+, M_S = -1/2\rangle = \bar{\sigma}^{-1} \equiv \mathbf{f}_A(M_S = -1/2), \quad (\text{C9})$$

are added to the molecular basis $\mathcal{B}_{\text{mol}}^{30}$ to form the $\mathcal{B}_{\text{mol}}^{32} = (\mathcal{B}_{\text{mol}}^{30}, \mathcal{B}_{\text{mol}}^{2-})$ basis that finally includes all the states from Table I. In this basis, the last two states (at positions 31 and 32) have $5\sigma^{-1}$ electronic configuration that corresponds to $A^2\Sigma^+$, the first excited state of HCl^+ . Namely, at $R \approx 4.7$ a.u., the PEC of this bound state intersects with PECs of a few dissociative final states from Table I, exhibiting at the same time a nonzero SO interaction with some of them. In fact, according to the single-configuration approximation the only new nonzero matrix elements of the final $\mathbf{H}_{\text{so}}^{32}$ matrix with respect to the $\mathbf{H}_{\text{so}}^{30}$ matrix are $\mathbf{H}_{\text{so}}^{32}(10, 31)$ and $\mathbf{H}_{\text{so}}^{32}(11, 32)$ (plus the complex-conjugated transposed matrix elements). In the vicinity of the potential crossing point the new matrix elements are set to 0.032i a.u., the value calculated a long time ago [37].

The presence of $a(R)$, the weight of the $3p_z(\text{Cl})$ atomic orbital in (B5) and (C8) makes SO coupling R -dependent. However, at any R the coupling effect depends also on differences between the diagonal matrix elements of $\mathbf{H}^{32}$, i.e., the effect of the SO-mixing is enhanced when the differences between the nonrelativistic PECs become comparable to ξ or smaller. We choose to refer all diagonal matrix elements of $\mathbf{H}^{32}(R)$ at any R to the $U_5(R)$ potential, the eigenvalue of f_{11x} and f_{11y} eigenstates of the nonrelativistic Hamiltonian $\mathbf{H}_0(R)$ (see Fig. 1). This makes the diagonal matrix elements $\mathbf{H}_{\text{so}}^{32}(i, i)$ equal to zero at any R when $5 \leq i \leq 12$ and refers all the eigenvalues of the $\mathbf{H}^{32}(R)$ matrix to the value of the $U_5(R)$ potential at the same internuclear distance.

APPENDIX D: CONSTRUCTION OF AUGER AMPLITUDES TO NONRELATIVISTIC MOLECULAR STATES

This appendix describes the procedure for determination of $L - vv'$ Auger amplitudes for transitions between the nonrelativistic dissociative state $2p^{-1}\sigma^*$ and the nonrelativistic dissociative states $v^{-1}v'^{-1}\sigma^*$ in the single-center approximation.

Firstly, the partial amplitudes describing the Auger transitions from $\text{HCl}^+ 2p^{-1}$ state to the $\text{HCl}^{2+} v^{-1}v'^{-1}({}^{2S_{vv'}+1}\Lambda)$ final states (the spectator-less transitions) are expressed by linear combination of direct and exchange two-electron integrals

$$A_{vv'} = J_{vv'}(S_{vv'}, \Lambda, l_\epsilon, m_\epsilon, m_c; R) + (-1)^{S_{vv'}} K_{vv'}(S_{vv'}, \Lambda, l_\epsilon, m_\epsilon, m_c; R). \quad (\text{D1})$$

Note that these amplitudes depend also on l_ϵ , the Auger partial wave (in our case only $l_\epsilon = 1$ contribution is significant) and on m_c , the projection of the orbital angular momentum of the initial $2p$ core hole. Although it completely neglects the coupling of the σ^* spectator with the rest of the electrons, the spectator-less case is different from the nonresonant case where the spectator electron is kicked out of the molecule by the primary photoionization event: here the amplitudes still depend on the internuclear distance because of the presence of the spectator electron, which modulates the content of $3p_z$ atomic orbital in the 5σ molecular orbital. The spectator-less amplitudes to the nine HCl^{2+} final states of interest are constructed using the data tables in Ref. [29]. The nonzero elements of A_{jm} Auger matrix can be reconstructed from data in Tables IV, VI, VII, and VIII. To obtain Auger rates to the nonrelativistic final states,

$$\Gamma_{fi}(R) = \frac{\pi}{6} \sum_{m=1}^9 \sum_{p=1}^8 |(A_{mf}(R) S_{f \rightarrow q})_{fp}|^2, \quad (\text{D2})$$

TABLE VIII. Auger coefficients w and their values for Slater integrals $R_0(2p, \epsilon p; 3p, 3p) = 0.012404$ a.u. and $R_2(2p, \epsilon p; 3p, 3p) = 0.007518$ a.u.

w_1	$(-R_0 + R_2/5)/\sqrt{2}$	-0.0072
w_2	$(-R_0 - R_2/25)\sqrt{2}$	-0.0085
w_3	$-R_0 + R_2/5$	-0.0101
w_{41}	$12R_0/25$	0.0037
w_{42}	$-2R_0 - 14R_2/25$	-0.0190
w_{51}	$2R_0 + 2R_2/25$	0.0239
w_{52}	R_0	0.0117
w_{61}	$2R_0 + 8R_2/25$	0.0258
w_{62}	$-6R_2/25$	-0.0018

the spectator-less amplitudes A_{mf} must be weighted by the spin matrix elements. The notation $S_{f \rightarrow p}$ means that for each final state index f in the $\mathcal{B}_{\text{mol}}^{32}$ basis, the q th row of $\mathbf{S}$ spin matrix is selected in such a way that the $(S_{vv'}, S, M_S)$ quantum numbers values for this line match the corresponding quantum numbers of the basis state f . The correspondence vector $T = (3, 4, 3, 4, 5, 6, 7, 8, 5, 6, 7, 8, 3, 4, 5, 6, 7, 8, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2, 1, 2)$ selects index q value for a given value of f index according to $q = T_f$. The spin matrix is given by

$$\mathbf{S} = \begin{bmatrix} (0, 0, \frac{1}{2}) & (0, 0, -\frac{1}{2}) & (1, 1, \frac{1}{2}) & (1, 1, -\frac{1}{2}) & (1, 0, \frac{1}{2}) & (1, 0, -\frac{1}{2}) & (1, -1, \frac{1}{2}) & (1, -1, -\frac{1}{2}) & \leftarrow (S', M'_S, m_{s\epsilon}) \\ \frac{1}{2} & 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{2} & 0 & 0 & 0 & (0, \frac{1}{2}, \frac{1}{2}) \\ 0 & \frac{1}{2} & 0 & 0 & 0 & \frac{1}{2} & -\frac{1}{\sqrt{2}} & 0 & (0, \frac{1}{2}, -\frac{1}{2}) \\ \frac{\sqrt{3}}{2} & 0 & 0 & -\frac{1}{\sqrt{6}} & \frac{1}{2\sqrt{3}} & 0 & 0 & 0 & (1, \frac{1}{2}, \frac{1}{2}) \\ 0 & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{1}{2\sqrt{3}} & \frac{1}{\sqrt{6}} & 0 & (1, \frac{1}{2}, -\frac{1}{2}) \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & (1, \frac{3}{2}, \frac{3}{2}) \\ 0 & 0 & 0 & \frac{1}{\sqrt{3}} & \sqrt{\frac{2}{3}} & 0 & 0 & 0 & (1, \frac{3}{2}, \frac{1}{2}) \\ 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{2}{3}} & \frac{1}{\sqrt{3}} & 0 & (1, \frac{3}{2}, -\frac{1}{2}) \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & (1, \frac{3}{2}, -\frac{3}{2}) \\ & & & & & & & & \uparrow (S_{vv'}, S, M_S) \end{bmatrix}. \quad (\text{D3})$$

In the nonrelativistic case, the calculated Γ_{fi} rates at large R are about 20% lower than recently published values [31] (see Fig. 8). Anticipating similar relative rate differences for other final states evolving towards $3s^{-1}3p^{-1}$ and $3s^{-2}$ states of Cl^+ , which are not included in this study, the total decay width of the $2p^{-1}\sigma^*$ resonance in HCl is estimated to $\Gamma_i(\infty) = 125$ meV. While Eq. (29) calculates Auger rates $\bar{\Gamma}_{fi}$ from SO-mixed states exactly, the Auger rates $\tilde{\Gamma}_{fi}$ are calculated from Eq. (30), which neglects

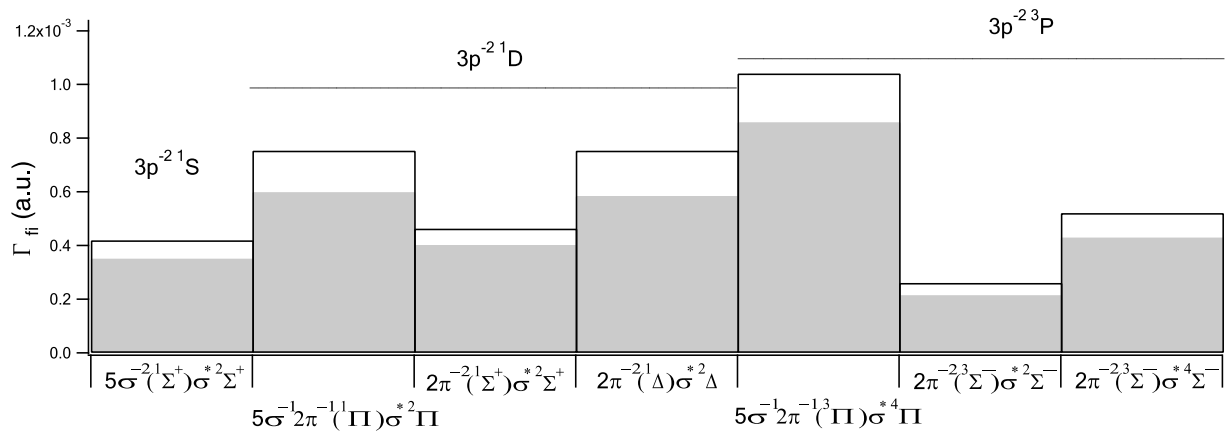


FIG. 8. Comparison with previously published nonrelativistic asymptotic rates [15] and the rates calculated from Eq. (D2) (gray bars).

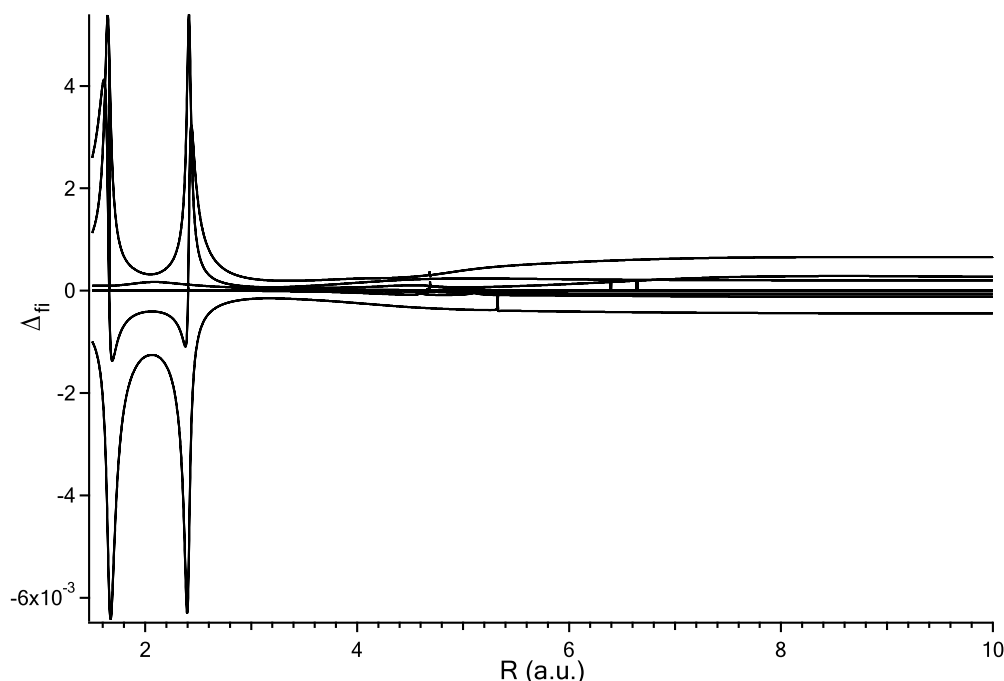


FIG. 9. Relative difference $\Delta_{fi}(R) = (\tilde{\Gamma}_{fi}(R) - \bar{\Gamma}_{fi}(R))/\bar{\Gamma}_{fi}(R)$ of the Auger partial rates to the 32 SO-coupled states.

the contribution of terms containing cross products of Auger amplitudes to nonrelativistic final states. In our specific case, both results match to better than 1% at any R , as shown in Fig. 9.

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