# Three-Dimensional Analytical Infinite Order Sudden Quantum Theory for Triatomic Indirect Photodissociation Processes

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## Abstract

Our previously developed analytical infinite order sudden (IOS) quantum theory of triatomic photodissociation is extended to describe indirect photodissociation processes through a real or virtual intermediate state. The theory uses the IOS approximation for the dynamics in the final dissociative channels and an Airy function approximation for the continuum states. These approximations enable us to evaluate the multi-dimensional non-separable transition amplitudes analytically (as one-dimensional quadratures), despite the different natural coordinates for the initial bound, the intermediate resonant, and the final dissociative states. The fragment internal energy distributions are described as a function of the initial and final quantum states and the photon excitation energy. The theory readily permits the evaluation of rotational distributions for high values of the total angular momentum $J$ in the initial bound molecular state, a feature that would be very difficult with close-coupled methods. Paper II applies the theory to describe the photofragment

yield spectrum of NOCl in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition.

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## I. INTRODUCTION

The enormous advancements with theories of the photodissociation dynamics and the explosion in computational power now enable the treatment of full three-dimensional quantum calculations for light tri- and tetra-atomic system dynamics.[1] These computations, however, encounter difficulties in situations with heavier atoms and/or higher energies and with nonadiabatic processes involving several potential energy surfaces, situations in which the number of relevant channels, etc., far exceeds computational capabilities. In addition, full quantum computations often cannot provide detailed physical insight into the mechanisms operative in the dynamics. Thus, it is necessary to have simple approximate models that are reasonably accurate, quick to implement, able to treat more complex systems, and that lend themselves to providing an understanding of the dynamics process.[2–12] These models become more indespensible when the potential surfaces are not known but are to be determined semiempirically by comparison of computed and experimental results and by iterating the potential until reasonable agreement is generated. Such iterative computations require the computational facility afforded by simple models. Full quantum mechanical computations may then be performed using the final potential surfaces, provided the system is simple enough and the approximation methods are sufficiently accurate.[13–17]

We have developed a simple infinite order sudden (IOS) approximation[18–20] and have generalized the Franck-Condon description of the three-dimensional photodissociation dynamics of triatomic molecules[2,3] to provide a useful model satisfying the requirements noted above.[20–23] The theory treats the dynamics in terms of the vastly differing natural dynamical coordinate systems for the bound and dissociative states, but this implies that the bound-continuum transition matrix elements are non-separable three-dimensional integrals.[9,10,22,23] The combination of IOS[13,18,24] and Airy function[3,20,21,23] approximations for the continuum wave functions have been exploited by us to perform the two radial integrals analytically, leaving the one-dimensional integral over the remaining bending degree of freedom to be resolved by use of a quadrature formula. Thus, the theory essentially produces an analytical treatment of the triatomic dissociation dynamics, the photoabsorption spectrum, and the fragment internal state distributions.

Our analytic IOS triatomic dissociation theory has several limitations, some of which are addressed by the extensions developed in the present work. First of all, the theory omits the influence of final state interactions, interactions that produce changes in the nascent Franck-Condon rotational and vibrational fragment distributions. Thus, the analytical IOS theory provides excellent agreement with close-coupled calculations[21,25] when final state interactions may be ignored on the dissociative potential energy surface. However, it is desirable to extend the theory to treat weak final state interactions perturbatively, an extension contained in the present paper. In addition, many photodissociation processes proceed indirectly and, therefore, involve the participation of, at least, three electronic states. When the intermediate resonant state is long lived,[26] our previous theory[21] may be applied by just treating the process as a direct dissociation from the "bound" resonant state to the continuum, but the situation becomes more complicated when the intermediate states are short lived such that the intermediate states strongly overlap.[27,28] However, both cases of weak final state interactions and of weak nonadiabatic interactions can basically be treated formally using the same mathematical tools[14,29] and the same two-potential description with the second order golden rule rate expression.[30,31] One of the potentials arises from the matter-radiation interaction,[32,33] while the second contains the final state interactions or the nonadiabatic coupling. The intermediate states may, therefore, be described as either continuum or quasi-bound states embedded in the continuum, depending on the situation at hand.

We extend our previous analytical IOS[20,21,23] to describe these second order "indirect" photodissociation processes. The use of qualitatively different coordinate systems for the initial, intermediate, and final states now produces the greater complexity of having the product of two three-dimensional non-separable transition matrix elements with sums over a wide range of intermediate states. The application of the IOS and Airy function approximations enables us to reduce the second order golden rule rate expression again to analytical expressions involving one-dimensional quadratures, but now with sums over a vast number of intermediate states. The IOS approximation for an indirect photodissociation process is appropriate provided the lifetimes of the intermediate state are short compared to periods of molecular motion, and this is the situation considered explicitly in paper II where typical intermediate state widths are of order of hundreds of $\mathrm{cm}^{-1}$. When the intermediate states are non-overlaping and long lived with lifetimes shorted than the rotational periods, our previous theory may be applied treating the intermediate state as the "initial" state for a direct photodissociation. Hence, the conditions for the validity of the IOS do not conflict with practical implementations of the theory of indirect photodissociation provided the IOS is applicable to the scattering on the repulsive potential energy surface.

The utility of the IOS formulation is illustrated in paper II by computations of the photofragment yield spectrum for the photodissociation of NOCl to $NO(X^2\Pi_{3/2})+Cl(^2P_{3/2})$ through the $T_1(1^3A'')$ state,[34–36] where experiments by Reisler and coworkers exhibit structure due to broad quasi-bound "intermediate" states on the $T_1$ state.[37]

Section II develops the general theory, while the appendices provide some subtle technical details and a distillation of necessary information from previous papers.[20,21,23]

## II. THEORY

The different photodissociation processes, such as direct photodissociation, scalar predissociation, and vibrational predissociation, may be described through the Hamiltonian

$$H = H_0 + V_I, \tag{2.1}$$

where $V_I$ is the interaction Hamiltonian which couples the intermediate and final continuum eigenstates of $H_0$. If the coupling $V_I$ is sufficiently weak, the rate of indirect dissociation $\Gamma_{fi}$ from the initial bound state $|i>$ to the unbound electronic state $|f>$, mediated by the intermediate states $|r>$, is given by the standard golden rule of second order perturbation theory,

$$\Gamma_{fi} = \frac{2\pi}{\hbar}\left|\sum_r < f\,|\,V_I\,G_r(E)\,\mu\,|\,i>\right|^2. \tag{2.2}$$

where $\mu$ is the photo-excitation interaction operator which couples the initial bound $|i>$ and resonant quasibound $|r>$ states. $G_r(E)$ is the contribution from the resonant state $|r>$,

$$G_r(E) = \frac{|r><r|}{\Delta E_r + i\hbar\,\Gamma_r/2}, \tag{2.3}$$

where $\Delta E_r = E_i + \hbar\,\omega - E_r$ is the energy difference between the initial (ground state energy $E_i$ plus excitation photon energy $\hbar\,\omega$) and resonant states. $\Gamma_r$ is the decay rate of the intermediate resonant state which is given by the usual golden rule expression[3,9,30]

$$\Gamma_r = \frac{2\pi}{\hbar}\sum_f |<f\,|\,V_I\,|\,r>|^2. \tag{2.4}$$

A summation is implicit in Eqs. (2.2) and (2.4) over the resonant state $|r>$ and all energetically allowed final rotational and vibrational quantum states available to the products labelled by $|f>$. The usual Born-Oppenheimer and Condon approximations are invoked. Hence, the initial $|i>$, resonant $|r>$, and final $|f>$ states are written as products of nuclear and electronic wave functions. The electronic matrix elements of $V_I$ are taken to be only weakly dependent on the nuclear coordinates in the region where there is non-negligible overlap between the final and resonant vibrational wave functions, but this approximation is readily lifted to handle weak variations.

### A. Initial and Resonant State Wave Functions

While the general theory may be formulated for situations in which the $|r>$ are either continuum or bound states, the theory is presented using the latter case for illustration and for application in paper II. The initial bound and intermediate resonant quasibound state nuclear wave functions for a bent triatomic molecule are represented in terms of a product basis set of rigid-rotor (asymmetric top) and harmonic oscillator functions,

$$\Psi_i(Q) = \sum_K g_K\,[(2J+1)/8\pi^2]^{1/2}\,D^{J*}_{MK}(\alpha,\beta,\gamma)\prod_{i=1}^{3}\psi_{n_i}(Q_i), \tag{2.5}$$

$$\Psi_r(Q') = \sum_{K'} g'_{K'}\,[2J'+1)/8\pi^2]^{1/2}\,D^{J'*}_{M'K'}(\alpha',\beta',\gamma')\prod_{i=1}^{3}\psi_{n'_i}(Q'_i), \tag{2.6}$$

for the initial $|i>$ and resonant $|r>$ states, respectively. The asymmetric top wave functions are formed from linear combinations of the appropriate symmetric-top functions $D^{J*}_{MK}$ and $D^{J'*}_{M'K'}$ with coefficients $g_K$ and $g'_{K'}$, respectively.[38] The $\psi_{n_i}(Q_i)$ and $\psi_{n'_i}(Q'_i)$ are products of harmonic oscillator wave functions of the normal coordinates $Q_i$ and $Q'_i$, which are generally different. The Euler angles $(\alpha,\beta,\gamma)$ and $(\alpha',\beta',\gamma')$ specify the orientation of the equilibrium principal axes of inertia for $|i>$ and $|r>$, respectively, relative to the space-fixed coordinate system.

The orientational coordinates generally differ for the three electronic states, and the evaluation of Eqs. (2.2) and (2.4) requires using the inter-relations between these different coordinates, which are described in Appendix A. Differences in the equilibrium axes for the two bound states produce the well-known axis switching phenomenon in bound-bound spectroscopy. Anharmonicities and vibration-rotation couplings in both initial and resonant states may be included by taking appropriate linear combinations of harmonic basis functions of the forms (2.5) and (2.6). Below we treat an individual harmonic term arising from the use of anharmonic potentials since the general case follows directly.

### B. Final State Wave Function

Jacobi scattering coordinates are the most appropriate for describing the dynamics on the final repulsive electronic state. The Jacobi coordinates $R$ and $\theta$ are, respectively, the distance between the diatom center of mass and the atom and the angle between the diatomic axis and the atom to diatom vector (Fig. 1). In the asymptotic region where the dissociation coordinate $R\to\infty$, the nuclear wave function on the final electronic surface is written in the scattering coordinate basis as

$$\Psi_f(R;\theta;r) \to \psi_{n_4}(r)\,\psi_{\hat{E}}(R;\theta)\sum_{\mu\, m} < J''M''|lj\mu\, m>\, Y_{jm}(\beta'',\alpha'')\,Y_{l\mu}(\theta_{SF},\phi_{SF}), \tag{2.7}$$

where $\psi_{n_4}(r)$ is a harmonic oscillator function for the vibration of the diatomic photofragment. The angular momentum quantum numbers $(j, m)$ refer to the rotation of the diatomic fragment and its z component, and $(l, \mu)$ are the quantum numbers for the orbital motion of the atom relative to the diatomic center of mass and its $z$ component. The angles $(\beta'', \alpha'')$ are the polar and azimuthal angles specifying the orientation of the diatomic molecule fragment relative to space-fixed axes, while $(\theta_{SF}, \phi_{SF})$ describe the orientation of the atom-diatom vector relative to the space-fixed frame (see Fig. 1). Assuming that no electronic angular momentum is present, the two angular momenta $l$ and $j$ are coupled to provide well-defined values of the total angular momentum and its z component $(J'', M'')$ using the Clebsch-Gordan coefficients $< J''M''|lj\mu m >$.[39–42] Finally, $\psi_{\hat{E}}(R;\theta)$ is the asymptotic continuum wave function for the relative translational motion of the photofragments with asymptotic kinetic energy $\hat{E}$. This wave function depends on $l$ through the centrifugal potential $l(l+1)/(2\mu_1' R^2)$, where $\mu_1'$ is the reduced mass for the relative motion of atom $C$ with respect to the diatomic fragment $A-B$.

Equation (2.7) describes the wavefunction that would result when applying the IOS approximation to a potential energy surface involving the sum of a harmonic oscillator potential in $r$ (with the isolated diatomic photofragment force constant) and a repulsive potential which is a function of $R$ and $\theta$. This dissociative potential energy surface for the continuum state is taken as having the general functional form

$$U(R;\theta) = F(\theta)\, exp[-f(\theta)\,(R-\overline{R})], \tag{2.8}$$

where $F(\theta)$ and $f(\theta)$ are general functions of $\theta$ and $\overline{R}$ is the equilibrium distance between the dissociating atom $C$ and the center of mass of the diatom $A-B$ in the initial bound state. The theory can readily be generalized to describe the adiabatic distortion of the diatomic fragment vibration and, in principle, should be directly applicable to treating final surface scattering wave functions containing a linear combination of terms of the form of Eq. (2.7) when the unbound surface is known to be strongly non-separable. In these cases, the translational wave functions $\Psi_{\hat{E}}(R;\theta)$ must be obtained through the numerical solution of coupled differential equations, and the large number of possible final quantum states involved in most photodissociation processes would require that a very large number of channels be retained in the expansion. Below this fragment wavefunction $\psi_{\hat{E}}(R;\theta)$ is taken to be given by the IOS and Airy approximations as described previously.[21,23]

### C. Evaluation of Matrix Elements

The description of the indirect photodissociation in Eq. (2.2) requires the evaluation of matrix elements beteween the resonant state wave function $\Psi_r(Q')$ of Eq. (2.6) and both the initial and asymptotic final state wave functions. Substituting Eq. (2.3) into Eq. (2.2) and using the notation for the wave functions as in Eqs. (2.5)-(2.7) convert Eq. (2.2) into

$$\Gamma_{fi} = \frac{2\pi}{\hbar}\left|\sum_r \frac{<\Psi_f(R;\theta;r)\,|\,V_I\,|\,\Psi_r(Q')><\Psi_r(Q')\,|\,\mu\,|\,\Psi_i(Q)>}{\Delta E_r + i\,\hbar\,\Gamma_r/2}\right|^2, \tag{2.9}$$

with $\Gamma_r$ given by Eq. (2.4) and $\Delta E_r$ defined after Eq. (2.3). One principal difficulty in evaluating the integrals in Eq. (2.8) stems from the fundamentally different coordinate systems, $Q$, $Q'$, and the Jacobi scattering coordinates, appropriate to the separate initial $|i>$, resonant $|r>$, and final $|f>$ states respectively. Consequently, the two integrals in the numerator of Eq. (2.9), as well as those for $\Gamma_r$ in the denominator, are six-dimensional nonseparable matrix elements. However, upon introduction of relations between the Euler angles specifying the molecular orientations in these three states (see Appendix A), integration is performed below over these molecular orientations, leaving the still nontrivial nonseparable three-dimensional transition matrix elements. As outlined below and as described in detail by previous papers,[21,23] use of the IOS approximation[18–20] for the rotational motion and a further Airy function approximation[3,20,21,23] for the continuum wave function enables this multidimensional nonseparable bound-continuum transition amplitude to be reduced to one-dimensional integrals which can be represented in analytical forms by the use of appropriate quadrature formulas. Thus, for the sake of analytical tractability, the unbound anisotropic potential surface $U(R;\theta)$ in Eq. (2.8) is linearized about the ($\theta$-dependent) classical turning point,[3] thereby generating the Airy function approximation to $\Psi_{\hat{E}}(R;\theta)$ in Eq. (2.7). The Airy function is normalized to a delta function in energy and represents semi-quantitatively the radial motion along the reaction coordinate $R$ for not too low available kinetic energies above the dissociation threshold.[3,13,20–23]

A previous paper[21] describes the relations between normal and scattering coordinates which are necessary for a proper evaluation of the bound-continuum matrix element $< f\,|\,V_I|r >$. Specifically, for a scalar coupling operator $V_I$ and a given rotational state $K'$, the use of the transformation between resonant and final state coordinate systems, the Clebsch-Gordan series, the orthogonality property of rotation matrices, and sum rules for Clebsch-Gordan coefficients[39–42] enable this transition matrix element to be reduced, after invoking the Condon approximation, to the three-dimensional matrix element,

$$
\begin{aligned}
&< \Psi_f(R;\theta;r)\,|\,V_I\,|\,\Psi_r(Q')>= \overline{V_I}\,g_{K'}\left(\frac{(2j+1)\,(2l+1)\,(2J''+1)}{2\,(2J'+1)}\right)^{1/2}\delta_{M'M''}\delta_{J'J''}\\
&\sum_{m'}(-1)^{l-j+m'}\begin{pmatrix} l & j & J''\\ m' & 0 & -m'\end{pmatrix}\\
&\left\langle \Psi_{n_4}(r)\,\Psi_{\hat{E}}(R;\theta)d^{j}_{0m'}(\theta)\,|\,J_B\,|^{1/2}\,|\,d^{J'}_{m'K'}(\phi'_2-\overline{\theta'}+\beta'_0)\prod_{i=1}^{3}\Psi_{n'_i}(Q'_i)\right\rangle\\
&\equiv \overline{V_I}\,g_{K'}\left(\frac{2j+1)\,(2l+1)\,(2J''+1)}{2\,(2J'+1)}\right)^{1/2}\delta_{M'M''}\delta_{J'J''}\\
&\sum_{m'}(-1)^{l-j+m'}\begin{pmatrix} l & j & J''\\ m' & 0 & -m'\end{pmatrix}\;I(j;m';J';K';n'_i;n_4),
\end{aligned}
\tag{2.10}
$$

where the (....) in the second line of this equation is a Wigner $3j$ symbol,[41] $J_B$ is the Jacobian of the transformation from the normal modes $Q'_i$ to the scattering coordinates $(R,\theta,r)$ [see Eq. (B11)], and $d^{j}_{0m'}$ and $d^{J'}_{m'K'}$ are Wigner rotation matrix elements.[41] Finally, the last line of Eq. (2.10) introduces the notation $I(j;m';J';K';n'_i;n_4)$ for the continuum-resonant transition matrix element, where we ignore the weak $l$-dependence of the integral introduced by the $l$-dependence of $\Psi_{\hat{E}}(R;\theta)$.

Introducing the transformation from normal modes to Jacobi coordinates[21] allows the straightforward integration over $r$. Linearization of the final state potential energy surface $U(R;\theta)$ in Eq. (2.8) about the classical turning point enables the resulting more complex radial coordinate $R$ integral in the bound-continuum transition matrix element in Eq. (2.10) to be performed analytically[21] after using the integral representation for the Airy function and an analytical continuation in the complex plane[3]. This process leaves only the one-dimensional integral over $\theta$, which is converted to a fully analytical expression upon introduction of standard quadrature procedures. Previous papers present the lengthy details of the transformation between the resonant state normal coordinates $Q_i'$ and the scattering coordinates $(R, \theta, r)$ on the repulsive potential energy surface[21] along with the details of different rotational coordinate systems[9] (see also Appendix A for a description of some of the equations used) and the relations between them that are necessary for deriving Eq. (2.10).

The angles in the arguments of the Wigner matrices in Eq. (2.10) are defined as follows: The angles $\phi_1'$ and $\phi_2'$ are, respectively, the angular displacements of the diatomic vector and of the atom to diatom vector of the vibrating molecule from their equilibrium resonant state positions. Reference[9] shows that the Jacobi scattering angle $\theta$ between the diatomic molecular axis and the atom to diatomic molecule vector (see Fig. 1) is related to these displacements by

$$\theta = \phi_1' - \phi_2' + \overline{\theta'}, \tag{2.11}$$

where $\overline{\theta'}$ is the equilibrium angle in the resonant quasibound state configuration. The angles $\phi_1'$, and $\phi_2'$ are functions of the internal coordinates of the molecule, and both $\phi_1'$ and $\phi_2'$ vanish, by definition, when the molecule is at the resonant state equilibrium configuration. These angles, in general, depend on all three Jacobi coordinates $(R, \theta, r)$, but as long as stretching vibrations have atomic displacements that are much smaller than bending amplitudes, these dependences can be ignored. Adopting the leading linear approximations[9] for $\phi_1'$ and $\phi_2'$ yields

$$\phi_1' = \rho' \, (\delta - \overline{\delta'}), \tag{2.12}$$

$$\phi_2' = [\rho' - (\partial\theta/\partial\delta)_{eq}] \, (\delta - \overline{\delta'}), \tag{2.13}$$

where $(\delta - \overline{\delta'})$ is the instantaneous displacement of the bond angle relative to the equilibrium angle in the bound resonant state. The molecular parameter $\rho'$ has been determined in Ref.[9] as a function of the atomic masses and interatomic distances, while the angle $\beta_0'$ in Eq. (2.10) has been evaluated in Ref.[23] as

$$\beta_0' = (1/2)\arctan[-2I'_{x'''y'''}/(I'_{x'''x'''} - I'_{y'''y'''})], \tag{2.14}$$

where $I'_{x'''x'''}$ and $I'_{y'''y'''}$ are the moments of inertia about the $x'''$ and $y'''$ axes for the bound resonant state of the triatomic molecule and $I'_{x'''y'''}$ is the product of inertia as evaluated in a body-fixed frame $\{x''', y''', z'''\}$ whose axes coincide with the principal axes of inertia of the resonant state (see Appendix A for a description of the different axes systems). Finally, since most of triatomic molecules are close to symmetric tops, we further assume that the triatomic molecule is a near prolate symmetric top. (Appendix C, however, treats the general case of asymmetric tops.) The solution of the Schrödinger equation for symmetric tops can be expressed in terms of normalized associated Legendre and Jacobi polynomials which then permits representing the reduced rotation matrices $d^j_{0m'}(\theta)$ and $d^{J'}_{m'K'}(\phi_2' - \overline{\theta'} + \beta_0')$ in Eq. (2.10) in terms of these analytical functions, respectively.[21,23,43]

The transition rate $\Gamma_r$ in the denominator of Eq. (2.9) is just the sum over the fragment rotational quantum number $j$ and the diatomic photofragment vibrational quantum number $n_4$ of the square of the same multidimensional transition amplitudes discussed above. Since scalar coupling is assumed for the resonant to final electronic state matrix element and since we simplify the algebra by approximating the rotational motions by symmetric top wave functions in both the initial and resonant states, this approximation permits the elimination of the sums over $K$ and $K'$ in Eqs. (2.5) and (2.6), and the resonant state widths $\Gamma_r$ may be written using Eq.(2.6) of Ref.[23] as

$$\Gamma_r(J';K';n_i') = \overline{V}_I^2 \sum_{j,n_4} \sum_{m'} (j+1/2) \Big| < \Psi_{n_4}(r)\, \Psi_{\hat{E}}(R;\theta)\, d^j_{0m'}(\theta)\, |J_B|^{1/2}\, | \\ d^{J'}_{m'K'}(\phi_2' - \overline{\theta'} + \beta_0') \prod_{i=1}^{3} \Psi_{n_i'}(Q_i') > \Big|^2 \delta_{J'J''}\, \delta_{M'M''}$$

$$\equiv \overline{V_I}^2 \sum_{j,n_4} \sum_{m'} (j+1/2) \left| I(j;m';J';K';n_i';n_4) \right|^2 \delta_{J'J''}\, \delta_{M'M''}. \tag{2.15}$$

Consequently, the integral $< .... >$ in Eq. (2.15) requires the calculation of the same integral $I(j;m';J';K';n_i';n_4)$ defined in Eq. (2.10) and evaluated previously.[23]

### D. Radiative (Dipole) and Scalar Couplings

The initial to resonant state transition matrix element may be written, using Eqs. (2.5) and (2.6), as

$$\begin{aligned}
&< \Psi_r(Q') \,|\, \mu \,|\, \Psi_i(Q) > \\
&= \left\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] \Psi^{J'}_{M'K'}(\alpha',\beta',\gamma') \,|\, \mu \,|\, \Psi^{J}_{MK}(\alpha,\beta,\gamma) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle \\
&= \frac{[(2J+1)\,(2J'+1)]^{1/2}}{8\pi^2} \\
&\left\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] D^{J'}_{M'K'}(\alpha',\beta',\gamma') \,|\, \mu \,|\, D^{J}_{MK}(\alpha,\beta,\gamma) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle,
\end{aligned} \tag{2.16}$$

where $\mu$ is the electronic transition dipole coupling. The matrix element in Eq. (2.16) involves integration over both the Euler angles specifying the orientation of the molecule and the internal vibrational coordinates. The angular integral from Eq. (2.16), containing the product of rotation matrices, may only be evaluated after introducing the relation between the orientations $(\alpha,\beta,\gamma)$ and $(\alpha',\beta',\gamma')$ of the molecule in the initial and intermediate states, respectively. The resolution of this integral and the intermediate-continuum state matrix element below require the specification of the different reference coordinate systems for the initial $|i>$, the intermediate resonance $|r>$, and the final $|f>$ states. (Appendix A describes these coordinate systems and their inter-relations).

The remainder of the integral in Eq. (2.16) involves the vibrational motions in the initial and resonant bound states. Although the evaluation of this integral over the stretching modes is straightforward, the extensive algebra is summarized in Appendix B. Equation (2.16) assumes the bent triatomic molecule in the initial and resonant states to be a near prolate symmetric top. As described in Appendix C, asymmetric top wave functions may be incorporated explicitly into the theory after lifting some approximations in the rotation transformations described in Appendix A. More general cases involving anharmonicities or vibration-rotation interactions are readily treated using linear combinations of wave functions of the forms of Eqs. (2.5) and (2.6). The following treatment may then be applied to the full wave function, *term by term.*

Introducing the Born-Oppenheimer wave functions of Eqs. (2.5) and (2.6) for the initial and resonant states, respectively, and a spherical tensor basis to express the polarization $\hat{e}$ of the photon and of the electonic coordinates, the *qth* spherical tensor component of the dipole operator[40] for the matter-radiation interaction Hamiltonian is given by[32]

$$\mu_q = A\,\mu_{ri} \sum_{M''} (-1)^q \hat{e_q}\, (\frac{4\pi}{3})^{1/2}\, Y_{1M''}(\beta''', \alpha''')\, D^1_{qM''}(\alpha, \beta, \gamma), \tag{2.17}$$

where A is a constant whose square is proportional to the energy density of photons for the given frequency and polarization $\hat{e}$,[33] and $\mu_{ri}$ is the electronic dipole transition matrix element between the initial and resonant states. The rotation matrix $D^1_{qM''}(\alpha, \beta, \gamma)$ can be expressed in terms of space-fixed coordinates, as in Eq. (A3), by

$$D^1_{qM''}(\alpha, \beta, \gamma) = \sum_{nn'} D^1_{qn}(\phi_{SF}, \theta_{SF}, \gamma_{SF})\, D^1_{nn'}(0, \phi_2 - \overline{\theta}, 0)\, D^1_{n'M''}(\alpha_0, \beta_0, \gamma_0), \tag{2.18}$$

while the definitions for the different coordinate systems (see Appendix A) produce the correspondence

$$\phi'_{SF} = \phi_{SF}; \theta'_{SF} = \theta_{SF}; \gamma'_{SF} = \gamma_{SF}. \tag{2.19}$$

The angles $\phi_2$ and $\overline{\theta}$ in the argument of the rotation matrix in Eq. (2.18) are, respectively, the angular displacement of the atom to diatom vector of the vibrating molecule from its equilibrium initial state position in the rotating coordinate system (defined by an analogous expression to Eq. (2.13) with $\overline{\delta'}$ replaced by $\overline{\delta}$ and $\rho'$ substituted by $\rho$) and the equilibrium Jacobi angle in the initial state configuration.

Equations (2.18) and (2.19) in combination with Eq. (A3) (and a similar one for the initial bound state) transform Eq. (2.16) into

$$\left\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] \Psi^{J'}_{M'K'}(\alpha',\beta',\gamma') \,|\, \mu_q \,|\, \Psi^{J}_{MK}(\alpha,\beta,\gamma) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle$$

$$= A\,\mu_{ri} \sum_{M''} (-1)^q\, \hat{e}_q \,(\frac{4\pi}{3})^{1/2}\, \frac{[(2\,J+1)\,(2\,J'+1)]^{1/2}}{8\,\pi^2}$$

$$\sum_{m\,m'} \sum_{n\,n'} \sum_{m''\,m'''} \left\langle \left[\prod_{i=1}^{3} \Psi_{n'_{i'}}(Q_i')\right] D^{J'}_{M'\,m''}(\phi_{SF},\theta_{SF},\gamma_{SF})\, D^{J'}_{m''\,m'''}(0,\phi_2'-\overline{\theta'},0)\right.$$

$$D^{J'}_{m'''\,K'}(\alpha_0',\beta_0',\gamma_0') \,|\, D^{1}_{q\,n}(\phi_{SF},\theta_{SF},\gamma_{SF})\, D^{1}_{n\,n'}(0,\phi_2-\overline{\theta},0)$$

$$D^{1}_{n'\,M''}(\alpha_0,\beta_0,\gamma_0) \,|\, D^{J}_{M\,m}(\phi_{SF},\theta_{SF},\gamma_{SF})\, D^{J}_{m\,m'}(0,\phi_2-\overline{\theta},0)$$

$$\left. Y_{1M''}(\beta''',\alpha''')\, D^{J}_{m'\,K}(\alpha_0,\beta_0,\gamma_0) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle, \tag{2.20}$$

where the integrals over the three internal motions are non-separable because of the bend-stretch coupling between vibrational degrees of freedom.[21,23] The Euler angle integral over $(\phi_{SF},\theta_{SF},\gamma_{SF})$ in Eq. (2.20) involves three rotation matrices and can be expressed in terms of Wigner $3j$ symbols as[40,41]

$$< D^{J'}_{M'\,m''}(\phi_{SF},\theta_{SF},\gamma_{SF}|D^{1}_{q\,n}(\phi_{SF},\theta_{SF},\gamma_{SF})|D^{J}_{M\,m}(\phi_{SF},\theta_{SF},\gamma_{SF} >$$
$$= 8\,\pi^2 \begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix}. \tag{2.21}$$

Assuming symmetric top wave functions in both initial $|JKM>$ and resonant $|J'K'M'>$ states produces the simplifications $\alpha_0=\gamma_0=\alpha_0'=\gamma_0'=0$, which allow the sums over $m'''$, $n'$, and $m'$ in Eq. (2.20) to be explicitly performed through use of the sum rules for the reduced rotation matrices,[39]

$$\sum_{m'''} d^{J'}_{m''\,m'''}(\phi_2'-\overline{\theta'})\, d^{J'}_{m'''\,K'}(\beta_0') = d^{J'}_{m''\,K'}(\phi_2'-\overline{\theta'}+\beta_0'), \tag{2.22}$$

$$\sum_{n'} d^{1}_{n\,n'}(\phi_2-\overline{\theta}) d^{1}_{n'\,M''}(\beta_0) = d^{1}_{n\,M''}(\phi_2-\overline{\theta}+\beta_0), \tag{2.23}$$

$$\sum_{m'} d^{J}_{m\,m'}(\phi_2-\overline{\theta}) d^{J}_{m'\,K}(\beta_0) = d^{J}_{m\,K}(\phi_2-\overline{\theta}+\beta_0). \tag{2.24}$$

We assume in Eq. (2.25), for illustration and for use in paper II, that the transition is polarized in the plane of the molecule (i.e., $\alpha'''=0$). Therefore, $\beta'''$ is the angle between the transition dipole moment and the body-fixed $z'''$ axis (see Appendix A). This assumption of an in-plane transition moment may readily be lifted as described in Appendix C. Given this choice of transition moment and applying the identity,[39,40]

$$Y_{1\,M''}(\beta''', \alpha''') = (\frac{3}{4\,\pi})^{1/2}\, D^{1*}_{M''\,0}(\alpha''', \beta''', 0) = (\frac{3}{4\,\pi})^{1/2}\, d^{1}_{M''\,0}(\beta'''), \tag{2.25}$$

in conjunction with Eqs. (2.21)-(2.24) enable Eq. (2.20) to be written as

$$\begin{aligned}
&\left\langle \left[\prod_{i=3}^{3} \Psi_{n_i'}(Q_i')\right] \Psi^{J'}_{M'K'}(\alpha', \beta', \gamma') \,|\, \mu_q \,|\, \Psi^{J}_{M\,K}(\alpha, \beta, \gamma) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle \\
&\quad = A\, \mu_{ri} \sum_{M''} (-1)^q\, \hat{e}_q\, [(2\,J+1)\,(2\,J'+1)]^{1/2} \\
&\quad \sum_m \sum_n \sum_{m''} \begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix} \\
&\quad \left\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] d^{J'}_{m''\,K'}(\phi_2' - \overline{\theta'} + \beta_0') \,|\, d^{1}_{n\,M''}(\phi_2 - \overline{\theta} + \beta_0) \,|\right. \\
&\quad \left. d^{J}_{m\,K}(\phi_2 - \overline{\theta} + \beta_0)\, d^{1}_{M''0}(\beta''') \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i\right] \right\rangle,
\end{aligned} \tag{2.26}$$

where we assume in Eq. (2.25), for illustration and for use in paper II, that the transition is polarized in the plane of the molecule (i.e., $\alpha''' = 0$). Therefore, $\beta'''$ is the angle between the transition dipole moment and the body-fixed $z'''$ axis (see Appendix A). This assumption of an in-plane transition moment may readily be lifted as described in Appendix C. The sum over $M''$ in Eq. (2.26) can be performed through further use of sum rules for reduced rotation matrices to yield

$$\sum_{M''} d^{1}_{n\,M''}(\phi_2 - \overline{\theta} + \beta_0)\, d^{1}_{M''\,0}(\beta''') = d^{1}_{n\,0}(\phi_2 - \overline{\theta} + \beta_0 + \beta'''), \tag{2.27}$$

which then permits Eq. (2.20) to be rewritten in the compact form,

$$\begin{aligned}
&\left\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] \Psi^{J'}_{M'K'}(\alpha', \beta', \gamma') \,|\, \mu_q \,|\, \Psi^{J}_{M\,K}(\alpha, \beta, \gamma) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle \\
&= A\, \mu_{ri}\, (-1)^q\, \hat{e}_q\, [(2\,J+1)\,(2\,J'+1)]^{1/2} \\
&\sum_m \sum_n \sum_{m''} \begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix} I_{ri}(J'; m''; K'; n; J; m; K; n_i; n_i'),
\end{aligned} \tag{2.28}$$

where $I_{ri}(J'; m''; K'; n; J; m; K; n_i; n_i')$ is the three-dimensional integral,

$$
\begin{aligned}
&I_{ri}(J'; m''; K'; n; J; m; K; n_i; n_i') \\
&= \Big\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] d^{J'}_{m''\,K'}(\phi_2' - \overline{\theta'} + \beta_0') \\
&\mid d^1_{n\,0}(\phi_2 - \overline{\theta} + \beta_0 + \beta''') \mid d^J_{m\,K}(\phi_2 - \overline{\theta} + \beta_0) \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \Big\rangle.
\end{aligned}
\tag{2.29}
$$

Assuming that the initial state is the ground vibrational state, i.e., $n_i = 0$ ($i = 1, 2, 3$) and performing the integration over the two stretching vibrations in the resonant state (see Appendix B), the three-dimensional integral in Eq. (2.29) may be reduced to the one-dimensional integral,

$$
\begin{aligned}
&I_{ri}(J'; m''; K'; n; J; m; K; n_i') \\
&=< d^{J'}_{m''K'}(\phi_2' - \overline{\theta'} + \beta_0') \mid F(\delta; n_i')\, d^1_{n\,0}(\phi_2 - \overline{\theta} + \beta_0 + \beta''') \mid d^J_{m\,K}(\phi_2 - \overline{\theta} + \beta_0) >,
\end{aligned}
\tag{2.30}
$$

where $F(\delta; n_i')$ is the matrix element resulting from the integration over the resonant state stretching modes as given explicitly by Eq. (B24).

Equation (2.28) is the final one-dimensional integral left from the full original six-dimensional matrix element for the rotational and vibrational motions when the transition is induced by in-plane dipole coupling. The argument $\chi \equiv \phi_2 - \overline{\theta} + \beta_0 + \beta'''$ in the reduced rotation matrix $d^1_{n0}$ of Eq. (2.30) is identical to Bersohn's parameter $\chi$[44] and is the instantaneous angle between the transtion dipole moment and the direction of photodissociation. This point is examined in detail in Ref.[10].

Upon substitution of Eqs. (2.10) and (2.28) into Eq. (2.9), assuming, for convenience, that the triatomic molecule is a prolate symmetric top, and performing a summation over all resonant and final state internal motion quantum numbers, lead to the rate $P_j(J; K; n_4)$ of production of photofragments in the state $|j\ n_4>$ as,

$$P_j(J;K;n_4) = \frac{2\,\pi}{\hbar}\, A^2\, \overline{V_I^2}\, \mu_{ri}^2\, |\hat{e_q}|^2\, \delta_{M\,M'} \sum_l \Bigg| \sum_{n_i'} \sum_{K'} \sum_{J'} \sum_{m'} \sum_{m} \sum_{n} \sum_{m''}$$
$$\Big[(2\,l+1)\,(j+1/2)\,(2\,J+1)\,(2\,J'+1)\Big]^{1/2} (-1)^{(l-j+m')} \begin{pmatrix} l & j & J' \\ m' & 0 & -m' \end{pmatrix}$$
$$\begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix} \frac{I(j;m';J';K';n_i';n_4)}{\Delta\,E_r + i\hbar\Gamma_r/2}$$
$$I_{ri}(J';m'';K';n;J;m;K;n_i')\Bigg|^2, \tag{2.31}$$

where the initial rotational state is $|J\ K>$, the photon energy is $\omega$, and $\hat{e_q}$ is the polarization vector for the incident radiation. The sum over the orbital angular momentum $l$ may be performed upon ignoring the dependence on $l$ of the continuum wave function in the integrand of Eq. (2.10) and using the orthogonality property of the Wigner $3j$ symbols,

$$\sum_l (2\,l+1) \begin{pmatrix} l & j & J'' \\ m' & 0 & -m' \end{pmatrix} \begin{pmatrix} l & j & J'' \\ m'' & 0 & -m'' \end{pmatrix} = \delta_{m'm''}. \tag{2.32}$$

The selective measurement of dissociation fragments with total space-fixed $z$ projection of angular momentum $M$ or with resolution of the fragment $M'$ quantum number is a technically difficult problem, so we consider the average over these two quantum numbers which may be evaluated analytically using the sum rule[41]

$$\sum_{M\,M'} \begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ M & q & M' \end{pmatrix} \delta_{M\,M'} = (2J'+1)^{-1}. \tag{2.33}$$

These steps convert Eq. (2.31) into the final expression for the state-to-state transition rate,

$$P_j(J;K;n_4) = \frac{2\,\pi}{\hbar}\, A^2\, \overline{V}_I^2\, \mu_{ri}^2\, |\hat{e_q}|^2 (j+1/2)\,(2\,J+1)$$
$$\sum_{m'} \Bigg| \sum_{n_i'} \sum_{K'} \sum_{J'} \sum_{m} \sum_{n} \sum_{m''} \begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix} \frac{I(j;m';J';K';n_i';n_4)}{\Delta E_r + i\hbar\Gamma_r/2}$$
$$I_{ri}((J';m'';K';n;J;m;K;n_i')\Bigg|^2. \tag{2.34}$$

When the dissociation is induced by nonadiabatic coupling between the initial and intermediate resonant states, $\mu$ is a scalar operator. The limit of $\mu$ as a scalar coupling operator may be obtained from Eq. (2.34) by replacing 1 by 0 and by setting the photon quantum number $n = 0$ in the Wigner $3j$ symbol and in the photon rotation matrix involved in $I_{ri}(J'; m''; K'; n; J; m; K; n_i; n_i')$ [see Eq. (2.29)], followed by the use of the relations,[41,42]

$$\begin{pmatrix} J & 0 & J' \\ m & 0 & m'' \end{pmatrix} = (-1)^{j-m-m''}(2J+1)^{-1/2}\delta_{JJ'}\delta_{mm''}, \tag{2.35}$$

$$\begin{aligned} &\sum_m d^{J*}_{mK}(\phi_2 - \overline{\theta} + \beta_0)\, d^{J'}_{mK'}(\phi_2' - \overline{\theta'} + \beta_0') \\ &= d^J_{K'K}(\phi_2 - \phi_2' + \overline{\theta'} - \overline{\theta} + \beta_0 - \beta_0')\,\delta_{JJ'} \equiv d^J_{K'K}(\vartheta)\,\delta_{JJ'}, \end{aligned} \tag{2.36}$$

thus allowing the unnormalized final state angular momentum distributions for scalar coupling to be written as

$$\begin{aligned} &P_j(J'; K; n_i; n_4) = \frac{2\pi}{\hbar}\,\overline{V_I}^2\,\overline{\mu}^2\,(j+1/2) \\ &\sum_{m'}\left|\sum_{K',n_i'} \frac{I'_{ri}(J; K'; K; n_i; n_i')\, I(j; m'; J'; K'; n_i'; n_4)}{\Delta E_r + i\hbar\,\Gamma_r/2}\right|^2 \delta_{M'M''}\,\delta_{J'J''}\,\delta_{MM''}\,\delta_{JJ'}, \end{aligned} \tag{2.37}$$

where $I'_{ri}(J; K'; K; n_i; n_i')$ is given by

$$I'_{ri}(J; K'; K; n_i; n_i') = \left\langle \left[\prod_{i=1}^{3} \Psi_{n_i'}(Q_i')\right] |\, d^J_{K'K}(\vartheta)\,| \left[\prod_{i=1}^{3} \Psi_{n_i}(Q_i)\right] \right\rangle, \tag{2.38}$$

which is the transition rate for initial excitation induced by a scalar coupling operator. Assuming again that the initial state is the ground vibrational state, this matrix element may be reduced to the one-dimensional integral,

$$I'_{ri}(J; K'; K; n_i') =< F(\delta; n_i')\,|\, d^J_{K'K}(\vartheta) >, \tag{2.39}$$

where $F(\delta; n_i')$ is the remaining bound-resonant state transition matrix element in Eq. (B.24) after analytical integration over the rotations and the stretching vibrational degrees of freedom.

The different quantum numbers and their associated angular momenta involved in Eqs. (2.34) and (2.37) are summarized in Table I, while the final one-dimensional integrals for the transition rate are presented in Eqs. (2.28) and (2.37) for dipole and scalar couplings, respectively. The integrals over the one-dimensional angular vibrational motion in these two equations can be performed numerically using standard quadrature methods.

## III. CONCLUSIONS

We have extended our previously developed three-dimensional analytical infinite order sudden (IOS) quantum- mechanical theory to study indirect and nonadiabatic photodissociaiton processes through a real or virtual unstable intermediate state. As an illustration of the general theory, the initial bound and intermediate states are described by harmonic potentials, while the dynamics in the final repulsive state are modeled as occuring on an anisotropic repulsive potential energy surface. In particular, the use of the Airy function approximation for the continuum wave function $\Psi_{\hat{E}}(R;\theta)$ in Eq. (2.7) allows us to treat general dissociative potential energy surfaces of the form of Eq. (2.8) which may be fit to available *ab initio* calculations. The theory uses the second order golden rule rate expression for weak nonadiabatic couplings or final state interactions. The initial and resonant state nuclear wave functions are represented in terms of a basis set of rigid-rotor and product harmonic oscillator functions in the natural (or local) modes appropriate to these bound states, while the dynamics on the dissociative surface are described using the IOS approximation and the natural asymptotic Jacobi scattering coordinates appropriate to this repulsive surface. This choice of bound and IOS wave functions leads to nonseparable three-dimensional transition amplitudes between the continuum and bound resonant states. Integration is performed analytically over two of the degrees of freedom after introducing the IOS and Airy approximations. We thus analytically compute all the transition matrix elements, since the remaining one-dimensional integrals are represented in analytic form using standard quadrature procedures.

Paper II applies the theory to the computation of the $J = 0$ photofragment yield spectrum of NOCl in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ absorption for producing the NO fragment in its vibrational states $n_{NO} = 0$, 1, and 2, along with calculations of the thermally averaged fragment rotational energy distributions. The latter computations involve the treatment of high total angular momenta $J$ and large numbers of final channels, a feature that would be rather expensive with close coupled methods.

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## APPENDIX A: COORDINATE SYSTEMS INVOLVED IN EVALUATING ROTATIONAL MATRIX ELEMENTS FOR BENT TRIATOMIC INDIRECT PHOTODISSOCIATIONS

The description of an indirect photodissociation process requires the use of different reference coordinate systems (see Fig. 1) and the relations between the Euler angles for the three states $|i>$, $|r>$, and $|f>$. The coordinate systems for the initial and final states have already been described[9,10] and are not repeated here. Similarly, the coordinate systems for the intermediate bound state are defined as follows:

$(x', y', z')$ is a space-fixed nonrotating frame in the resonant bound state.

$(\hat{x}', \hat{y}', \hat{z}')$ is a body-fixed frame for the resonant state, with the vector from atom A to atom B parallel to the $\hat{z}'$ axis, with $\hat{z}'_A > \hat{z}'_B$, with atom C in the $\hat{x}' - \hat{z}'$ plane, and with $\hat{x}'_C > \hat{x}'_B$.

$(\hat{x}'_0, \hat{y}'_0, \hat{z}'_0)$ is a body-fixed frame which satisfies the Eckart conditions for the resonant bound state configuration and which is coincident with $(\hat{x}', \hat{y}', \hat{z}')$ when the molecule is in its resonant state equilibrium position.

$(\hat{\hat{x}}', \hat{\hat{y}}', \hat{\hat{z}}')$ is a body-fixed frame for the resonant state, with $\hat{\hat{z}}'$ coincident with the vector from the diatomic center of mass to the atom and with the molecule lying in the $\hat{\hat{x}}' - \hat{\hat{z}}'$ plane with $\hat{\hat{x}}'_B > 0$.

$(\hat{\hat{x}}'_0, \hat{\hat{y}}'_0, \hat{\hat{z}}'_0)$ is a body-fixed frame which satisfies the Eckart conditions for the resonant bound state configuration and which coincides with $(\hat{\hat{x}}', \hat{\hat{y}}', \hat{\hat{z}}')$ when the molecule is in its resonant state equilibrium position.

$(x''', y''', z''')$ is a body-fixed frame for the resonant state, with axes coincident with the principal axes of inertia in that bound state configuration and with $z'''$ along the axis whose moment of inertia differs most from the other two.

$(x'''', y'''', z'''')$ is a body-fixed frame with $z''''$ along the transition dipole moment for the photodissociative transition.

If $R(\alpha', \beta', \gamma')\{x', y', z'\}$ denotes the rotation of the $\{x', y', z'\}$ coordinate system by the

Euler angles $(\alpha', \beta', \gamma')$,[39] then these axis systems are related by the following rotation operations:

$$
\begin{aligned}
&R(\alpha',\beta',\gamma')\{x',y'z'\} \to \{x''',y''',z'''\},\\
&R(\alpha'',\beta'',\gamma'')\{x',y',z'\} \to \{\hat{x}',\hat{y}',\hat{z}'\},\\
&R(\phi'_{SF},\theta'_{SF},\gamma'_{SF})\{x',y',z'\} \to \{\hat{\hat{x}}',\hat{\hat{y}}',\hat{\hat{z}}'\},\\
&R(\alpha'_0,\beta'_0,\gamma'_0)\{\hat{x}'_0,\hat{y}'_0,\hat{z}'_0\} \to \{x''',y''',z'''\},\\
&R(\alpha''',\beta''',\gamma''')\{x''',y''',z'''\} \to \{x'''',y'''',z''''\},\\
&R(0,\phi'_1,0)\{\hat{x}',\hat{y}',\hat{z}'\} \to \{\hat{x}'_0,\hat{y}'_0,\hat{z}'_0\},\\
&R(0,\phi'_2,0)\{\hat{\hat{x}}',\hat{\hat{y}}',\hat{\hat{z}}'\} \to \{\hat{\hat{x}}'_0,\hat{\hat{y}}'_0,\hat{\hat{z}}'_0\},\\
&R(0,\overline{\theta'},0)\{\hat{x}'_0,\hat{y}'_0,\hat{z}'_0\} \to \{\hat{\hat{x}}'_0,\hat{\hat{y}}'_0,\hat{\hat{z}}'_0\},
\end{aligned} \tag{A1}
$$

The equations (A1) may be considered as definitions of the angles appearing in the various rotation operators and rotational functions for the resonant state, consistent with the various coordinate systems already defined. In particular, the identity

$$
R(\alpha',\beta',\gamma')\{x',y',z'\} = R(\alpha'_0,\beta'_0,\gamma'_0)R^{-1}(0,\overline{\theta'},0)R(0,\phi'_2,0)R(\phi'_{SF},\theta'_{SF},\gamma'_{SF})\{x',y',z'\}, \tag{A2}
$$

and the addition theorem of rotation matrices[41,42] enable the rotational part of the resonant state wave function in Eq. (2.6) to be written as

$$
\begin{aligned}
D^{J'*}_{M'K'}(\alpha',\beta',\gamma') = \sum_{m''m'''} & D^{J'*}_{M'm''}(\phi'_{SF},\theta'_{SF},\gamma'_{SF})\\
& D^{J'*}_{m''m'''}(0,\phi'_2-\overline{\theta'},0)\, D^{J'*}_{m'''K'}(\alpha'_0,\beta'_0,\gamma'_0),
\end{aligned} \tag{A3}
$$

with a similar expression for the rotational part of the initial state wave function in Eq. (2.5).

## APPENDIX B: ANALYTICAL EVALUATION OF THE BOUND-BOUND MATRIX ELEMENT INVOLVING THE STRETCHING MODES FOR BENT TRIATOMIC PHOTODISSOCIATIONS

The evaluation of the integral over the vibrational motions in Eq.(2.16) requires first the transformation from normal modes to internal coordinates in both initial and resonant states of the bound triatomic molecule.

The vibrational wave functions for the initial bound state are given explicitly as the products ($i = 1, 2, 3$) of the individual mode functions,

$$\Psi_{n_i}(Q_i) = 2^{-n_i/2}(n_i!)^{-1/2}\left(\frac{\omega_i}{\pi\hbar}\right)^{1/4}\exp(-\frac{1}{2}Q_i^2)H_{n_i}(Q_i), \tag{B1}$$

with a similar equation for the resonant state in which primes are on the $Q_i$ and $n_i$. The coordinates $(Q_i, Q_i')$ are mass weighted and the transformation from the normal modes $(Q_i, Q_i')$ to the internal coordinates $(r_1 \equiv r_{AB}, r_2 \equiv r_{BC}, \delta)$ can be expressed as $(q_i = (\omega_i/\hbar)^{1/2}Q_i)$,

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} (\omega_1/\hbar)^{1/2} & 0 & 0 \\ 0 & (\omega_2/\hbar)^{1/2} & 0 \\ 0 & 0 & (\omega_3/\hbar)^{1/2} \end{pmatrix} A^{-1} \begin{pmatrix} r_1 - r_1^o \\ r_2 - r_2^o \\ \delta - \overline{\delta} \end{pmatrix} \equiv M \begin{pmatrix} r_1 - r_1^o \\ r_2 - r_2^o \\ \delta - \overline{\delta} \end{pmatrix}, \tag{B2}$$

with a similar equation containing primes again applying for the resonant state. The matrices $A^{-1}$ and $A'^{-1}$ are the transformations from internal coordinates to normal modes[45] in the initial and resonant states; $(r_1^o \equiv \overline{r}_{AB}, r_2^o \equiv \overline{r}_{BC}, \overline{\delta})$ and $(r'^o_1 \equiv \overline{r'}_{AB}, r'^o_2 \equiv \overline{r'}_{BC}, \overline{\delta'})$ are the equilibrium values of the internal coordinates in the initial and resonant states, respectively.

Introducing a vector notation in which $q$, $q'$, $(r - r_o)$ , $(r - r_o')$ are column vectors, enables Eq. (B2) to be expressed in matrix form as

$$q = M\,(r - r_o), \tag{B3}$$

where the transpose operation implies, for example, $(\widetilde{r - r_0}) \equiv (r_1 - r_1^0, r_2 - r_2^0, \delta - \overline{\delta})$ and a similar equation applies for $(\widetilde{r - r_0'})$. Combining Eq. (B3) and a similar one for the resonant state provides the transformation between resonant and initial state normal modes,

$$q' = M'M^{-1}q + M'\,(r_o - r'_o) \equiv \Lambda\, q + \Delta. \tag{B4}$$

Equation (B4) enables deriving the useful relation

$$\begin{aligned} \tilde{q}'q' = q'^2 &= (\Lambda\, \widetilde{q + \Delta})\,(\Lambda\, q + \Delta) \\ &= \tilde{q}\,\tilde{\Lambda}\,\Lambda\, q + \tilde{\Delta}\,\Delta + 2\,\tilde{\Delta}\,\Lambda\, q, \end{aligned} \tag{B5}$$

which is now applied.

Substituting Eqs. (B4) and (B5) into Eq. (B2) and using the usual generating functions for Hermite polynomials[31] allow recasting the product of vibrational wave functions in Eqs. (2.5) and (2.6) to the convenient form,

$$\begin{aligned} \prod_{i=1}^{3} \Psi_{n_i}(Q_i) = 2^{-\sum_{i=1}^{3} n_i/2} \frac{1}{(\pi\hbar)^{3/4}} &\left[ \prod_{i=1}^{3} (n_i!)^{-1/2} (\omega_i)^{1/4} \left(\frac{\partial}{\partial t_i}\right)^{n_i} \right] \\ &\exp\left[ -\frac{1}{2}\tilde{q}q + 2\tilde{t}q - \tilde{t}t \right]\Bigg|_{t_i=0} \end{aligned} \tag{B6}$$

$$\begin{aligned} \prod_{i=1}^{3} \Psi_{n'_i}(Q'_i) = 2^{-\sum_{i=1}^{3} n'_i/2} \frac{1}{(\pi\hbar)^{3/4}} &\left[ \prod_{i=1}^{3} (n'_i!)^{-1/2} (\omega'_i)^{1/4} \left(\frac{\partial}{\partial t'_i}\right)^{n'_i} \right] \\ \exp\left[ -\frac{1}{2}(\tilde{q}\tilde{\Lambda}\Lambda q + \tilde{\Delta}\Delta + 2\tilde{\Delta}\Lambda q) + 2\tilde{t'}(\Lambda q + \Delta) - \tilde{t'}t' \right]&\Bigg|_{t'_i=0}, \end{aligned} \tag{B7}$$

where the multiple differential operators $(\partial/\partial t_i)$ and $(\partial/\partial t'_i)$ for the generating functions apply to the initial and resonant states, respectively. Equations (B6) and (B7) also employ the vector notation $\tilde{t} = (t_1, t_2, t_3)$ and $\tilde{t} = (t'_1, t'_2, t'_3)$, with $t$ and $t'$ column vectors. Combining all these ingredients the integral over the vibrational degrees of freedom in Eq. (2.16) may be evaluated from

$$\begin{aligned} &< \prod_{i=1}^{3} \Psi_{n_i}(Q_i) | \prod_{i=1}^{3} \Psi_{n'_i}(Q'_i) > \\ &= 2^{-\frac{1}{2}\sum_{i=1}^{3}(n_i+n'_i)} \frac{1}{(\pi\hbar)^{3/2}} \left[ \prod_{i=1}^{3} (n_i! n'_i!)^{-1/2} (\omega_i \omega'_i)^{1/4} \left(\frac{\partial}{\partial t_i}\right)^{n_i} \left(\frac{\partial}{\partial t'_i}\right)^{n'_i} \right] \\ &\int_{-\infty}^{\infty} \prod_{i=1}^{3} dq_i \exp\left[ -\frac{1}{2}[\tilde{q}(\tilde{\Lambda}\Lambda + \hat{1})q] + 2(\tilde{t} - \frac{1}{2}\tilde{\Delta}\Lambda + \tilde{t'}\Lambda)q \right. \\ &\left. -\frac{1}{2}\tilde{\Delta}\Delta + 2\tilde{t'}\Delta - \tilde{t}t - \tilde{t'}t' \right]\Bigg|_{t_i=t'_i=0} |J_{vv'}|^{1/2}, \end{aligned} \tag{B8}$$

where $\hat{1}$ is the unit matrix and $J_{vv'}$ is the Jacobian of the transformation in Eq. (B4). The Jacobian is evaluated as follows: First, observe that when integrating over the $Q$ - space coordinates, the normalization condition in $Q'$ - space can be expressed as

$$\prod_{i=1}^{3}\int_{-\infty}^{\infty}\left|\Psi_{n_i'}(Q_i'(Q_i))\right|^2\left|\frac{\partial Q_i'}{\partial Q_i}\right|dQ_i = 1, \tag{B9}$$

while use of the transformation from mass weighted coordinates $(Q_i', Q_i)$ to the reduced coordinates $(q_i', q_i)$ converts Eq. (B9) into

$$\prod_{i=1}^{3}\int_{-\infty}^{\infty}\left|\Psi_{n_i'}(q_i'(q_i))\right|^2\left|\frac{\partial q_i'}{\partial q_i}\right|\frac{\hbar}{(\omega_i\omega_i')^{1/2}}\,dq_i = 1. \tag{B10}$$

Thus, introducing the linear transformation (B4) into (B10) the square root of the Jacobian in Eq. (B8) is seen to be given by

$$|J_{vv'}|^{1/2} = \left|\frac{Det M'}{Det M}\right|^{1/2}\frac{\hbar^{3/2}}{\prod_{i=1}^{3}(\omega_i\omega_i')^{1/4}}. \tag{B11}$$

Define the row vector $\tilde{b}$ and the (symmetric) matrix $S$ by

$$\tilde{b} = 2(\tilde{t} - \frac{1}{2}\tilde{\Delta}\Lambda + \tilde{t}'\Lambda), \tag{B12}$$

$$S = \tilde{\Lambda}\Lambda + \hat{1}. \tag{B13}$$

The integral in Eq. (B8) reduces to a standard multivariate Gaussian integral, which can be evaluated to yield ($dq = \prod_{i=1}^{3} dq_i$)

$$\int_{-\infty}^{\infty} dq \exp\left[-\frac{1}{2}\tilde{q}Sq + \tilde{b}q\right] = \frac{(2\pi)^{3/2}}{(Det S)^{1/2}}\exp\left[\frac{1}{2}\tilde{b}S^{-1}b\right]. \tag{B14}$$

The integral $I_{ri}(J'; m''; K'; n; J; m; K; n_i; n_i')$ on the right hand side of (2.28) is a non-separable three-dimensional integral, which involves the normal modes wavefunctions for both the initial and resonant states in their respective but different natural coordinate systems. Evaluation of this integral over the stretching modes can be performed as follows: The argument of the exponential function in the integral of Eq. (B14) is expressed in terms of the internal coordinates of the initial state through the linear transformation (B3), thereby converting this argument to

$$-\frac{1}{2}\,\tilde{q}\,S\,q+\tilde{b}\,q=-\frac{1}{2}\,\widetilde{(r-r_0)}\,\tilde{M}\,S\,M\,(r-r_0)+\tilde{b}\,M\,(r-r_0). \tag{B15}$$

Defining the two- and three-dimensional vectors $\tilde{s}$ and $\tilde{W}$ and the matrix B by

$$\tilde{s}=(r_1-r_1^0,r_2-r_2^0), \tag{B16}$$

$$\tilde{W}=\tilde{b}\,M, \tag{B17}$$

$$B=\tilde{M}\,S\,M, \tag{B18}$$

and performing the matrix multiplications convert Eq. (B15) into

$$-\frac{1}{2}\,\tilde{q}\,S\,q+\tilde{b}\,q=-\frac{1}{2}\tilde{s}\,U\,s+\tilde{V}\,s+W_3\,(\delta-\overline{\delta})-\frac{1}{2}\,B_{33}\,(\delta-\overline{\delta})^2, \tag{B19}$$

where matrix elements of $U$ and $V$ are given by

$$U_{ij}=B_{ij},\quad (i,j\leq 2), \tag{B20}$$

$$V_i=W_i-B_{i3}\,(\delta-\overline{\delta}),\quad (i=1,2). \tag{B21}$$

Thus, the integral in Eq. (B14) is transformed to

$$\exp\left[W_3\,(\delta-\overline{\delta})-\frac{1}{2}\,B_{33}\,(\delta-\overline{\delta})^2\right]\int_{-\infty}^{\infty}ds\,|J_{vv'}|^{1/2}\exp\left[-\frac{1}{2}\,\tilde{s}\,U\,s+\tilde{V}\,s\right], \tag{B22}$$

where $ds=ds_1\,ds_2=d(r_1-r_1^0)\,d(r_2-r_2^0)$ and $J_{vv'}$ is the Jacobian in Eq. (B11) for the transformation from normal modes to internal coordinates. The two-dimensional integral in Eq. (B22) is a standard Gaussian integral, which can be evaluated to give [omitting the constant Jacobian factor $|J_{vv'}|^{1/2}$ of Eq. (B11)]

$$\int_{-\infty}^{\infty}ds\,\exp\left[-\frac{1}{2}\,\tilde{s}\,U\,s+\tilde{V}\,s\right]=\frac{2\,\pi}{(Det\,U)^{1/2}}\,\exp\left[\frac{1}{2}\,\tilde{V}\,U^{-1}\,V\right]. \tag{B23}$$

Introducing Eq. (B23) into (B22), incorporating the Jacobian, collecting the $t'$ parameters in Eq. (B8), and assuming the initial state is the ground vibrational state, i.e., $t_i=0$ and

$n_i = 0$ ($i = 1,2,3$), allow, after some rather involved rearrangement, the integral over the resonant state stretching degrees of freedom in Eq. (B8) to be written as

$$< \prod_{i=1}^{3} \Psi(Q_i) \,|\, \prod_{i=1}^{3} \Psi(Q_i') >_{(q_1,q_2)} = \frac{2}{\pi^{1/2}} \, 2^{-\sum_{i=1}^{3} n_i'/2} \prod_{i=1}^{3} (n_i'!)^{-1/2}$$

$$\exp\left[-\frac{1}{2}\,\tilde{\Delta}\,\Delta + \sum_{j=0}^{2} A_j\,(\delta - \overline{\delta})^j\right] T(n_1', n_2', n_3') \left|\frac{Det\ M'}{Det\ M\ Det\ U}\right|^{1/2} \equiv F(\delta; n_i'), \tag{B24}$$

where $F(\delta; n_i')$ is a one-dimensional function of the bending angle $\delta$. The three-dimensional array $T(n_1', n_2', n_3')$ is given by

$$T(n_1', n_2', n_3') = \prod_{i=1}^{3} \left(\frac{\partial}{\partial t_i'}\right)^{n_i'} \exp\left[\sum_{i=1}^{3} \gamma_i t_i' + \sum_{i \le j = 1}^{3} \gamma_{ij} t_i' t_j'\right]\Bigg|_{t_i'=0}, \tag{B25}$$

and can be evaluated recursively for any combination of the resonant state vibrational quantum numbers $n_i'$.[20] The molecular parameters $\gamma_n$ and $\gamma_{m\,n}$ in Eq. (B25) are defined by

$$\gamma_n = 2\,\Delta_n - 2 \sum_{j\,l=1}^{2} \sum_{i\,k\,m=1}^{3} \Delta_m\,\Lambda_{m\,i}\,M_{i\,j}\,U_{j\,l}^{-1}\,\Lambda_{n\,k}\,M_{k\,l}$$

$$+2\left[-\sum_{i=1}^{3}\sum_{j\,l=1}^{2} \Lambda_{ni}\,M_{i\,j}\,U_{j\,l}^{-1}\,B_{l\,3} + \sum_{i=1}^{3} \Lambda_n i\,M_{i\,3}\right](\delta - \overline{\delta}), \tag{B26}$$

$$\gamma_{m\,n} = 2\,\epsilon_{m\,n} \sum_{j\,l=1}^{2} \sum_{i\,k=1}^{3} \Lambda_{m\,i}\,M_{i\,j}\,U_{j\,l}^{-1} \Lambda_{n\,k}\,M_{k\,l} - \delta_{m\,n}. \tag{B27}$$

with $\epsilon_{ij} = 1$ if $i = j$ and $\epsilon_{ij} = 2$ if $i \neq j$. The parameters $A_0$, $A_1$, and $A_2$ in Eq. (B24) are given by

$$A_0 = \frac{1}{2} \sum_{j\,l=1}^{2} \sum_{i\,k\,m\,n=1}^{3} \Delta_m\,\Lambda_{m\,i}\,M_{i\,j}\,U_{j\,l}^{-1}\,\Delta_n\,\Lambda_{n\,k}\,M_{k\,l}, \tag{B28}$$

$$A_1 = \sum_{j\,l=1}^{2} \sum_{i\,k=1}^{3} \Delta_k\,\Lambda_{k\,i}\,M_{i\,j}\,U_{j\,l}^{-1}\,B_{l,3} - \sum_{i\,k=1}^{3} \Delta_k\,\Lambda_{k\,i}\,M_{i\,3}, \tag{B29}$$

$$A_2 = \frac{1}{2}\left[\sum_{j\,l=1}^{2} B_{j\,3}\,U_{j\,l}^{-1}\,B_{l\,3} - B_{3\,3}\right]. \tag{B30}$$

Although Eq. (B24) is presented assuming that the initial state is the ground vibrational state, this restriction can easily be lifted. The integral over the resulting stretching modes in Eq. (B8) may be evaluated for any combination of vibrational quantum numbers for the initial and resonant states using the $Q$ centroid method.[46]

## APPENDIX C: ANALYTICAL EVALUATION OF MATRIX ELEMENTS FOR ASYMMETRIC TOP BENT TRIATOMIC MOLECULES

If the triatomic molecule is an asymmetric top, the coefficients $g_K$ and $g'_{K'}$ in Eqs. (2.5) and (2.6) must be explicitly determined by any of the standard methods.[38,47] In such cases, Eqs. (2.22) - (2.24) must be replaced by

$$\sum_{m'''} D^{J'}_{m''m'''}(0,\phi'_2-\overline{\theta'},0)\, D^{J'}_{m'''K'}(\alpha'_0,\beta'_0,\gamma'_0) = D^{J'}_{m''K'}(\psi'_1,\psi'_2,\psi'_3), \tag{C1}$$

$$\sum_{n'} D^{1}_{n\,n'}(0,\phi_2-\overline{\theta},0)\, D^{1}_{n'\,M''}(\alpha_0,\beta_0,\gamma_0) = D^{1}_{n\,M''}(\psi_1,\psi_2,\psi_3), \tag{C2}$$

$$\sum_{m'} D^{J}_{m\,m'}(0,\phi_2-\overline{\theta},0)\, D^{J}_{m'\,K}(\alpha_0,\beta_0,\gamma_0) = D^{J}_{m\,K}(\psi_1,\psi_2,\psi_3), \tag{C3}$$

where the closure relation for rotation matrices has been used[40]. The angles $(\psi'_1,\psi'_2,\psi'_3)$ or $(\psi_1,\psi_2,\psi_3)$ in Eqs. (C1) - C(3) are the resultants of first rotating with $(\alpha'_0,\beta'_0,\gamma'_0)$ or $(\alpha_0,\beta_0,\gamma_0)$ and then with $(0,\phi'_2-\overline{\theta'},0)$ or $(0,\phi_2-\overline{\theta},0)$, respectively. Lifting the assumption of an in-plane transition moment (i.e., of $\alpha'''=0$) in Eq. (2.25) and applying symmetry property of rotation matrices,[40]

$$D^{1*}_{M''0}(\alpha''',\beta''',0) = D^{1}_{0\,M''}(0,-\beta''',-\alpha'''), \tag{C4}$$

transforms the dipole coupling initial to resonant state transition integral of Eq. (2.30) into

$$\begin{aligned} I_{ri}(J';m'';K';n;J;m;K;n'_i) = \sum_{M''} &< D^{J'}_{m''\,K'}(\psi'_1,\psi'_2,\psi'_3)\,| \\ F(\delta;n'_i)\, D^{1}_{n\,M''}(\psi_1,\psi_2,\psi_3)\, D^{1}_{0\,M''}(0,-\beta''',-\alpha''')\,&|\, D^{J}_{m\,K}(\psi_1,\psi_2,\psi_3) > . \end{aligned} \tag{C5}$$

Similarly, the initial to resonant state transition matrix element for an asymmetric top triatomic and scalar coupling becomes, afer using Eq. (2.35),

$$I'_{ri}(J;K';K;n'_i) = \sum_{m} < F(\delta;n'_i)\,|\, D^{J'}_{m\,K'}(\psi'_1,\psi'_2,\psi'_3)\, D^{J}_{K\,m}(-\psi_3,-\psi_2,-\psi_1) > . \tag{C6}$$

Transformation to the body-fixed $(\hat{\hat{x}}',\hat{\hat{y}}',\hat{\hat{z}}')$ frame for the resonant state (see Appendix A) and using the Clebsch-Gordan series, the orthogonality of rotation matrices, and the sum rules for Clebsch-Gordan coefficients permit reducing the expression for $I(j;m';J';K';n_i';n_4)$ in Eq. (2.10) to

$$I(j;m';J';K';n_i';n_4) = \sum_{m''} < \Psi_{n_4}(r)\,\Psi_{\hat{E}}(R;\theta)\,d^{j}_{0\,m'}(\theta)\,|J_B|^{1/2}\,|\,d^{J'}_{m'\,m''}(\phi_2' - \overline{\theta'})$$
$$D^{J'}_{m''\,K'}(\alpha_0',\beta_0',\gamma_0')\prod_{i=1}^{3}\Psi_{n_i'}(Q_i')\ > . \tag{C7}$$

The presence of the rotation matrix $D^{1}_{0\,M''}(0,-\beta''',-\alpha''')$ in Eq. (C7) accounts for the general orientation of the transition moment. Introducing the coefficientes $g_K$ and $g'_{K'}$ for the initial and resonant state asymmetric top rotational wave functions [see Eqs. (2.5) and (2.6)] and performing a summation over the initial state rotational quantum number $K$ convert the dipole coupling state-to-state transition rate of Eq. (2.34) into

$$P_j(J;n_4) = \frac{2\,\pi}{\hbar}\,A^2\,\overline{V}_I^2\,\mu_{ri}^2\,|\hat{e}_q|^2\,(j+1/2)\,(2J+1)$$
$$\sum_{m'}\Bigg|\sum_{n_i'}\sum_{K}\sum_{K'}\sum_{K''}\sum_{J'}\sum_{m}\sum_{n}\sum_{m''} g_K\,g'_{K'}\,g'_{K''}\begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix}\frac{I(j;m';J';K'';l;n_i';n_4)}{\Delta E_r + i\,\hbar\,\Gamma_r/2}$$
$$I_{ri}(J';m'';K';n;J;m;K;n_i')\Bigg|^2, \tag{C8}$$

where $K''$ designates the resonant state rotational quantum number involved in the continuum-resonant state transition matrix element $I(j;m';J';K'';n_i';n_4)$ [see Eqs. (2.10) and (2.15)] and where $I(j;m';J';K';n_i';n_4)$ and $I_{ri}(J';m'';K';n;J;m;K;n_i')$ are replaced by Eqs. (C5) and (C7), respectively. Similarly, the unnormalized final state angular momentum distributions for scalar coupling and asymmetric top wave functions become

$$P_j(J';n_4) = \frac{2\,\pi}{\hbar}\,\overline{V}_I^2\,\overline{\mu}^2\,(j+1/2)\sum_{m'}\Bigg|\sum_{K',n_i'}\sum_{K}\sum_{K''} g_K\,g'_{K'}\,g'_{K''}$$
$$\frac{I'_{ri}(J;K';K;n_i')\,I(j;m';J';K'';n_i';n_4)}{\Delta E_r + i\,\hbar\,\Gamma_r/2}\Bigg|^2\,\delta_{M'M''}\,\delta_{J'J''}\,\delta_{JJ'}, \tag{C9}$$

where the resonant-initial state transition matrix element $I'_{ri}(J;K';K;n_i')$ is given by Eq. (C6) and the initial state is taken to be in the ground vibrational level as in Eq. (2.39).

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TABLE I. Quantum Numbers and Associated Angular Momenta for the Rotational Motions Involved in Indirect Triatomic Photodissociation Processes

| Quantum Number | State | Associated Momentum |
|---|---|---|
| $j$ | $\|f>$ | Diatomic Rotational Angular Momentum |
| $l$ | $\|f>$ | Orbital Angular Momentum |
| $K$ | $\|i>$ | Rotational Angular Momentum |
| $K'$ | $\|r>$ | Rotational Angular Momentum |
| $J$ | $\|i>$ | Total Angular Momentum |
| $J'$ | $\|r>$ | Total Angular Momentum |
| $J''$ | $\|f>$ | Total Angular Momentum |
| $M$ | $\|i>$ | $z$-component of $J$ |
| $M'$ | $\|r>$ | $z'$-component of $J'$ |
| $M''$ | $\|f>$ | $z''$-component of $J''$ |
| $m$ | $\|f>$ | $z''$-component of $j$ |
| $\mu$ | $\|f>$ | $z''$-component of $l$ |

## APPENDIX: FIGURE CAPTION

**Fig. 1:** Body-fixed coordinate systems for a bent triatomic molecule. The angles $(\beta, \alpha)$ give the orientation of the principal axis of smallest moment of inertia (along the $z''$ axis), $(\theta_{SF}, \phi_{SF})$ give the orientation of the atom to diatom vector (along the $\hat{\hat{z}}$ axis), and $(\beta'', \alpha'')$ give the orientation of the diatomic molecule (along the $\hat{z}$ axis), all relative to to the space-fixed frame. The $(\hat{x}\hat{y}\hat{z})$, $(x'y'z')$, and $(\hat{\hat{x}}\hat{\hat{y}}\hat{\hat{z}})$ frames are all body fixed frames specified with the $z$ axis along the three vectors mentioned above. The molecular center of mass is located at the origin, and the diatomic center of mass is indicated by an asterisk. $R$ is the distance from atom C to the center of mass of the diatomic photofragment, and $r$ is the interatomic distance for A-B.