Theory of nuclear motion in RABBITT spectra

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Reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) is a powerful photoelectron spectroscopy, offering direct access to internal dynamics of the target. It is being increasingly applied to molecular systems, but a general, computationally tractable theory of RABBITT spectra in molecules has so far been lacking. We show that under quite general assumptions, RABBITT spectra in molecules can be expressed as a convolution of the vibronic cross-correlation functions and two-electron photoionization matrix elements. We specialize the general expressions to the commonly encountered special cases. We expect our theory to enable accurate modeling and interpretation of molecular RABBITT spectra in most medium-sized molecules.

I. INTRODUCTION

Reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) is an ingenious photoelectron spectroscopy, offering direct access to the photoelectron phases [1], and consequently to the intricate details of the electronic and nuclear dynamics in atoms and molecules [2–6]. Driven by recent improvements in experimental techniques (see, e.g., Refs. [7,8]), RABBITT spectroscopy is being increasingly applied to molecular systems, with many notable recent theory developments (see, e.g., Refs. [4,9,10] and references therein). An essential factor affecting all molecular spectroscopies is nuclear motion, which, however, received only limited attention in the literature so far [4,11,12]. This oversight is likely partially due to the enormous cost of the brute-force treatment of the electron-nuclear coupling in photoionization, which so far limited practical calculations to a very few nuclear degrees of freedom. A similar difficulty arises in molecular spectroscopy of bound-to-bound transitions, where it has been long recognized [13,14] that the problem can nonetheless be made numerically tractable by recasting it in a time-dependent form. The observable effects of the nuclear motion are then compactly summarized by vibronic auto- and cross-correlation functions [13,14]. The utility of the nuclear auto- and cross-correlation functions has also been appreciated in the strong-field and attosecond domain, where they have been used to describe nuclear-motion effects in high-harmonics generation [15–17] and attosecond electron-hole migration [18–20]. Very recently, an elegant theory of the molecular electron-streaking spectra has been developed [21], with the single-surface nuclear autocorrelation functions taking the central role.

In this contribution, we extend the approach of Ref. [21] to the theory of molecular RABBITT photoelectron spectra. We derive a compact, general expression for the relevant transition amplitudes in terms of vibronic cross-correlation functions. Our treatment includes, at least in principle, all nuclear motion effects relevant for RABBITT transitions. In particular, it describes the effects of the coherent averaging over the initial vibrational function, including the zero-point effects (ZPE), the redistribution of the absorbed photon energy between the photoelectron and internal degrees of freedom, the effects of absorption and emission of additional IR photons by the cationic core, and the effects of the finite pulse duration. The treatment naturally includes complex vibronic dynamics in the vicinity of conical intersections as well.

The rest of this manuscript is organized as follows: Sec. II develops the general theory of RABBITT spectra in molecules. Section III considers some relevant special cases, which allow further simplifications of the general expression. Finally, Sec. IV summarizes the work and presents an outlook for follow-up investigations and applications.

II. THEORY

We are interested in modeling photoelectron spectra of a molecular system, described by a field-free, time-independent Hamiltonian $\hat{H}_0$, produced as a result of simultaneously interacting with an infrared laser field and its harmonics in the extreme-ultraviolet (XUV) spectral range. The fields are assumed to be sufficiently weak, so that at most second-order interactions need to be considered (one order in IR and one in XUV). Under these assumptions, it is sufficient to consider a three-color field. The individual spectral components of this field, all taken to be linearly polarized, are given by

$$F_{\mathrm{IR}}(t) = f_{\mathrm{IR}}(t)\vec{n}_{\mathrm{IR}} \cos{(\omega t)} \tag{1}$$

$$F_i(t) = f_i(t)\vec{n}_i \cos{(\Omega_i t + \Phi_i)}, \tag{2}$$

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where $i = 1, 2$, $\vec{n}$ is field polarization direction, and $f(t)$ is a slowly varying envelope. The corresponding terms in the total Hamiltonian are given by

$$\hat{V}_{\text{IR}} = \tfrac{1}{2}\hat{\mu}_{\text{IR}} f_{\text{IR}}(t)[e^{i\omega t} + e^{-i\omega t}], \qquad (3)$$

$$\hat{V}_i = \tfrac{1}{2}\hat{\mu}_i f_i(t)\left[e^{i\Omega_i t + i\Phi_i} + e^{-i\Omega_i t - i\Phi_i}\right], \qquad (4)$$

where the terms in brackets correspond to the emission $(+)$ and absorption $(-)$ of a photon. We assume that the field parameters are such that only absorption is possible for the XUV fields $(\hat{V}_i)$, while the IR photons can be both absorbed and emitted. Operators $\hat{\mu}$ incorporate the specific form of the field-interaction Hamiltonian and field polarization properties. Equations (3) and (4) implicitly assume that the laser field is treated in the length gauge and dipole approximation.

In addition to the field-free Hamiltonian $\hat{H}_0$, we will also consider Hamiltonians $\hat{H}_{\text{IR}}$ and $\hat{H}_i$, defined as

$$\hat{H}_{\text{IR}} = \hat{H}_0 + \hat{V}_{\text{IR}}, \qquad (5)$$

$$\hat{H}_i = \hat{H}_0 + \hat{V}_{\text{IR}} + \hat{V}_i, \qquad (6)$$

corresponding to our preferred order of treating the perturbations. For each Hamiltonian $\hat{H}_a$, the corresponding propagator $\hat{U}_a$ is symbolically given by

$$\hat{U}_a(t', t; E) = e^{-i\int_t^{t'} dt'' (\hat{H}_a - E)}, \qquad (7)$$

where we have chosen to pull the rapidly oscillating phase e^{-iEt} out. The "characteristic energy" E is in principle arbitrary; however, we expect that it is selected such as to make $\hat{U}_a$ a slow function of time. We note that a propagator in Eq. (7) satisfies the energy-origin transformation

$$\hat{U}_a(t', t; E) = e^{i(E - E')(t' - t)}\hat{U}_a(t', t; E'). \qquad (8)$$

A. Wave function response to a two-color, XUV + IR, field

Our first task is to calculate the wave function response to the combined effects of the IR and *one* of the XUV fields. The overall signal is obtained by combining the response to the separate harmonics below, in Sec. II B. We will consider only the contribution bilinear in the two fields, and assume that the contributions due to each field alone can be neglected (e.g., because they are energetically separated from the signal of interest). The detailed derivation, including all the intermediate steps, is given in the Appendixes A–C. Here, we summarize the key expressions needed to understand the final result.

We start by treating $\hat{H}_{\text{IR}}$ as the zeroth-order Hamiltonian, and $\hat{V}_i$ as the perturbation. The usual time-dependent perturbation theory then yields [14,22,23]

$$\left|\Psi_i^{(1)}(t)\right\rangle = -i\int_{t_0}^t dt'\, e^{-iE_I(t - t')}\hat{U}_i(t, t'; E_I)\hat{V}_i(t')e^{-iE_N(t' - t_0)}$$
$$\times \hat{U}_{\text{IR}}(t', t_0; E_N)\left|\Psi^{(0)}(t_0)\right\rangle, \qquad (9)$$

where E_N and E_I are, respectively, characteristic energies of the system before and after XUV photon absorption, and t_0 is chosen before the start of the XUV pulse [i.e., $f_i(t' < t_0) = 0$]. We will also assume that the observation time t is past the end of the laser pulse. The initial wave function $|\Psi^{(0)}\rangle$ is a vibronic wave function, including both electronic and nuclear degrees of freedom.

So far, we have avoided choosing a specific representation of the vibronic wave functions. For the initial wave function $\Psi^{(0)}$, we use the standard adiabatic Born-Huang ansatz:

$$|\Psi^{(0)}(t)\rangle = \sum_a |\psi_a(r; q)\rangle\, |\chi_a(q, t)\rangle, \qquad (10)$$

where ψ_a are the discrete, time-independent electronic states of the neutral species, which depend on the electronic coordinates r and parametrically on the nuclear coordinates q. Time-dependent nuclear wave packets χ_a propagate on these electronic surfaces. We take that the electronic states ψ_a and the corresponding surfaces are available to us through some other means. [If desired, e.g., for treating the situation where the initial, neutral wave packet finds itself in a vicinity of a conical intersection, Eq. (10) can be taken as a diabatic vibronic ansatz, with minimal changes to the treatment.]

Under our assumptions, absorption of an XUV photon brings the molecule into a highly excited electronic state, with one of the electrons either ionized or in a Rydberg state. If we assume that at most one electron is ionized or excited, while the others remain tightly bound, it is natural to expand the wave function after XUV absorption in the form

$$|\Psi^{(1)}(t)\rangle = \sum_c \int dk\, |\psi_{ck}(r; q)\rangle\, |\chi_c(q, t)\rangle, \qquad (11)$$

where discrete index c is understood to run over the asymptotically populated, tightly bound states of the residual ion, while the general index k labels the full electronic state (continuum or discrete) associated to this ion core. As before, functions ψ_{ck} and the corresponding energy surfaces are assumed to be available to us.

After some tedious but straightforward manipulations, relying on the set of electronic wave functions in Eqs. (10) and (11) being complete (see Appendix A), Eq. (9) can be rewritten in the form

$$\left|\Psi_i^{(1)}(t)\right\rangle = -\frac{i}{2}e^{-i\Phi_i + iE_N t_0}\sum_d \int dp\, e^{-iE_I t} |\psi_{dp}(r; q)\rangle$$
$$\times |\chi_{dpi}(q, t)\rangle, \qquad (12)$$

$$|\chi_{dpi}(q, t)\rangle = \sum_{a,c}\int dk \int_{t_0}^t dt'\, e^{i(E_I - E_N - \Omega_i)t'} f_i(t')$$
$$\times \hat{u}_{dp,ck}(t, t'; E_I)\hat{\mu}_{ck,a} |\chi_a(q, t')\rangle, \qquad (13)$$

$$\hat{u}_{dp,ck}(t, t'; E_I) = \langle\psi_{dp}(r; q)|\hat{U}_{\text{IR}}(t, t'; E_I)|\psi_{ck}(r; q)\rangle, \qquad (14)$$

$$\hat{\mu}_{ck,a}(q) = \langle\psi_{ck}(r; q)|\hat{\mu}_i|\psi_a(r; q)\rangle. \qquad (15)$$

In Eq. (13), $\chi_{dpi}(q, t)$ is the final amplitude of the ion state d and photoelectron state p, at nuclear coordinates q and time t, generated by the XUV field F_i. Propagator (14) describes evolution of the initially prepared ionized (or excited) state under the influence of the IR field. Operator $\hat{\mu}_{ck,a}$ is the transition dipole for ionization (or excitation) of an electronic state $|\psi_a(r; q)\rangle$, forming state $|\psi_{ck}(r; q)\rangle$. This operator depends parametrically on the nuclear coordinates q.

We would now like to examine the propagator $\hat{u}_{dp,ck}(t, t'; E_I)$ of Eq. (14) a bit more closely. Without

attempting any formal justification, we introduce the crucial approximation of our treatment. We will assume that

$$\hat{u}_{dp,ck}(t, t'; E_I) \approx \hat{u}_{p,k}(t, t'; E_I - E_C)\hat{u}_{d,c}(t, t'; E_C), \quad (16)$$

$$\hat{u}_{d,c}(t, t'; E_C) = \langle \psi_d(r; q)| \hat{U}_{\text{IR}}(t, t'; E_C) |\psi_c(r; q)\rangle, \quad (17)$$

$$\hat{u}_{p,k}(t, t'; E_I - E_C) = \langle \psi_p(r; q)| \hat{U}_{\text{IR}}(t, t'; E_I - E_C) \\ \times |\psi_k(r; q)\rangle, \quad (18)$$

$$[\hat{u}_{d,c}, \hat{u}_{p,k}] = 0. \quad (19)$$

In Eq. (17), E_C is the characteristic energy of the cationic manifold, while $|\psi_c(r; q)\rangle$ are Born-Oppenheimer electronic wave functions of the cation. As before, we assume that efficient means of evaluating Eq. (17) are available to us. Propagator (18) could have been formally (and tautologically) defined as

$$\hat{u}_{p,k}(t, t'; E_I - E_C) \overset{?}{=} \hat{u}_{dp,ck}(t, t'; E_I)\hat{u}_{c,d}(t', t; E_C). \quad (20)$$

(Note, however, that the putative definition (20) does not satisfy the commutator relation (19), except for the degenerate case of a single-state cationic manifold.)

From Eq. (20), it is clear that in adopting Eq. (16), we neglect the possibility of a transition in the (c, d) manifold inducing a transition in the (k, p) manifold and vice versa. Examples of such transitions are collisionally induced (de)excitation in the ion core, as well as shake-off and shake-up transitions. By our initial assumptions, the two manifolds (the compact ion core and the extended photoelectron-Rydberg orbital) are energetically and spatially separated, so that such transitions are expected to have low relative cross sections. If necessary, they could be treated as higher-order perturbations.

We should also emphasize that partitioning of the Hamiltonian implied by Eq. (16) does *not* introduce the single-particle approximation. This can be clearly seen in the special case where the cationic manifold consists of an isolated, nondegenerate ground state. Then, the propagator $\hat{u}_{d,c}$ amounts to a q-dependent phase change, and Eq. (16) is exact, rather than an approximation. Indices k, p then enumerate all electronic states in the system, both excited and ionized. The energies of these states must, however, be taken relative to the energy of the target state E_C.

We can now evaluate the propagator of Eq. (18), treating the IR field as a perturbation to the zeroth-order Hamiltonian. Following the sequence of steps detailed in Appendix B, we obtain

$$\hat{u}_{p,k,\pm}(t, t'; E_k) = \frac{1}{2} e^{-i(E_p - E_k)t} f_{\text{IR}}(t') \langle \psi_p(r; q)| \hat{\mu}_{\text{IR}} |\psi_k(r; q)\rangle \\ \times \frac{e^{i(E_p - E_k \pm \omega)t'}}{(E_p - E_k \pm \omega) - i0^+}, \quad (21)$$

where $E_k = E_I - E_C$ is the "excess" characteristic energy of the state $|\psi_{kc}\rangle$ relative to E_C, the characteristic energy of the cation, and the index $\pm$ stands for the emission ($+$) or the absorption ($-$) of an IR photon.

Substituting Eqs. (21) and (16) into Eqs. (12) and (13), we finally obtain (see Appendix C) the second-order wave function response $\Psi_{i\pm}^{(2)}$, where we have chosen to sepa-

rate contributions due to emission and absorption of the IR photons:

$$\left|\Psi_{i\pm}^{(2)}(t)\right\rangle = -\frac{i}{2} e^{-i\Phi_i - iE_C t + iE_N t_0} \sum_d \int dp \, e^{-iE_p t} |\psi_{dp}(r; q)\rangle \\ \times |\tilde{\chi}_{dpi\pm}(q, t)\rangle, \quad (22)$$

$$|\tilde{\chi}_{dpi\pm}(q, t)\rangle = \frac{1}{2} \sum_{a,c} \int_{t_0}^t dt' e^{-i\epsilon_{cp,a\pm} t'} f_i(t') f_{\text{IR}}(t') \hat{u}_{d,c}(t, t'; E_C) \\ \times \hat{D}_{cp,a\pm}(q) |\chi_a(q, t')\rangle, \quad (23)$$

$$\epsilon_{cp,a\pm} = (\Omega_i \mp \omega) - (E_p + E_C - E_N), \quad (24)$$

$$\hat{D}_{cp,a\pm}(q) = \int dk \frac{\hat{\mu}_{p,ck}\hat{\mu}_{ck,a}}{(E_p - E_k \pm \omega) - i0^+}, \quad (25)$$

$$\hat{\mu}_{p,ck}(q) = \langle \psi_p(r; q)| \hat{\mu}_{\text{IR}} |\psi_k(r; q)\rangle, \quad (26)$$

where we used $E_I = E_k + E_C$, and moved the phase contribution in $|\chi_{dpi}\rangle$ dependent solely on t into the definition of $\Psi_i^{(2)}$.

The individual terms in Eqs. (22)–(26) have a transparent physical interpretation. The quantity $(E_p + E_C)$ is the total electronic energy of the final state of the system. The nontrivial dynamics in the system is described by nuclear wave packets $|\tilde{\chi}_{dpi\pm}\rangle$, which propagate on ionic surface d and are entangled with final photoelectron momentum p. The operator $\hat{D}_{cp,a\pm}$ is the standard electronic matrix element for two-photon absorption. The quantity $\epsilon_{cp,a\pm}$ is the amount of energy deposited into the nuclear degrees of freedom of the system. Finally, Eq. (23) describes time evolution of the nuclear wave packet on the (generally coupled) ionic energy surfaces. The Fourier transform in Eq. (23) picks out the relevant spectral component of the nuclear wave packet.

B. RABBITT signal: General case

Using Eqs. (22) and (23), we are ready to describe the RABBITT sidebands. Sideband M arises due to interference between two-photon transitions involving two neighboring harmonics:

$$\Omega_1 = (M - 1)\omega, \quad (27)$$

$$\Omega_2 = (M + 1)\omega. \quad (28)$$

The signal at final photoelectron momentum p is given by a sum of three contributions:

$$I(p) = I_{1-,1-}(p) + I_{2+,2+}(p) + 2\Re[I_{1-,2+}(p)]. \quad (29)$$

The first contribution is the photoelectron signal due to the simultaneous absorption of an Ω_1 and ω photons. The second term describes absorption of an Ω_2 and emission of ω photons. The remaining term, which arises from the complex-conjugate pair $I_{1-,2+}(p) + I_{2+,1-}(p)$, describes the delay-dependent interference.

From Eq. (22), the individual contributions are given by (see Appendix D)

$$I_{l,r}(p) = \langle \Psi_l^{(2)}(t)|p'\rangle\langle p|\Psi_r^{(2)}(t)\rangle\big|_{p' \to p} \\ = \frac{1}{4} \delta\left(\frac{\vec{p}' - \vec{p}}{2\pi}\right) e^{i(\Phi_l - \Phi_r)} \sum_d \langle \tilde{\chi}_{dpl}(q, t)|\tilde{\chi}_{dpr}(q, t)\rangle,$$

where $l, r = 1-, 2+$, and we assumed that the continuum functions are normalized to $\delta(\frac{\vec{p'}-\vec{p}}{2\pi})$. Any other normalization choice will lead to an equivalent expression, provided that a consistent choice is made in Eq. (25). We will therefore omit the continuum normalization factor from now on.

Substituting $|\tilde{\chi}_{dpi\pm}\rangle$ from Eq. (23) and using completeness relation for $\hat{u}_{d,c}$ (see Appendix D), we finally get

$$I_{l,r}(p) = e^{i(\Phi_l-\Phi_r)}\tilde{I}_{l,r}(p), \qquad (30)$$

where

$$\tilde{I}_{l,r}(p) = \frac{1}{16}\int_{t_0}^{t}dt''\int_{t_0}^{t}dt'\,e^{+i\epsilon_p(t''-t')}f_l(t'')f_{\mathrm{IR}}(t'')f_r(t')f_{\mathrm{IR}}(t')$$

$$\times\sum_{a,b,c,e}\langle\chi_b(q,t'')|\,\hat{D}_{ep,bl}^\dagger(q)\hat{u}_{e,c}(t'',t';E_C)$$

$$\times\hat{D}_{cp,ar}(q)\,|\chi_a(q,t')\rangle. \qquad (31)$$

The quantity $\tilde{I}_{l,r}$ is the "intrinsic" part of the RABBITT matrix element, which does not depend on the relative delay of the XUV and the IR fields. The entire delay dependence is encapsulated by the phase prefactor $e^{i(\Phi_l-\Phi_r)}$ in Eq. (30). As expected on physical grounds, the initial and observation times (t_0 and t) drop out of the final expression, provided that the envelopes of all pulses are zero outside of the $[t_0 : t]$ interval. These integration limits can therefore be replaced by $[-\infty : +\infty]$ if desired. Equations (29)–(31) are our general-case result for the RABBITT spectrum. Below, we consider some of the relevant special cases.

III. RABBITT SIGNAL: SPECIAL CASES

Although the result of Eq. (31) is compact and physically transparent, it is invokes a rather complex object: a weighted two-time nuclear cross-correlation function [$\langle\chi_b|...|\chi_a\rangle$]. We would like to consider possible simplifications to Eq. (31). For weak IR fields and short pulses, it is reasonable to neglect vibrational excitation by the IR field, both in the neutral and in the cationic manifolds. Then, the propagator $\hat{u}_{e,c}$ can be replaced by the field-free propagator $\hat{u}_{e,c}^0$, which is invariant with respect to shift of the time origin:

$$\hat{u}_{e,c}(t'',t';E_C)\approx\hat{u}_{e,c}^0(t''-t';E_C) \qquad (32)$$

$$\hat{u}_{e,c}^0(\tau;E_C) = \langle\psi_e(r;q)|\,\hat{U}_0(\tau,0;E_C)\,|\psi_c(r;q)\rangle. \qquad (33)$$

Furthermore, the initial, neutral vibronic wave function in many stable molecules is well represented by a single-surface Born-Oppenheimer product, so that the a, b sums in Eq. (31) collapse to a single, time-independent term:

$$|\chi_a(q,t)\rangle\approx|\chi_0(q)\rangle. \qquad (34)$$

Additionally, the characteristic decay time scale for the cationic autocorrelation functions is often short, on the order of a few femtoseconds or tens of femtoseconds [14,17]. On these time scales, the difference between pulse envelopes at t' and t'' can be neglected (the continuous wave approximation). Furthermore, in the diabatic representation, the cationic cross-correlation functions remain small on the timescale of the IR and XUV pulse duration, and only the diabatic autocorrelations need to be considered:

$$\hat{u}_{e,c}^0(\tau;E_C)\approx\delta_{ec}\hat{u}_{c,c}^0(\tau;E_C)\equiv\hat{u}_c^0(\tau;E_C). \qquad (35)$$

Applying the approximations above to the general Eq. (30), we obtain

$$I_{l,r}(p) = e^{i(\Phi_l-\Phi_r)}P_{l,r}\sum_c M_{c,l,r}(p), \qquad (36)$$

$$P_{l,r} = \frac{\pi}{8}\int d\tau\,f_l(\tau)f_r(\tau)f_{\mathrm{IR}}^2(\tau), \qquad (37)$$

$$M_{c,l,r}(p) = \frac{1}{2\pi}\int d\tau\,e^{+i\epsilon_p\tau}\,\langle\chi_0(q)|\,\hat{D}_{cp,0l}^\dagger(q)$$

$$\times\hat{u}_c^0(\tau;E_C)\hat{D}_{cp,0r}(q)\,|\chi_0(q)\rangle, \qquad (38)$$

where time integrals are over all times, and we have chosen to apply normalization factor $\frac{1}{2\pi}$ to the definition of the matrix element $M_c(p)$, for reasons which will become clear in the following section. In Eq. (36), the pulse-envelope parameters ($P_{l,r}$) are cleanly separated from the molecular factors ($M_{c,l,r}$), while the entire time-delay dependence is encapsulated by the phase prefactor $e^{i(\Phi_l-\Phi_r)}$, similar to the familiar atomic case [1]. While at first glance the conditions under which the approximate Eq. (36) is obtained do appear very restrictive, a closer examination shows that they are expected to be satisfied for a large fraction of small, rigid molecules.

It is instructive to examine some limiting cases of Eq. (38).

A. No nuclear motion: The "atomic" case

We first consider the case of nuclear motion being entirely absent in the center-of-mass coordinate system, so that the molecule has well-defined coordinates q_0, which are unchanged by the action of the propagator $\hat{u}_c^0$. Then

$$M_{c,l,r}(p)\overset{\mathrm{fixed}}{=}\hat{D}_{cp,0l}^\dagger(q_0)\hat{D}_{cp,0r}(q_0)\frac{1}{2\pi}\int d\tau\,e^{+i\epsilon_p\tau}$$

$$= \hat{D}_{cp,0l}^\dagger(q_0)\hat{D}_{cp,0r}(q_0)\delta(\epsilon_p). \qquad (39)$$

This result coincides with the familiar atomic case: The RABBITT sidebands appear at the photoelectron energy of $M\omega - IP$, where IP is the ionization potential. Their width is determined by the combined bandwidth of the XUV and IR pulses. Obviously, no vibrational or isotope effects are possible in this approximation.

B. Nuclear motion: Condon approximation

The next natural approximation to consider is to treat the electronic part of the matrix element (38) as q independent: the Condon approximation. Then

$$M_{c,l,r}(p)\overset{\mathrm{Condon}}{=}\hat{D}_{cp,0l}^\dagger(q_0)\hat{D}_{cp,0r}(q_0)N_c(\epsilon_p), \qquad (40)$$

$$N_c(\epsilon_p) = \frac{1}{2\pi}\int d\tau\,e^{+i\epsilon_p\tau}A_c(\tau;E_C), \qquad (41)$$

$$A_c(\tau;E_C) = \langle\chi_0(q)|\,\hat{u}_c^0(\tau;E_C)\,|\chi_0(q)\rangle, \qquad (42)$$

where N_c is the Fourier transform of nuclear autocorrelation function on (diabatic) cationic surface c. The field-free autocorrelation function is Hermitian with respect to time reversal [14]:

$$A_c(-\tau) = A_c(\tau)^\dagger, \tag{43}$$

so that N_c is guaranteed to be real. As long as the time integration domain in Eq. (41) is not truncated, N_c is also guaranteed to be positive semidefinite [14]:

$$N_c(\epsilon_p) \geqslant 0. \tag{44}$$

An important consequence of Eq. (44) is that vibrational dynamics in the Condon approximation *does not introduce additional time delays* in the RABBITT spectrum. Time delays remain an exclusively electronic property in this approximation, similar to the atomic case. Nuclear motion, however, imposes a finite, intrinsic photoelectron energy profile onto the RABBIT spectrum. In the Condon approximation, this profile coincides with the vibration profile in one-photon photoionization spectrum at the same photoelectron energy.

Isotopic dependence can arise in two ways in this approximation. First, the initial wave packet $|\chi_0\rangle$ and the propagator $\hat{u}_c^0$ depend on the nuclear masses, so that the factor N_c is isotope dependent. This contribution affects the photoelectron-energy profile, but not the time delays or the contrast of the signal oscillations with time. Additional isotope dependence could arise if the characteristic geometries q_0, where the electronic matrix elements are determined, are not the same for the isotopomers involved.

C. Nuclear motion: Zero-point effects

In the Condon approximation [Eq. (40)], the electronic part of the matrix element $M_{c,l,r}$ is evaluated at a single, characteristic geometry q_0. A natural refinement is to consider the consequences of the finite spatial extent of the wave packet, by averaging the electronic matrix element over the initial wave packet. All nuclear wave packets will have nonzero spatial extent due to the effects of the zero-point motion. Vibrational excitation will also affect the extent of the wave packet. If the overall shape of the wave packet, apart from the central position, is unaffected by nuclear motion, we obtain

$$M_{c,l,r}(p) \overset{\text{ZPE}}{=} G_{c,l,r}(p)N_c(\epsilon_p), \tag{45}$$

$$G_{c,l,r}(p) = \langle \chi_0(q)| \hat{D}_{cp,0l}^\dagger(q)\hat{D}_{cp,0r}(q) |\chi_0(q)\rangle, \tag{46}$$

where $N_c(\epsilon_p)$ is given by Eq. (41) above.

For the most important special case, where $|\chi_0\rangle$ is the ground-state vibrational wave function of a multidimensional harmonic oscillator, the integral (46) can be readily evaluated. The result is (see Appendix E)

$$G_{c,l,r}(p) \overset{\text{ZPE}}{=} \left(D_l^{(0)}\right)^\dagger D_r^{(0)} + \sum_k \frac{1}{4\omega_k}\left[\left(D_l^{(0)}\right)^\dagger D_r^{(k,k)} + 2\left(D_l^{(k)}\right)^\dagger D_r^{(k)} + \left(D_l^{(k,k)}\right)^\dagger D_r^{(0)}\right]$$

$$+ \sum_k \frac{3}{16\omega_k^2}\left(D_l^{(k,k)}\right)^\dagger D_r^{(k,k)} + \sum_{k \neq m} \frac{1}{16\omega_k\omega_m}\left(D_l^{(k,k)}\right)^\dagger D_r^{(m,m)} + \cancel{\sum_{k \neq m} \frac{1}{8\omega_k\omega_m}\left(D_l^{(k,m)}\right)^\dagger D_r^{(k,m)}}, \tag{47}$$

where $D_x^{(0)} = \hat{D}_{cp,0x}(q_0)$ and $D_x^{(i)}, D_x^{(i,j)}$ are its derivatives with respect to the normal coordinates q_i, q_j. Quantities ω_i are the corresponding normal-node frequencies.

The last three terms in Eq. (47) are of the fourth order in q, higher than the formal second order of the Taylor expansion used to derive it (see Appendix E). The two terms containing the diagonal part of the second-derivative matrix of D ensure that the approximated $G_{c,l,r}$ remains positive semidefinite. These terms must be kept to obtain physically meaningful results. The last contribution to Eq. (47), which is expensive to evaluate, can be safely omitted.

If analytical derivatives of the matrix elements in Eq. (47) are not available, they can be obtained using the standard finite-difference formulas. It is particularly convenient to use the turning points of the normal modes. Then

$$D_x^{(k)} \approx \frac{\sqrt{\omega_k}}{2}[D_x(\sqrt{\omega_k}) - D_x(-\sqrt{\omega_k})], \tag{48}$$

$$D_x^{(k,k)} \approx \omega_k[D_x(\sqrt{\omega_k}) + D_x(-\sqrt{\omega_k}) - 2D_x(q_0)], \tag{49}$$

where $x = l, r$. Substituting into Eq. (47), we then obtain the final working expression:

$$G_{c,l,r}(p) \overset{\text{ZPE FD}}{=} D_l^\dagger D_r + \sum_k D_l^\dagger W_{r,k} + \sum_k W_{l,k}^\dagger D_r$$

$$+ \sum_k V_{l,k}^\dagger V_{r,k} + 3\sum_k W_{l,k}^\dagger W_{r,k} + \sum_{k \neq m} W_{l,k}^\dagger W_{r,m}, \tag{50}$$

$$D_x = \hat{D}_{cp,0x}(q_c), \tag{51}$$

$$V_{x,k} = \frac{1}{\sqrt{8}}[\hat{D}_{cp,0x}^\dagger(q_0 + \sqrt{\omega_k}) - \hat{D}_{cp,0x}^\dagger(q_0 - \sqrt{\omega_k})], \tag{52}$$

$$W_{x,k} = \frac{1}{4}[\hat{D}_{cp,0x}(q_0 + \sqrt{\omega_k}) + \hat{D}_{cp,0x}(q_0 - \sqrt{\omega_k}) - 2\hat{D}_{cp,0x}(q_0)]. \tag{53}$$

Equation (50) can be applied to the situation where the nuclear motion after ionization is negligible. In this case, the characteristic geometry q_c and the neutral equilibrium geometry q_0 coincide. If the characteristic geometry does not coincide with

the neutral equilibrium geometry, Eq. (50) still guarantees that the matrix element $G_{c,l,r}$ remains positive semidefinite.

IV. SUMMARY AND OUTLOOK

In this work, we develop the formal theory of RABBITT photoionization spectra in molecular systems. Our most general result is given by Eqs. (17), (25), and (29)–(31). It includes the effects of the nuclear motion in the initial (neutral) and final (cation) state (including vibrational heating by the IR field and IR-induced electronic transitions); coordinate dependence of the two-electron photoionization matrix elements; and effects of the finite pulse duration. It neglects the possibility of collisional (de)excitation of the final ion, as well as of the shake-off and shake-up processes. The possibility of multiphoton transitions due to the XUV or absorption-emission of multiple IR photons by the ionized electron are also neglected. The vibronic dynamics, including dynamics at conical intersections, is treated fully, both in the initial and the final molecular states.

We further analyze important special cases. We demonstrate that in the lowest-order, Condon approximation, nuclear motion does not introduce additional time delays in the RABBITT spectra. The photoelectron energy profile in this approximation coincides with the vibrational profile in one-photon ionization spectra. In contrast, the zero-point motion leads to nonvanishing phase contributions, and therefore time delays. We develop numerically tractable expressions for the ZPE contributions, both for the case where analytical derivatives of the electronic matrix elements are available and for the finite-difference evaluation.

The expressions we have developed can be readily evaluated by combining the existing molecular photoionization codes, utilizing fixed-nuclei approximation, *ab initio* potential energy surfaces, and molecular vibronic-dynamics simulations. We envision routine applications of our theory to molecules with tens and potentially hundreds of vibrational degrees of freedom, which are entirely out of reach for brute-force, coupled electron-nuclear simulations. Given the number and the extent of the approximations, necessary to obtain numerically tractable formulation of the theory, only a comparison with experiment can serve as the ultimate arbiter of its validity. Work in this direction is currently underway, with the initial results reported elsewhere [24].

APPENDIX A: DERIVATION OF EQ. (12)

Starting with Eq. (9) of the main text, we obtain [14,22,23]

$$\left|\Psi_i^{(1)}(t)\right\rangle = -i \int_{t_0}^{t} dt' e^{-iE_I(t-t')} \hat{U}_i(t,t';E_I) \hat{V}_i(t') e^{-iE_N(t'-t_0)} \hat{U}_{\text{IR}}(t',t_0;E_N) \left|\Psi^{(0)}(t_0)\right\rangle \tag{9}$$

$$= -i \int_{t_0}^{t} dt' e^{-iE_I(t-t')} \hat{U}_i(t,t';E_I) \frac{1}{2}\hat{\mu}_i f_i(t') e^{-i\Omega_i t' - i\Phi_i} e^{-iE_N(t'-t_0)} \hat{U}_{\text{IR}}(t',t_0;E_N) \left|\Psi^{(0)}(t_0)\right\rangle$$

$$= -\frac{i}{2} e^{-i\Phi_i + iE_N t_0} \int_{t_0}^{t} dt' e^{-iE_I t} e^{i(E_I - E_N - \Omega_i)t'} f_i(t') \hat{U}_i(t,t';E_I) \hat{\mu}_i \hat{U}_{\text{IR}}(t',t_0;E_N) \left|\Psi^{(0)}(t_0)\right\rangle$$

$$\approx -\frac{i}{2} e^{-i\Phi_i + iE_N t_0} \int_{t_0}^{t} dt' e^{-iE_I t} e^{i(E_I - E_N - \Omega_i)t'} f_i(t') \hat{U}_{\text{IR}}(t,t';E_I) \hat{\mu}_i \hat{U}_{\text{IR}}(t',t_0;E_N) \left|\Psi^{(0)}(t_0)\right\rangle, \tag{A1}$$

where E_N and E_I are, respectively, characteristic energies of the system before and after XUV photon absorption, t_0 is before the start of the XUV pulse, and t is past the end of the pulse. In the last line, we replaced $\hat{U}_i(t,t';E_I)$ with $\hat{U}_{\text{IR}}(t,t';E_I)$, thus neglecting the possibility of absorbing additional XUV photons.

We now use the ansatz (10) for the initial wave function, and assume that the set of electronic states ψ_a is complete with respect to the action of the propagator $\hat{U}_{\text{IR}}$. One can then define an identity operator $\hat{1}_N$, which can be inserted between operators $\hat{\mu}_i$ and $\hat{U}_{\text{IR}}(t',t_0;E_N)$ in Eq. (A1):

$$\hat{1}_N = \sum_a \left|\psi_a(r;q)\right\rangle \left\langle\psi_a(r;q)\right|, \tag{A2}$$

where the brackets are understood to imply integration over electronic coordinates r alone. The result is

$$\left|\Psi_i^{(1)}(t)\right\rangle = -\frac{i}{2} e^{-i\Phi_i + iE_N t_0} \sum_a \int_{t_0}^{t} dt' e^{-iE_I t} e^{i(E_I - E_N - \Omega_i)t'} f_i(t')$$
$$\times \hat{U}_{\text{IR}}(t,t';E_I) \hat{\mu}_i \left|\psi_a(r;q)\right\rangle \left|\chi_a(q,t')\right\rangle, \tag{A3}$$

$$\left|\chi_a(q,t')\right\rangle = \sum_b \hat{u}_{ab}(t',t_0;E_N) \left|\chi_b(q,t_0)\right\rangle, \tag{A4}$$

$$\hat{u}_{ab}(t',t_0;E_N) = \left\langle\psi_a(r;q)|\hat{U}_{\text{IR}}(t',t_0;E_N)|\psi_b(r;q)\right\rangle, \tag{A5}$$

where we have chosen to introduce vibrational propagator $\hat{u}_{ab}(t',t_0;E_N)$.

The quantity $\left|\chi_a(q,t')\right\rangle$ is to be understood as a vibrational wave packet on an electronic surface a at time t'. We assume that efficient means of propagating these wave packets are available to us. In the most common special case, where $\left|\Psi^{(0)}(t_0)\right\rangle$ is an eigenstate of the field-free Hamiltonian with energy E_N, and the effects of the IR field on the initial neutral wave function can be neglected, Eq. (A4) reduces simply to

$$\left|\chi_a(q,t')\right\rangle \overset{\text{G.S.}}{=} \left|\chi_a(q,t_0)\right\rangle. \tag{A4a}$$

Analogously to Eq. (A2), we introduce identity-resolution operator $\hat{1}_C$ in the ion space, using wave functions defined in

Eq. (11) of the main text:

$$\hat{1}_C = \sum_c \int dk \, |\psi_{ck}(r;q)\rangle \langle\psi_{ck}(r;q)| \,. \tag{A6}$$

Inserting $\hat{1}_C$ into Eq. (A3) between $\hat{U}_{IR}$ and $\hat{\mu}_i$ and rearranging the terms, we obtain

$$\left|\Psi_i^{(1)}(t)\right\rangle = -\frac{i}{2}e^{-i\Phi_i + iE_N t_0}\sum_{a,c}\int dk \int_{t_0}^t dt' e^{-iE_I t} e^{i(E_I - E_N - \Omega_i)t'}$$
$$\times f_i(t')\hat{U}_{IR}(t,t';E_I)|\psi_{ck}(r;q)\rangle\,\hat{\mu}_{ck,a}|\chi_a(q,t')\rangle\,, \tag{A7}$$

where operator $\hat{\mu}_{ck,a}$ has been defined by Eq. (15) of the main text.

We can now introduce yet another identity-resolution operator $\hat{1}_{C'}$, in the form

$$\hat{1}_{C'} = \sum_d \int dp \, |\psi_{dp}(r;q)\rangle \langle\psi_{dp}(r;q)| \,, \tag{A8}$$

where the (discrete) index d and general parameter p are understood as the labels of the final state of the photoion and photoelectron, respectively. Inserting $\hat{1}_{C'}$ to the left of the operator $\hat{U}_{IR}$ in Eq. (A7) and rearranging, we obtain

$$\left|\Psi_i^{(1)}(t)\right\rangle = -\frac{i}{2}e^{-i\Phi_i + iE_N t_0}\sum_d \int dp \, e^{-iE_I t}\,|\psi_{dp}(r;q)\rangle$$
$$\times |\chi_{dpi}(q,t)\rangle\,, \tag{12}$$

$$|\chi_{dpi}(q,t)\rangle = \sum_{a,c}\int dk \int_{t_0}^t dt' e^{i(E_I - E_N - \Omega_i)t'}$$
$$\times f_i(t')\hat{u}_{dp,ck}(t,t';E_I)\hat{\mu}_{ck,a}|\chi_a(q,t')\rangle\,, \tag{13}$$

$$\hat{u}_{dp,ck}(t,t';E_I) = \langle\psi_{dp}(r;q)|\hat{U}_{IR}(t,t';E_I)|\psi_{ck}(r;q)\rangle\,. \tag{14}$$

In Eq. (13), $\chi_{dpi}(q,t)$ is the final amplitude of the ion state d and photoelectron state p, at nuclear coordinates q and time t, generated by the XUV field F_i. Propagator (14) describes evolution of the initially prepared ionized (or excited) state under the influence of the IR field. We note that the meaning of the phase factor $e^{-iE_I t}$ is subtly different between Eqs. (A7) and (12). In Eq. (A7), it is a global overall phase, while in Eq. (12) E_I is permitted to be p dependent. This change amounts to a gauge transformation of $|\chi_{dpi}(q,t)\rangle$, which is compensated for by the counteracting transformation of the $\hat{u}_{dp,ck}$ propagator in Eq. (13).

APPENDIX B: DERIVATION OF EQ. (21)

We evaluate the propagator of Eq. (18), treating the IR field as a perturbation to the zeroth-order Hamiltonian:

$$\hat{U}_{IR}(t,t';E_k)|\psi_k(r;q)\rangle = \cancel{\hat{U}_0(t,t';E_k)|\psi_k(r;q)\rangle}$$
$$- i\int_{t'}^t dt'' \hat{U}_{IR}(t,t'';E_k)\hat{V}_{IR},$$
$$\times \hat{U}_0(t''t';E_k)|\psi_k(r;q)\rangle\,, \tag{B1}$$

where $E_k = E_I - E_C$ is the "excess" characteristic energy of the state $|\psi_{kc}\rangle$ relative to E_C. The first term on the right-hand side of Eq. (B1) preserves k, leading to the δ_{p-k} contribution upon substitution into Eq. (18). Because we are interested in the RABBITT sidebands, rather than in the main harmonic line, we are permitted to drop this contribution. Then, substituting $\hat{V}_{IR}$ from Eq. (3), we obtain, separately for emission (+) and absorption (−) of an IR photon,

$$\hat{u}_{p,k,\pm}(t,t';E_k) \overset{\text{s.b.}}{=} -\frac{i}{2}\int_{t'}^t dt'' f_{IR}(t'')e^{\pm i\omega t''}\langle\psi_p(r;q)|\hat{U}_{IR}(t,t'';E_k)\hat{\mu}_{IR}\hat{U}_0(t'',t';E_k)|\psi_k(r;q)\rangle$$

$$\approx -\frac{i}{2}\int_{t'}^t dt'' f_{IR}(t'')e^{\pm i\omega t''}\langle\psi_p(r;q)|\hat{U}_0(t,t'';E_k)\hat{\mu}_{IR}\hat{U}_0(t'',t';E_k)|\psi_k(r;q)\rangle$$

$$= -\frac{i}{2}\int_{t'}^t dt'' f_{IR}(t'')e^{\pm i\omega t''}e^{i(E_k - E_p)(t-t'')}\langle\psi_p(r;q)|\hat{U}_0(t,t'';E_p)\hat{\mu}_{IR}\hat{U}_0(t'',t';E_k)|\psi_k(r;q)\rangle$$

$$= -\frac{i}{2}e^{-i(E_p - E_k)t}\int_{t'}^t dt'' f_{IR}(t'')e^{i(E_p - E_k \pm \omega)t''}\langle\psi_p(r;q)|\hat{\mu}_{IR}|\psi_k(r;q)\rangle$$

$$= -\frac{i}{2}e^{-i(E_p - E_k)t}\langle\psi_p(r;q)|\hat{\mu}_{IR}|\psi_k(r;q)\rangle\int_{t'}^t dt'' f_{IR}(t'')e^{i(E_p - E_k \pm \omega)t''}\,, \tag{B2}$$

where in the second line, we have neglected the possibility of absorbing the second IR photon. In the third line, we shifted the energy origin of the left-most propagator and rearranged the terms. In the fourth line, we have used the assumption that $|\psi_k\rangle$ are eigenfunctions of the field-free Hamiltonian with energy E_k, so that

$$\hat{U}_0(t_2,t_1;E_k)|\psi_k(r;q)\rangle = |\psi_k(r;q)\rangle\,, \tag{B3}$$

and moved the IR-dipole matrix element outside of the integral.

To progress further, we now evaluate the dt'' integral in Eq. (B2) by parts, using the adiabatic turn-on procedure (see §42 of Ref. [25]):

$$
\int_{t'}^{t} dt'' f_{\mathrm{IR}}(t'') e^{\lambda t''} e^{i(E_p - E_k \pm \omega)t''} = \int_{t'}^{t} dt'' f_{\mathrm{IR}}(t'') \frac{d}{dt''} \left(-i \frac{e^{\lambda t'' + i(E_p - E_k \pm \omega)t''}}{(E_p - E_k \pm \omega) - i\lambda} \right)
$$

$$
= -i f_{\mathrm{IR}}(t'') \frac{e^{\lambda t'' + i(E_p - E_k \pm \omega)t''}}{(E_p - E_k \pm \omega) - i\lambda} \Bigg|_{t'}^{t} + i \int_{t'}^{t} dt'' \frac{df_{\mathrm{IR}}(t'')}{dt''} \frac{e^{\lambda t'' + i(E_p - E_k \pm \omega)t''}}{(E_p - E_k \pm \omega) - i\lambda}
$$

$$
\approx i f_{\mathrm{IR}}(t') \frac{e^{\lambda t' + i(E_p - E_k \pm \omega)t'}}{(E_p - E_k \pm \omega) - i\lambda} \overset{\lambda \to +0}{=} i f_{\mathrm{IR}}(t') \frac{e^{i(E_p - E_k \pm \omega)t'}}{(E_p - E_k \pm \omega) - i0^+}, \tag{B4}
$$

where we have used the slowly varying envelope approximation to neglect the time derivative of the envelope f_{IR}, and assumed that the observation time t is past the end of the IR pulse. Inserting Eq. (B4) into Eq. (B2), we then obtain our final expression (21) for $\hat{u}_{p,k,\pm}$.

APPENDIX C: DERIVATION OF EQ. (22)

Substituting Eqs. (21) and (16) into Eqs. (12) and (13), we obtain

$$
\left| \Psi_{i\pm}^{(2)}(t) \right\rangle = -\frac{i}{2} e^{-i\Phi_i + iE_N t_0} \sum_d \int dp \, e^{-i(E_C + E_p)t} \left| \psi_{dp}(r; q) \right\rangle e^{+i(E_p - E_k)t} \left| \chi_{dpi\pm}(q, t) \right\rangle,
$$

$$
= -\frac{i}{2} e^{-i\Phi_i - iE_C t + iE_N t_0} \sum_d \int dp \, e^{-iE_p t} \left| \psi_{dp}(r; q) \right\rangle \left| \tilde{\chi}_{dpi\pm}(q, t) \right\rangle,
$$

$$
\left| \tilde{\chi}_{dpi\pm}(q, t) \right\rangle = e^{+i(E_p - E_k)t} \sum_{a,c} \int dk \int_{t_0}^{t} dt' e^{i(E_C + E_k - E_N - \Omega_i)t'} f_i(t') \frac{1}{2} e^{-i(E_p - E_k)t} f_{\mathrm{IR}}(t') \left\langle \psi_p(r; q) \right| \hat{\mu}_{\mathrm{IR}} \left| \psi_k(r; q) \right\rangle
$$

$$
\times \frac{e^{i(E_p - E_k \pm \omega)t'}}{(E_p - E_k \pm \omega) - i0^+} \hat{u}_{d,c}(t, t'; E_C) \hat{\mu}_{ck,a} \left| \chi_a(q, t') \right\rangle
$$

$$
= \frac{1}{2} \sum_{a,c} \int_{t_0}^{t} dt' e^{i(E_p + E_C - E_N - \Omega_i \pm \omega)t'} f_i(t') f_{\mathrm{IR}}(t') \hat{u}_{d,c}(t, t'; E_C) \int dk \frac{\left\langle \psi_p(r; q) \right| \hat{\mu}_{\mathrm{IR}} \left| \psi_k(r; q) \right\rangle \hat{\mu}_{ck,a}}{(E_p - E_k \pm \omega) - i0^+} \left| \chi_a(q, t') \right\rangle
$$

$$
= \frac{1}{2} \sum_{a,c} \int_{t_0}^{t} dt' e^{-i\epsilon_{cp,a\pm}t'} f_i(t') f_{\mathrm{IR}}(t') \hat{u}_{d,c}(t, t'; E_C) \hat{D}_{cp,a\pm}(q) \left| \chi_a(q, t') \right\rangle,
$$

where $\epsilon_{cp,a\pm}$, $\hat{D}_{cp,a\pm}(q)$, and $\hat{\mu}_{p,ck}(q)$ are given by Eqs. (24), (25), and (26) of the main text, respectively.

APPENDIX D: DERIVATION OF EQS. (30) AND (31)

From Eq. (22), the individual contributions $I_{l,r}(p)$ in Eq. (29) are given by

$$
I_{l,r}(p) = \left\langle \Psi_l^{(2)}(t) | p' \right\rangle \left\langle p | \Psi_r^{(2)}(t) \right\rangle \Big|_{p' \to p}
$$

$$
= \left(-\frac{i}{2} e^{-i\Phi_l - iE_C t + iE_N t_0} \sum_c e^{-iE_{p'} t} \left| \psi_{cp'}(r; q) \right\rangle \left| \tilde{\chi}_{cp'l}(q, t) \right\rangle \right)^{\dagger}
$$

$$
\times \left(-\frac{i}{2} e^{-i\Phi_r - iE_C t + iE_N t_0} \sum_d e^{-iE_p t} \left| \psi_{dp}(r; q) \right\rangle \left| \tilde{\chi}_{dpr}(q, t) \right\rangle \right) \Bigg|_{p' \to p}
$$

$$
= \frac{1}{4} e^{i(\Phi_l - \Phi_r)} \sum_{cd} \left\langle \tilde{\chi}_{cp'l}(q, t) \right| \left\langle \psi_{cp'}(r; q) \right| e^{i(E_{p'} - E_p)t} \left| \psi_{dp}(r; q) \right\rangle \left| \tilde{\chi}_{dpr}(q, t) \right\rangle \Bigg|_{p' \to p}
$$

$$
= \frac{1}{4} e^{i(\Phi_l - \Phi_r)} \sum_{cd} \left\langle \tilde{\chi}_{cp'l}(q, t) \right| \delta_{cd} \delta \left(\frac{\vec{p'} - \vec{p}}{2\pi} \right) \left| \tilde{\chi}_{dpr}(q, t) \right\rangle \Bigg|_{p' \to p}
$$

$$
= \frac{1}{4} \delta \left(\frac{\vec{p'} - \vec{p}}{2\pi} \right) e^{i(\Phi_l - \Phi_r)} \sum_d \left\langle \tilde{\chi}_{dpl}(q, t) | \tilde{\chi}_{dpr}(q, t) \right\rangle, \tag{D1}
$$

where $l, r = 1-, 2+$, and we assumed that the continuum functions are normalized to $\delta(\frac{\vec{p}'-\vec{p}}{2\pi})$. Omitting the continuum normalization factor (see the main text) and substituting $|\tilde{\chi}_{dpi\pm}\rangle$ from Eq. (23), we get

$$
\begin{aligned}
I_{l,r}(p) &= \frac{1}{4} e^{i(\Phi_l - \Phi_r)} \sum_d \left(\frac{1}{2} \sum_{b,e} \int_{t_0}^t dt'' e^{-i\epsilon_{ep,bl}t''} f_l(t'') f_{\mathrm{IR}}(t'') \hat{u}_{d,e}(t,t'';E_C) \hat{D}_{ep,bl}(q) |\chi_b(q,t'')\rangle \right)^\dagger \\
&\quad \times \left(\frac{1}{2} \sum_{a,c} \int_{t_0}^t dt' e^{-i\epsilon_{cp,ar}t'} f_r(t') f_{\mathrm{IR}}(t') \hat{u}_{d,c}(t,t';E_C) \hat{D}_{cp,ar}(q) |\chi_a(q,t')\rangle \right) \\
&= \frac{1}{16} e^{i(\Phi_l - \Phi_r)} \sum_{b,e,a,c} \int_{t_0}^t dt'' \int_{t_0}^t dt' e^{+i\epsilon_p(t''-t')} f_l(t'') f_{\mathrm{IR}}(t'') f_r(t') f_{\mathrm{IR}}(t') \\
&\quad \times \langle \chi_b(q,t'') | \hat{D}_{ep,bl}^\dagger(q) \left(\sum_d \hat{u}_{e,d}(t'',t;E_C) \hat{u}_{d,c}(t,t';E_C) \right) \hat{D}_{cp,ar}(q) |\chi_a(q,t')\rangle ,
\end{aligned}
\tag{D2}
$$

where we used $\epsilon_{ep,bl} = \epsilon_{cp,ar} = \epsilon_p$, which holds due to our choice of Ω_1 and Ω_2, and $\hat{u}_{d,e}(t,t'';E_C)^\dagger = \hat{u}_{e,d}(t'',t;E_C)$.

We further use the ion-state completeness assumption to replace

$$
\sum_d \hat{u}_{e,d}(t'',t;E_C)\hat{u}_{d,c}(t,t';E_C) = \hat{u}_{e,c}(t'',t';E_C), \tag{D3}
$$

yielding Eqs. (30) and (31) of the main text.

APPENDIX E: DERIVATION OF EQ. (47)

For a one-dimensional harmonic oscillator of unit effective mass and force constant ω_i^2,

$$
\left(-\frac{1}{2}\frac{\partial^2}{\partial q_i^2} + \frac{1}{2}\omega_i^2 q_i^2 - \frac{1}{2}\omega_i \right) \chi_{0,i}(q_i) = 0, \tag{E1}
$$

the ground-state eigenfunction is given by

$$
\chi_{0,i}(q_i) = \left(\frac{\omega_i}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\omega_i}{2}q_i^2}, \tag{E2}
$$

$$
|\chi_0(q)\rangle = \prod_i \chi_{0,i}(q_i), \tag{E3}
$$

where q_i is the displacement from the equilibrium position $q_{0,i}$ and ω_i is the vibrational quantum. The multidimensional vibrational ground state is a product of $\chi_{0,i}$ for all modes. The first few nonzero moments of $\chi_{0,i}$, which are required below, are given by

$$
\int dq_i \chi_{0,i}^2(q_i) = 1, \tag{E4}
$$

$$
\int dq_i q_i^2 \chi_{0,i}^2(q_i) = \frac{1}{2\omega_i}, \tag{E5}
$$

$$
\int dq_i q_i^4 \chi_{0,i}^2(q_i) = \frac{3}{4\omega_i^2}. \tag{E6}
$$

The classical turning points of the ground-state vibrational wave function of mode i are found at $q_i = \pm\omega_i^{-\frac{1}{2}}$.

As long as matrix elements $\hat{D}$ are sufficiently smooth, they can be expanded in Taylor series:

$$
\hat{D}_{cp,0x} \approx D_x^{(0)} + \sum_i D_x^{(i)} q_i + \frac{1}{2}\sum_{ij} D_x^{(i,j)} q_i q_j, \tag{E7}
$$

$$
D_x^{(0)} = \hat{D}_{cp,0x}(q_0), \tag{E8}
$$

$$
D_x^{(i)} = \frac{\partial}{\partial q_i}\hat{D}_{cp,0x}(q_0), \tag{E9}
$$

$$
D_x^{(i,j)} = \frac{\partial^2}{\partial q_i \partial q_j}\hat{D}_{cp,0x}(q_0), \tag{E10}
$$

Inserting Eqs. (E3) and (E7) in Eq. (46), we obtain

$$
\begin{aligned}
G_{c,l,r}(p) &\stackrel{\mathrm{ZPE}}{=} \iiint_{-\infty}^{+\infty} \prod_k dq_k \prod_{i,j} \left(\frac{\omega_i}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\omega_i}{2}q_i^2} \left(\frac{\omega_j}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\omega_j}{2}q_j^2} \\
&\quad \times \left(D_l^{(0)} + \sum_k D_l^{(k)} q_k + \frac{1}{2}\sum_{ko} D_l^{(k,o)} q_k q_o \right)^\dagger \left(D_r^{(0)} + \sum_m D_r^{(m)} q_m + \frac{1}{2}\sum_{mn} D_r^{(m,n)} q_m q_n \right) \\
&= \iiint_{-\infty}^{+\infty} \prod_k dq_k \prod_{i,j} \left(\frac{\omega_i}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\omega_i}{2}q_i^2} \left(\frac{\omega_j}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\omega_j}{2}q_j^2} \\
&\quad \times \left[\left(D_l^{(0)} \right)^\dagger D_r^{(0)} + \left(D_l^{(0)} \right)^\dagger \frac{1}{2}\sum_k D_r^{(k,k)} q_k^2 + \sum_k \left(D_l^{(k)} \right)^\dagger D_r^{(k)} q_k^2 + \frac{1}{2}\sum_k \left(D_l^{(k,k)} \right)^\dagger D_r^{(0)} q_k^2 \right.
\end{aligned}
$$

$$+ \frac{1}{4} \sum_k \left(D_l^{(k,k)}\right)^\dagger D_r^{(k,k)} q_k^4 + \frac{1}{4} \sum_{k \neq m} \left(D_l^{(k,k)}\right)^\dagger D_r^{(m,m)} q_k^2 q_m^2 + \frac{1}{2} \sum_{k \neq m} \left(D_l^{(k,m)}\right)^\dagger D_r^{(k,m)} q_k^2 q_m^2 \Bigg]$$

$$= \left(D_l^{(0)}\right)^\dagger D_r^{(0)}$$

$$+ \sum_k \frac{1}{4\omega_k} \left[\left(D_l^{(0)}\right)^\dagger D_r^{(k,k)} + 2 \left(D_l^{(k)}\right)^\dagger D_r^{(k)} + \left(D_l^{(k,k)}\right)^\dagger D_r^{(0)} \right]$$

$$+ \sum_k \frac{3}{16\omega_k^2} \left(D_l^{(k,k)}\right)^\dagger D_r^{(k,k)} + \sum_{k \neq m} \frac{1}{16\omega_k \omega_m} \left(D_l^{(k,k)}\right)^\dagger D_r^{(m,m)} + \sum_{k \neq m} \frac{1}{8\omega_k \omega_m} \left(D_l^{(k,m)}\right)^\dagger D_r^{(k,m)}, \tag{47}$$

where we used parity arguments to drop vanishing contributions containing odd powers of any of the q_i coordinates.

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