Three-dimensional infinite order sudden quantum theory for indirect photodissociation processes. Application to the photofragment yield spectrum of NOCl in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition. Fragment rotational distributions and thermal averages

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Abstract

The analytical infinite order sudden (IOS) quantum theory of triatomic photodissociation, developed in paper I, is applied to study the indirect photodissociation of NOCl 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 functions. The transition is taken as polarized in the plane of the molecule; symmetric top wave functions are used for both the initial and intermediate bound states; and simple semiempirical model potentials are employed for each state. The theory provides analytical expressions for the photofragment yield spectrum for producing particular final fragment ro-vibrational states as a function of the photon excitation energy. Computations are made of the photofragment excitation spectrum of NOCl in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition for producing the NO fragment in the vibrational states $n_{NO} = 0$, 1, and 2. The computed spectra for the unexcited $n_{NO} = 0$ and excited $n_{NO} = 2$ states are in reasonable agreement with experiment. However, some discrepancies are observed for the singly excited $n_{NO} = 1$ vibrational state, indicating deficiencies in the semiempirical potential energy surface. Computations for two different orientations of the in-plane transition dipole moment produce very similar excitation spectra. Calculations of fragment rotational distributions are performed for high values of the total angular momentum J, a feature that would be very difficult to perform with close-coupled methods. Computations are also made of the thermally averaged rotational energy distributions to simulate the conditions in actual supersonic jet experiments.

I. INTRODUCTION

The photodissociation of triatomic molecules has long been recognized as a prototypical dynamical process that is amenable to both detailed experimental study[1–5] and theoretical calculations.[6–13] Although full quantum descriptions are possible for some triatomic dissociations, approximate theoretical treatments and models of photofragmentation dynamics provide invaluable insights into the interpretation of experimental photoabsorption spectra.[14–19] Consequently, various approximate quantum methods have been developed based upon corresponding approaches to inelastic molecular scattering theory, and several have been applied successfully to describe photodissociation dynamics. These approximate approaches include distorted wave treatments, within both adiabatic[20–22] and diabatic[16,17,23,24] representations, as well as infinite order sudden (IOS)[15,25,26] and coupled states methods.[15,27] Another approach for calculating approximate photofragment quantum state distributions is the generalized Franck-Condon theory,[28–34] which explicitly treats the influence of fundamentally different natural coordinate systems for describing the nuclear motions on the bound and dissociative potential energy surfaces.

Previous papers in this series have developed the extension of the generalized analytical Franck-Condon theory to include anisotropic repulsive potential surfaces in the treatment of the photodissociation of linear and bent triatomic molecules.[35–38] This generalized Franck-Condon model is based on an IOS formulation for the rotational motions and on a further Airy function approximation for the continuum wave functions.[28,35,36,38] These approximations enable the highly non-trivial, multidimensional nonseparable transitions amplitudes to be reduced analytically to one-dimensional integrals which are then represented in analytical forms by use of appropriate quadrature formulas. Prior generalized Franck-Condon theory calculations of photofragment energy and angular distributions demonstrate that this analytical quantum theory accurately reproduces close-coupled quantum fragment rotational distributions with a wide variety of potential functions for which the IOS approximation is applicable and for which final state interactions may be ignored.[35–38]

The preceding paper[39] (hereafter called paper I) extends our IOS approximation[36,38] to treat the indirect photodissociation of triatomic molecules. The approach in paper I provides a useful model in situations a) where there is poor prior knowledge of the repulsive potential energy surfaces, b) where the presence of non-adiabatic interactions couples several potential energy surfaces, and/or c) where the presence of heavier atoms and/or higher energies make close-coupled computations prohibitively expensive or unwarranted. This latter situation is especially relevant when the repulsive potential surfaces are poorly characterized. The treatment in paper I considers weak final state interactions and non-adiabatic photodissociation processes by using the standard golden rule of second-order perturbation theory. The analytical IOS theory again provides closed analytical expressions for the state-to-state transition rates and final state angular momentum distributions.

The present paper illustrates the utility of the analytical IOS formulation by computations of the photodissociation of NOCl to $NO(X^2\Pi_{3/2})$ + $Cl(^2P_{3/2})$ through the $T_1(1^3A'')$ state,[40–42] where experiments by Reisler and coworkers exhibit structure due to broad quasibound "intermediate" states on the T_1 state.[43] Thus, the system is modeled by having the intermediate states described as a bound electronic state coupled to the dissociative continuum by weak final state interactions. The widths of the intermediate state range in the hundreds of cm^{-1}, enabling the IOS approximation to be applied to the intermediate states. The bound portion of the intermediate state surface is modeled based on experimental quasibound vibrational frequencies and photofragment specific absorption intensities, while the dissociative portion is fit to older *ab initio* computations.[42] We use this previously determined potential[38] to focus on the development of the theoretical method, rather than on providing the most complete description of the experiments. Nevertheless, this simple model does display many observed features, thereby providing some insights into the experimental data.

The theory of paper I is applied to the indirect NOCl photodissociation by assuming that the initial rotational state of NOCl (in the ground electronic state) may appropriately be described by symmetric top wave functions and that this initial state is the $(0,0,0)$

ground vibrational level. Computations are presented for the rate of production of the $NO(X^2\Pi_{3/2})$ fragment in the ground $n_{NO} = 0$ and excited $n_{NO} = 1$ and 2 vibrational states as a function of the incident photon energy (the photofragment excitation yield spectrum). The in-plane transition dipole moment is taken as either parallel to the Cl-N or N-O bonds. Calculations show that variation in the direction of this in-plane transition moment does not significantly affect the overall structure of the spectra, but only introduces a small change in the intensities.

Even for initial triatomic states with total vanishing total angular momenta ($J = K = 0$), the computations access 523 intermediate vibrational states, and each is coupled to the order of 40 diatomic rotational channels. The total number of channels included increases by a factor of $(2J+1)$ for the initially rotating states ($J \neq 0$) that are involved in the computations of the thermally averaged NO fragment rotational distributions. Hence, this example serves to illustrate both the need for analytical models such as ours and the capabilities of this approach. Close-coupled computations are possible for this system with massively parallel computers, but the computational labor scales with the number of channels N as N^3, while wavepacket methods[45] reduce this scaling to better than N^2. Our computations, on the other hand, are quite inexpensive and scale linearly with the number of channels, thus affording a huge simplification. In addition, our calculations provide a powerful tool for interpreting the final results since previous tests[35–38] demonstrate the accuracy of our methods when the basic model assumptions are met. For example, computations with only a few intermediate vibrational states provide insights into limitations of the experimental assignments of the NOCl photofragment excitation spectra. Moreover, the present treatment of the thermally averaged fragment rotational state distributions further emphasizes the power of the theory and the interpretive capabilities that would be difficult to extract from enormous close-coupled computations.

Section II briefly reviews the basic assumptions invoked in paper I, while Section III discusses the simple model potentials. Section IV describes the applications of the theory to the NOCl photodissociation in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition. The photofragment excitation spectra for producing the $n_{NO} = 0$, 1, and 2 NO fragment vibrational states are provided as a function of the photon excitation energy for initial states with $J = 0$. State specific ($J > 0$) and thermally averaged fragment rotational distributions are computed at selected photon energies. While some state specific distributions are highly structured, a small degree of thermal averaging provides relatively smooth distributions containing fairly broad structures.

II. GENERAL THEORY

Paper I develops a three-dimensional analytical quantum model based on the infinite order sudden (IOS) approximation to study triatomic indirect photodissociation processes. The model is formulated assuming that the rate of indirect dissociation Γ_{fi} from the initial bound state $|i\rangle$ to the unbound electronic state $|f\rangle$ is mediated by the quasibound states $|r\rangle$ and is given by the standard golden rule of second-order perturbation theory,

$$\Gamma_{fi} = \frac{2\pi}{\hbar} \left| \sum_r \langle f \,| V_I \, G_r(E) \, \mu \,|\, i \rangle \right|^2 , \tag{2.1}$$

where V_I is the interaction Hamiltonian which couples the resonant quasi-bound state $|r\rangle$ and continuum eigenstates $|f\rangle$ of the unperturbed Hamiltonian, μ is the photoexcitation interaction operator which couples the initial bound $|i\rangle$ and resonant quasibound $|r\rangle$ states, and $G_r(E)$ is the contribution from the resonant states $|r\rangle$,

$$G_r(E) = \frac{|r\rangle\langle r|}{\Delta E_r + i\,\hbar\,\Gamma_r/2}. \tag{2.2}$$

In Eq. (2.2), ΔE_r is the energy difference between the initial (ground state plus excitation photon energy $\hbar\,\omega$) and resonant states, i.e.,

$$\Delta E_r = E_i + \hbar\,\omega - E_r , \tag{2.3}$$

and Γ_r is the decay rate of the intermediate resonant state which is given by the usual golden rule expression,

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

A summation is implicit in Eqs. (2.1) over the resonant states $|r\rangle$ and over all energetically allowed final rotational and vibrational quantum states available to the products labelled by $|f\rangle$. 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. The usual Born-Oppenheimer and Condon approximations are invoked. Hence, the initial $|i\rangle$, resonant $|r\rangle$, and final $|f\rangle$ states are written as products of nuclear and electronic wave functions. As described in paper I, the initial bound and intermediate resonant quasibound state nuclear wave functions for the bent triatomic molecule are represented in terms of a product basis set of rigid-rotor (symmetric top)[44] and harmonic oscillator functions,

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

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

for the initial $|i\rangle$ and resonant $|r\rangle$ states, respectively. D^{J*}_{MK} and $D^{J'*}_{M'K'}$ are the appropriate symmetric top functions[46] for the initial $|i\rangle$ and resonant $|r\rangle$ states, respectively, and the $\psi_{n_i}(Q_i)$ and $\psi_{n'_i}(Q'_i)$ are harmonic oscillator wave functions for the normal coordinates Q_i and Q'_i. The Euler angles (α,β,γ) and (α',β',γ') specify the orientation of the equilibrium principal axes of intertia for the $|i\rangle$ and $|r\rangle$ states, respectively, relative to the space-fixed coordinate system.

The final state wave function Ψ_f for the dynamics on the final repulsive electronic state is written in terms of the Jacobi scattering coordinates R (distance between the diatom center of mass and the atom), θ (angle between the diatomic axis and the atom to diatom vector), and r (internuclear distance of the diatomic photofragment). Thus, Ψ_f is taken in the IOS approximation as a product of the harmonic oscillator function $\psi_{n_4}(r)$ for the diatomic photofragment, the continuum wave function, and the rotational part,

$$\Psi_f(R;\theta;r) = \psi_{n_4}\,\psi_{\hat{E}}(R;\theta)\sum_{\mu\,m}\langle\, J''\,M''\,|\,l\,j\,\mu\,m\,\rangle\, Y_{j\,m}(\beta'',\alpha'')\,Y_{l\,\mu}(\theta_{SF},\phi_{SF}). \qquad (2.7)$$

The angular momentum quantum numbers (l,μ) describe the orbital motion of the atom relative to the diatomic center of mass and its z component, while (j,m) describe the rotational angular momentum of the diatomic molecule and its z component. The angles (β'',α'') are the polar and azimuthal angles specifying the orientation of the diatomic molecule fragment relative to space-fixed axes, while (θ_{SF},ϕ_{SF}) describe the orientation of the atom-diatom vector relative to the space-fixed frame, as explained in paper I. It is further assumed that no electronic angular momentum is present, so that the diatomic photofragment rotational angular momentum j and the orbital angular momentum l are coupled to give well-defined values of the total angular momentum J'' and its z component M'' through Clebsch-Gordan coefficients. The continuum wave function $\psi_{\hat{E}}$ for the relative translational motion of the photofragments is taken to be given by infinite order sudden (IOS) and Airy approximations, as described in previous papers.[36,39]

As discussed below, the NOCl molecule in both the resonant quasibound and initial bound states is well approximated as a near prolate symmetric top. All transitions are taken as originating from the ground vibrational of the initial electronic state, and we assume that the molecule in this inital state is well described by a prolate symmetric top. Introducing the further assumption that the transition is polarized in the plane of the molecule, Paper I provides the expression for the state-to-state transition rate $P_j(J;K;n_4)$ for producing photofragments in a final rotational and vibrational states $|f\rangle = |j\,n_4\rangle$ as,

$$P_j(J;K;n_4) = \frac{2\,\pi}{\hbar}\,A^2\,\overline{V_I}^2\,\mu_{ri}^2\,|\hat{e}_q|^2\,(j+1/2)\,(2J+1)$$
$$\sum_{m'}\left|\sum_{n_i'}\sum_{K'}\sum_{J'}\sum_{m}\sum_{n}\sum_{m''}\begin{pmatrix} J & 1 & J' \\ m & n & m'' \end{pmatrix}\frac{I(j;m';J';K';n_i';n_4)}{\Delta E_r + i\,\hbar\,\Gamma_r/2}\right.$$
$$\left. I_{ri}(J';m'';K';n;J;m;K;n_i')\right|^2, \qquad (2.8)$$

where $|J\,K\rangle$ is the initial rotational state. A is a constant whose square is proportional to the energy density of photons for the given frequency and polarization vector $\hat{e}_q$ of the incident radiation, μ_{ri} is the electronic dipole transition matrix element between the initial and resonant states, and J' and K' are, respectively, the total angular momentum and rotational quantum number of the intermediate resonant state. The quantities $I(j; m'; J'; K'; n_i'; n_4)$ and $I_{ri}(J'; m''; K'; n; J; m; K; n_i')$ are, respectively, one-dimensional angular qudratures[36,38,39] that remain after performing the analytical integration over the other coordinates for the continuum-resonant and resonant-initial state transition matrix elements. Explicit analytical expressions are presented in paper I using quadrature formulas for the integrals over the Jacobi scattering angle θ. The expressions in Paper I [Eqs. (2.11) - (2.13)] use as the integration variables the angles describing the instantaneous displacement $(\delta - \overline{\delta'})$ of the bond angle relative to the equilibrium angle in the resonant bound state of the molecule.[39] The integrand in $I_{ri}(J'; m''; K'; n; J; m; K; n_i')$ also depends on the angle between the transition dipole moment and the body-fixed z'''-axis for the resonant state, and calculations are performed for two different orientations of the in-plane transition dipole moment. (Paper I presents the general theory for arbitrary directions of the transition moment.)

The transition rate Γ_r in the denominator of Eq. (2.2) contains squared integrals with a sum over the fragment vibrational n_i and rotational j quantum numbers, where the integral is the same multidimensional transition amplitudes described in paper I. Since the coupling operator V_I between the resonant and final electronic states is assumed to be a scalar, the resonant state widths Γ_r in Eq. (2.8) may be evaluated, using Eq. (2.9) of Ref.[38] as

$$\Gamma_r(J'; K'; n_i') \equiv \overline{V_I}^2 \sum_{j,\, n_4} \sum_{m'} (j + 1/2) \left| I(j; m'; J'; K'; n_i'; n_4) \right|^2 \delta_{J'J''}\, \delta_{M'M''}. \tag{2.9}$$

The computation of $P_j(J'; K; n_4)$ from Eq. (2.8) requires knowledge of these widths Γ_r and the specification of the energy difference ΔE_r between the initial and resonant states internal (i.e., rotational and vibrational) degrees of freedom in the denominator of $G_r(E)$ [see Eq. (2.2)]. The calculated widths Γ_r for NOCl [Eq. (2.9)] are found to vary very slowly with energy E and rotational states J' and K', differing rather little from the $J' = 0$ case. Thus, for states of not too high total angular momentum J', it is possible to ignore the J' and K' dependence of Γ_r. Consequently, the required Γ_r in Eq. (2.8) are computed from Eq. (2.9) assuming that the triatomic molecule is in the nonrotating $J' = 0$ level of the resonant state.

The energies of the initial and resonant states are defined by the usual equations,

$$E_{JK} = \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2}\right) K^2, \tag{2.10}$$

$$E'_{J'K'} = n'_1\omega'_1 + n'_2\omega'_2 + n'_3\omega'_3 + \frac{B'+C'}{2} J'(J'+1) + \left(A' - \frac{B'+C'}{2}\right) K'^2 + E_{0r}, \tag{2.11}$$

where ω_i and ω'_i are the frequencies of the initial and resonant states, respectively, and A, B, C and A', B', C' are the corresponding rotational constants (see Table I). E_{0r} in Eq. (2.11) is the energy of the ground level of the resonant state (see Table I). The calculations all assume that the initial state is the $(0,0,0)$ vibrational level, but there is no difficulty in extending the calculations to initial excited vibrational levels. Further simplification follows by observing that for states of low total angular momentum J' the rotational energy difference between Eqs. (2.10) and (2.11) is much smaller than the absolute value of the other terms (e.g., Γ) in the denominator of Eq. (2.8). Hence, we set $K' = K$ in the calculation of ΔE_r in the denominator of Eq. (2.8).

III. MODEL POTENTIALS

The present calculations consider a simple model for the indirect photodissociation of NOCl in the $T_1(1^3A'')$ state to produce $\mathrm{NO}(X^2\Pi_{3/2})$. The geometry, valence force constants, and normal mode frequencies for the initial ground NOCl state and for the $\mathrm{X}^2\Pi_{3/2}$ electronic state of NO are taken from Refs.[47,48] and are summarized in Table I along with other relevant parameters. The T_1 surface is decomposed into a final state scattering problem by describing the system in terms of two diabatic surfaces and a perturbation V_I. As described in Sect. II A of paper I, we assume that the bound diabatic surface for the bent triatomic molecule can be represented in terms of a harmonic potential in the internal coordinates. This potential is characterized by force constants K_i, K_{23}, and K'_i, K'_{23} $(i = 1,2,3)$ for the initial bound and virtual quasibound states, respectively (see Table I). Thus, the potential energy for the initial state is expressed in terms of the internal coordinates as

$$V_i(r_{NO};r_{NCl};\delta) = \frac{1}{2}K_1\,(r_{NO}-\overline{r}_{NO})^2 + \frac{1}{2}K_2\,(r_{NCl}-\overline{r}_{NCl})^2 + \frac{1}{2}K_3\,(\delta-\overline{\delta})^2$$
$$+K_{23}\,(r_{NCl}-\overline{r}_{NCl})\,(\delta-\overline{\delta}), \tag{3.1}$$

with a similar equation for the resonant state. The geometry and frequencies of the intermediate virtual resonant state are repeatedly adjusted so that the Franck-Condon factors for transitions from the initial ground $(0,0,0)$ vibrational state to the resonant state vibrational levels $\{n_i'\}$ roughly resemble those observed for the experimental photofragment yield spectra of NOCl in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition.[43] The equilibrium configuration geometry and frequencies for this intermediate resonant state are given in Table I.

Computations of the decay rates Γ_r in the denominator of Eq. (2.2) require the determination of the (scalar) coupling operator V_I in Eq. (2.9). In general, this operator must be a function of the internal coordinates of the triatomic molecule. However, we take V_I, for simplicity, as a single constant. More general cases can readily be treated with an explicit dependence of V_I on the internal nuclear coordinates. A value for V_I has been determined by comparing the available experimental widths in the photofragment yield spectra of NOCl[43] with the computed widths, where V_I is the only free parameter. Thus, Eq. (2.9) produces, for a particular NO photofragment vibrational state n_4, the semiempirical value

$$V_I = \left[\frac{\Gamma_{r,\,exp}}{\sum_j (j+1/2)\,|\langle\Psi_f(R;\theta;r)|\Psi_r(Q')\rangle|^2}\right]^{1/2}, \tag{3.2}$$

where $\Gamma_{r,exp}$ is the experimental width[43] for producing that fragment state. The procedure is repeated for each of the nine vibrational states of Table II. The matrix element in the denominator of Eq. (3.2) is the continuum-resonant state transition integral appearing on the right hand side of Eq. (2.9). This matrix element can be reduced analytically to a one-dimensional quadrature $I(j;m';J';K';n_i';n_4)$ after transforming from the modes Q' to the dissociative Jacobi coordinates R, θ, r, followed by an analytical integration over the R and r involved in the nuclear wave function $\Psi_f(R;\theta;r)$ for the final electronic surface and the transformed wave function $\Psi_r(Q')$ for the intermediate resonant state. Complete details of the different steps required to perform these analytical developments are given in a previous paper.[36] Table I also summarizes the equilibrium values of the Jacobi coordinates R, r, and θ in the initial and intermediate resonant states. Averaging over the nine calculations of V_I from Eq. (3.2) and the experimental values thus yields $V_I = 176.44$ cm^{-1}. The individual computed $\Gamma_{r,calc}$ are presented in Table II and agree with experiment to better than a factor of two.

In general, the rotational motion of a triatomic molecule is given by an asymmetric top wave function, and the treatment of these wavefunctions within our theoretical framework is described in Appendix C of paper I. For the case of NOCl, the rotational motion in both the initial and resonant states is well approximated by symmetric top functions, since the Ray's asymmetry parameter is $\kappa = -0.9920$ and $\kappa' = -0.9925$ for the initial and resonant states, respectively (see Table I). In both cases this is very close to the prolate symmetric top value of $\kappa = -1.0$.

The present computations treat the transition as polarized in the plane of the molecule because the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition dipole moment of NOCl is typical of a parallel transition.[43] Thus, we consider the in-plane transition dipole as either parallel to the Cl-N bond or parallel to the NO bond. Computations are easily made for the other orientations. The angle β''', involved in the initial-resonant states transition integral $I_{ri}(J'; m''; K'; n; J; m; K; n_i')$ [see Eq. (2.30) of paper I], is provided in Table I for these two orientations of the transition dipole moment.

Although the use of the Airy function approximation for the continuum wave function $\psi_{\hat{E}}(R;\theta)$ allows us to treat general potentials in a fashion similar to that described in previous papers,[35,36,38] the dissociative potential energy surface for the continuum state is fit to older *ab initio* calculations for the repulsive portion of the $T_1(1^3A'')$ state potential for NOCl. Since the use of anisotropic repulsive potentials for the continuum is an important feature of the theory, the fit for this repulsive potential is generated using the functional form,

$$U(R;\theta) = F(\theta)\, exp[-f(\theta)\,(R - \overline{R})], \tag{3.3}$$

where $F(\theta)$ and $f(\theta)$ are expansions in powers of cos θ,

$$F(\theta) = \sum_n c_n \cos^n \theta, \tag{3.4}$$

$$f(\theta) = \sum_n c'_n \cos^n \theta, \tag{3.5}$$

and $\overline{R}$ is the equilibrium distance of atom C (the Cl atom) from the center of mass of the diatom $A - B$ (the NO diatomic photofragment) in the initial bound state. The coefficients c_n and c'_n in Eqs. (3.4) and (3.5) have been evaluated through standard fitting procedures[51] using 40 Gauss-Legendre quadrature points. The angular functions $F(\theta)$ and $f(\theta)$ in the dissociative potential energy surface are displayed as a function of $\cos\theta$ in Fig. 1. The functions $F(\theta)$ and $f(\theta)$ are very smooth in the vicinity of the ground state Franck-Condon region, which is centered about $cos\,\overline{\theta'} = 0.60$ (see Table I).

IV. RESULTS AND DISCUSSION

The determination of the final state fragment energy distribution from Eq. (2.8) requires a multiple summation over the intermediate state vibrational quantum numbers n'_i. This requires that the widths Γ_r in Eq. (2.9) must be computed for each of the contributing intermediate state vibrational levels. Table II shows that the agreement between the experimental and calculated widths is satisfactory, differing by at most a factor of 1.5, where Γ_r is overestimated for the vibrational excited states with $n_4 = 1$ and 2, while those for $n_4 = 0$ are underestimated. If we allowed V_I to depend on the vibrational coordinates, we could obtain better agreement, but at the expense of additional adjustable parameters.

As a test of the convergence of the calculated photodissociation excitation spectra with respect to the number of intermediate states retained in the summations, computations of the final state fragment energy distributions have been performed by varying this number until the spectrum for each $n_4 = 0, 1$ or 2 no longer changes. The inclusion of 523 vibrational states (i.e., all resonant vibrational states in the energy range of 16,207 to 22,413 cm^{-1}) yields convergence of the spectral structure over the range of photon energies from 16,207 to 20,000 cm^{-1}. The results presented in the figures and text below all incorporate these 523 resonant states.

Figures 2-4 display the calculated photofragment yield spectra of NOCl in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition for producing the NO fragment in the vibrational states $n_4 = 0, 1$, and 2 and for the initial and resonant state $J = 0$ and $J' = 1$ rotational levels, respectively. The computations in these figures all assume that the transition dipole moment is along the Cl-NO bond. Similar calculations (not shown) with the transition moment along the N-O bond exhibit the same overall spectral structure as shown in Figs. 2-4, except that the intensities are enhanced on average by a factor of 20%. This behavior can be attributed to the fact that the angle β''', used to specify the different orientations of the transition dipole moment, only enters the theory through a factor of the reduced rotation matrix element d^1_{n0} in the integrand of $I_{ri}(J'; m''; K'; n; J; m; K; n'_i)$ [see Eq. (2.30) of paper I]. This angle β''' only differs by 0.34 rad (see Table I) for the two orientations of the transition dipole moment.

The inset of each figure exhibits the corresponding experimental spectrum for comparison. The calculated intensities for $n_4 = 1$ and $n_4 = 2$ are multiplied by a factor of 100 and 10, respectively (the relative experimental intensities are not given[43]). Table II presents the calculated resonant state energies $E_{r,calc}$, the calculated widths $\Gamma_{r,calc}$, and the peaks in the calculated photofragment spectra for producing NO in particular vibrational states, along with the corresponding experimental quantities taken from Ref.[43].

The three peak structure for producing the $n_4 = 0$ and $n_4 = 2$ NO vibrational states is fairly well reproduced by Figs. 2 and 4 respectively, although the relative intensities of the two highest peaks for $n_4 = 0$ are inverted. The peaks at 16,162, 16,580, and 16,981 cm^{-1} in the computed $n_4 = 0$ photofragment spectrum of Fig. 2 correspond rather well to the bending progression $n'_3 = 0$, 1, and 2 in the zeroth order intermediate resonant state (for which $E_r = 16,207$, 16,588, and 16,967 cm^{-1}, respectively). Moreover, the spacings of 418 and 401 cm^{-1} in this bending progression for the $n'_1 = 0$ NO resonant state stretching mode are very close to the spacings 405 and 424 cm^{-1}, respectively, of the experimental peak energies (see Table II). This correspondence agrees with the experimental assignment of the three peaks to the bending progression $n_3' = 0$, 1, and 2 in the resonant state. Moreover, the dashed curve in Fig. 2 demonstrates that this spectrum contains the same three peak structure when we incorporate in the calculations only the progression of bending vibrational states $n_3' = 0$, 1, and 2 in the sum over intermediate states in Eq. (2.8). While the peaks in Fig. 2 correspond nicely to the experimental assignment, the computed spectrum between the first and second peaks and in the higher energy tail contains contributions from many other resonant states.

The assignment of the calculated peaks in the photofragment spectrum of Fig. 4 for producing NO in the excited $n_4 = 2$ state follows similarly. The calculated positions for the two higher peaks at 19,223 and 19,617 cm^{-1} are very close to the resonant state energies $E_r = 19,219$ and 19,599 cm^{-1}, corresponding, respectively, to the unexcited $n_3' = 0$ and the excited $n_3' = 1$ levels in the resonant state (see Table II). The spacing of 394 cm^{-1} in this bending progression (see Fig. 4) compares favorably with the experimental spacing of 340 cm^{-1} and with the bending frequency $\omega_3' = 380$ cm^{-1} for our resonant state potential. Therefore, these transitions may be assigned to the bending progression in accord with the experimental interpretation. The computed relative intensities of these two peaks again differ from experiment and have significant contributions from many other intermediate resonant states. However, the small intensity lower photon energy peak at 18,588 cm^{-1} lies too far from the computed resonant state energy for it to be from the unexcited $n_3' = 0$ bending vibrational state. This discrepancy exhibits some obvious deficiencies in our simple potential function for the resonant state. The dashed curve in Fig. 4 shows the photofragment spectrum for producing the $n_4 = 2$ fragment NO vibrational state as computed by including only the bending progression $n_3' = 0$, 1, and 2 in the sum of Eq. (2.8). The dashed curve clearly exhibits a third peak at 20,000 cm^{-1} in agreement with the experimental spectrum. This third peak corresponds to the slight shoulder in the full computation.

Globally, the computed photofragment spectrum for $n_4 = 1$ in Fig. 3 exhibits very different structure than that obtained experimentally, again due to inadequacies in the potential energy surface. Nevertheless, the three peaks at 17,723, 17,895, and 18,332 cm^{-1} in the central region of the spectrum qualitatively appear to follow the bending progression $n_3' = 0, 1$, and 2 (with the accompanying excitation $n_1' = 1$ in the NO streching mode). The two resolved peaks in Fig. 3 at 17,723 and 17,895 cm^{-1} of rather similar intensities might be assigned to the bending progression $n_3' = 0$ and 1. Although the absolute positions of the second and third peaks at 17,895 and 18,332 cm^{-1}, respectively, differ from experiment by about 200 cm^{-1} (see Table II), the spacing between the peaks for $n_3' = 1$ and 2 is 437 cm^{-1}, in reasonable agreement with the experimental spacing of 385 cm^{-1} and with the resonance state energy difference 380 cm^{-1}. Moreover, the experimental peak assigned to the unexcited bending mode $n_3' = 0$ lies at 17,723 cm^{-1}, an energy which differs by only 7 and 10 cm^{-1} from the experimental value and the resonance state energy, respectively (see Table II). However, incorporation of only the bending progression vibrational states $n_3' = 0$, 1, and 2 in Eq. (2.8) for this $n_4 = 1$ excited mode does not reproduce the expected three peak structure, as occurs for the dashed curves in Figs. 2 and 4 for the unexcited $n_4 = 0$ and excited $n_4 = 2$ states, respectively. Instead, the three resonance state model yields only a single low intensity (10% of spectrum in Fig. 3) peak (not shown) at around 17,600 cm^{-1}, thereby representing a serious deficiency of our potential energy surfaces.

In summary, the assignment of certain individual peaks in Figs. 2 and 4 (see also Table II) to the bending vibrational mode of the resonant state of NOCl follows the observation[52] that the spacing 400 cm^{-1} between these peaks closely matches the frequency 380 cm^{-1} of this mode in the ground state of NOCl. The photofragment yield experiments of Reisler and coworkers[43] (see inserts in Figs. 2-4) each exhibit three peaks for each n_4 corresponding to the bending progression $n_3' = 0, 1$ and 2. Moreover, the three groups of three peaks for $n_4 = 0$ and 2, listed in Table II, are separated, respectively, by $\sim$ 3000 cm^{-1}, twice the frequency of the NO stretch, again in agreement with the experimental assignment. These assignments are readily tested by computing the photofragment spectra using only selected intermediate states, a process demonstrating the poor correspondence of the $n_4 = 1$

spectrum with experiment but emphasizing the interpretative capabilities of the theoretical methods.

We have also computed the normalized final fragment rotational distributions for specific photon excitation energies. These distributions are illustrated for final states with the NO fragment unexcited ($n_4 = 0$) and for excitations corresponding to the two highest energy peaks in Fig. 2, the minimum between them, and for the photon energy of 15,800 cm^{-1} (see Table II) which lies on the low energy side of the first peak. These computations also assume that the transition dipole moment is along the Cl-NO bond and have been performed for the ten rotational states $J = 0$ up to $J = 9$ and with $J = K$. Figures 5a (for $J = 0$) and 5b (for $J = K = 3$) present the NO fragment rotational distributions produced at the lower photon energy and at an excitation energy corresponding to the lowest energy maximum in Fig. 2. The distribution in Fig. 5a for the lower photon energy is centered at rather low rotational states, between $j = 2$ and $j = 8$, with a relatively rapid fall off. The rotational distributions in Fig. 5a for excitation at the higher photon energy 16,162 cm^{-1} are broader, more oscillatory, and shifted to higher j, between $j = 12$ and $j = 18$. Both of these distributions become even broader and more structureless for processes originating from the initial $J = K = 3$ rotational state (Fig. 5b), with a $j_{max} \sim 15$ for the unexcited bending state located at the higher energy, in close agreement with the experimental value for the P_{12} branch spectrum but without the peak for $j \sim 0$.[43] The latter peak may arise, in part, from the influence of electronic angular momenta which are ignored here and are expected to affect the low j populations most. Computations performed for $J = K = 1$ and $J = K = 2$ (not shown) yield fairly similar type final fragment rotational distributions as computed for $J = 0$.

Figures 5c-5d display the final NO fragment rotational distributions produced by excitation at the first minimum and the second maximum in Fig. 2. The overall difference in the rotational excitation in both distributions is not as pronounced as in Figs. 5a-5b, and the difference in photon energies is smaller. The distributions in both cases show well pronounced oscillations characteristic of an interference pattern with a "wavelength" Δj of

~ 3.5 between adjacent minima or maxima for $J = 0$. When $J = K = 3$ (Fig. 5d), the rotational distributions contain a broadening similar to that involved in the transition from Figs. 5a to 5b. In particular, the calculated NO rotational distribution, produced following the decay of the bending resonance $n_3' = 1$, in Fig. 5d has a symmetric, Gaussian-type shape with a maximum at $j \sim 15$. Experimental excitation in the region of the second maximum produces a Gaussian-like distribution between $j = 10.5$ and $j = 20.5$ and with the peak at $j \sim 15$.[43] The structure of final fragment rotational distributions computed at the two higher photon energies for $J = K = 1$ and $J = K = 2$ are again very similar to that calculated for the $J = 0$ case.[32] However, the experiments also display a lower j component not present in our computations and probably influenced by the neglected electronic angular momenta. As shown in the calculations of Vegiri *et al.*,[53] the NOCl rotational distributions are quite sensitive to the potential function, so it is likely that simple adjustment of the potentials would produce improved agreement with experiment.

The above computations consider the influence of parent internal excitations on the product state rotational distributions for individually selected initial rotational states. However, the experiments do not select the initial state but instead contain a quasi-thermal average over J and K. Thus, it is of interest to determine if the oscillations in the computed $J = 0$ photofragment spectrum become washed out by thermal averaging even at the very low temperature present in supersonic jet experiments. Hence, we have computed the normalized, thermally averaged rotational distributions,

$$P_j(T; n_4) = \frac{I(j; T; n_4)}{\sum_j I(j; T; n_4)}, \tag{4.1}$$

where $I(j; T; n_4)$ is given by

$$I(j; T; n_4) = \frac{\sum_{J=0}^{J_{max}} \sum_{K=-J}^{J} (2J+1)\, P_j(J; K; n_4)\, exp(-E_{JK}/kT)}{\sum_{J=0}^{J_{max}} \sum_{K=-J}^{J} (2J+1)\, exp(-E_{JK}/kT)}, \tag{4.2}$$

with the unnormalized rotational distributions $P_j(J; K; n_4)$ determined from Eq. (2.8), T the absolute temperature, and the initial state rotational energy E_{JK} given by Eq. (2.10). The calculations include states of total angular momentum J from $J = 0$ through $J_{max} = 7$

for the same photon energies as in Figs. 5a and 5b and from $J = 0$ through $J_{max} = 9$ for the photon energies corresponding to the excitation of the resonant state bending progression (0,0,0) and (0,0,1).

Figure 6 displays the thermally averaged $n_4 = 0$ state NO rotational distributions for two different temperatures. The $T = 1\,K$ spectra in Figs. 6a and 6c still contain some slight structure in the individual thermal rotational distributions, but when the temperature is raised to $T = 5\,K$ (Figs. 6b and 6d), the thermally averaged $P_j(T; n_4)$ become structureless and broad. In particular, the rotational state distributions of the NO fragment, produced following the decay of the two lowest bending resonances with $n'_3 = 0$ or 1 (Figs. 6c and 6d), have the form of a Gaussian with peaks at $j \sim 14$ and $j \sim 16$, respectively, for $n'_3 = 0$ and $n'_3 = 1$. In addition, the rotational distributions from this bending progression are more symmetric than the rotational distribution at the lowest photon energy. The computed rotational distributions again lack the $j = 0$ peak observed experimentally.

V. CONCLUSIONS

We illustrate the three-dimensional analytical infinite order sudden (IOS) quantum-mechanical theory from paper I by studying the indirect NOCl photodissociaiton process 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. The initial and resonant state nuclear wave functions are represented in terms of symmetric-top and product harmonic oscillator functions in the different natural 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. The transition is taken polarized in the plane of the molecule, and the initial bound state $|i\rangle$ is chosen as the $(0, 0, 0)$ ground vibrational state in various rotational sublevels.

One important aspect of the theory lies in the large number of intermediate states included in the computations, a number which must be included in order to compute the photofragment excitation spectrum. For example, when the initial state has total angular momentum J, the present computations require 523 intermediate state vibrational levels, translating into roughly $1569(2J+1)$ intermediate state channels. While close-coupled computations are possible for low J, the computations are still quite large compared to the present treatment where calculations have been performed for $J = 0$ through 9 in order to evaluate the thermally averaged photofragment rotational distributions, a task which may be prohibitive using three-dimensional close-coupled methods. Very rapid computations with fewer intermediate channels serve to aid in assigning the structure present in the computed photofragment spectra.

The theory is applied 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. The semiempirical harmonic potential for the intermediate state is chosen based on approximate experimental frequencies, while the final anisotropic repulsive potential surface is a fit of an anisotropic exponential repulsion using older *ab initio* calculations. Computations are conducted assuming that the transition dipole moment lies either along the Cl-N bond or along the N-O bond, and both provide very similar calculated excitation spectra. The computations for producing the NO fragment in the $n_{NO} = 0$ and $n_{NO} = 2$ vibrational states reproduce the three peak structure observed experimentally and assigned to the progression for the intermediate (resonant) state bending vibrational levels $n_3' = 0$, 1, and 2. The spacings between the peaks in the computed photofragment spectrum agree with both the experimental and theoretical frequencies of the bending vibrational mode in the resonant state. The three groups of three peaks for $n_{NO} = 0$ and 2 are separated by ~ 3000 cm^{-1}, twice the stretch frequency in the intermediate resonant state. The inadequacies of the simple intermediate harmonic state potential energy surface are apparent in the computed $n_{NO} = 1$ photofragment spectrum which exhibits a more complex structure than found experimentally.

We have also investigated the NO fragment rotational state distributions for producing the $n_{NO} = 0$ vibrational state following the decay of the resonant states at photon energies corresponding to excitation of the $n'_3 = 0$ and 1 resonant state bending vibrational levels. The final NO fragment rotational distributions, arising from excitation at the first minimum in Fig. 2 and from the excited bending mode $n'_3 = 1$, show pronounced oscillations for $J = 0$, oscillations which become broader upon excitation to the $J = K = 3$ rotational state. In particular, the calculated NO distributions, obtained following the decay of the excited bending mode $n'_3 = 1$ display a maximum at $j \sim 15$, in agreement with the experimental excitation in the P_{12} and Q_{22} branches. However, the experimental rotational distributions exhibit, in addition, a high intensity peak at a rather low rotational excitation energy. Such behavior is not present in our computations and probably arises from the neglect of electronic angular momenta and other limitations in the potentials.

Finally, the computed thermally averaged rotational distributions, performed for two different temperatures, show that the $n_{NO} = 0$ state distributions become structureless and broad at $T = 5K$, displaying the form of a Gaussian with peaks located at $j \sim 14$ and $j \sim 16$, respectively, for $n'_3 = 0$ and $n'_3 = 1$, in close agreement with the peak found experimentally. However, the calculations again fail to exhibit the $j = 0$ peak observed experimentally.

It is, on one hand, gratifying to find that an analytical theory with rather simple semiempirical potential functions captures many observed facets of the photodissociation dynamics. On the other hand, it comes as no surprise that these potentials are inadequate for some finer details of the dynamics. The computational simplicity of the analytical IOS theory would permit the iterative adjustment of the potentials to provide improved agreement with experiment or the use of more accurate *ab initio* potentials to generate our surfaces. However, the focus is primarily on developing and illustrating the theory, and for this purpose, the simple potentials are quite adequate.

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TABLE I. Spectroscopic Data[a] and Relevant Parameters[b] used in the Two Step Model Photodissociation NOCl $\rightarrow$ NO($X^2\Pi_{3/2}$) +Cl($^2P_{3/2}$)

Initial State	Resonant State
$\omega_1 = 1799.7$ cm^{-1} N=O stretch (99%)	$\omega_1' = 1505.7$ cm^{-1}
$\omega_2 = 332.0$ cm^{-1} N-Cl stretch (71%), ClNO bend (29%)	$\omega_2' = 210.82$ cm^{-1}
$\omega_3 = 595.9$ cm^{-1} N-Cl strech (32%), ClNO bend (68%)	$\omega_3' = 380.01$ cm^{-1}
$K_1 = 14.087$ mdyn/$\AA$ (N=O stretch)	$K_1' = 10.103$ mdyn/$\AA$
$K_2 = 1.243$ mdyn/$\AA$ (N-Cl stretch)	$K_2' = 0.8024$ mdyn/$\AA$
$K_3 = 1.15$ mdyn $\AA$/rad^2 (ONCl bend)	$K_3' = 0.300$ mdyn $\AA$/rad^2
$K_{23} = 0.089$ mdyn/rad	$K_{23}' = 0.069$ mdyn/rad
$\overline{r}_{NO}$=1.15 $\AA$	$\overline{r'}_{NO}$=1.13 $\AA$
$\overline{r}_{NCl}$=1.975 $\AA$	$\overline{r'}_{NCl}$=2.09 $\AA$
$\overline{\delta} = 2.007$ rad	$\overline{\delta'} = 1.977$ rad
$\rho = 0.8270$	$\rho' = 0.84778$
$\overline{R} = 2.3020$ $\AA$	$\overline{R'} = 2.3930$ $\AA$
$\overline{\theta} = 0.89077$ rad	$\overline{\theta'} = 0.93118$ rad
$A = 2.959448$ cm^{-1}	$A' = 2.852559$ cm^{-1}
$B = 0.186615$ cm^{-1}	$B' = 0.174312$ cm^{-1}
$C = 0.175546$ cm^{-1}	$C' = 0.164274$ cm^{-1}
$\kappa = -0.9920475$	$\kappa' = -0.9925317$
$\beta_0 = 2.3080$ rad	$\beta_0' = 2.2608$ rad
$\beta''' = 0.39738$ rad (along the Cl-NO bond)	$E_{0r} = 16,207$ cm^{-1}
$\beta''' = 0.73722$ rad (along the N-O bond)	$V_I = 176.44$ cm^{-1}

[a] The interatomic distance, frequency, and rotational constant of N=O are respectively $\overline{r}_{NO}$(N=O) = 1.1508 Å, ω_{NO} = 1903.68 cm^{-1}, $B_v(NO)$ = 1.7 cm^{-1} (see Ref.[49]). [b] The molecular parameters ρ and ρ' are involved in describing the angular displacements of the diatomic vector and of the atom to diatom vector of the vibrating molecule from their equilibrium initial and resonant state positions [see Eqs. (2.12) and (2.13) of Ref.[39]], while β_0 and β_0' are the angles in the transformation which diagonalizes the inertial tensor in the initial and resonant states, respectively [see Eq. (2.14) of Ref.[39]].

TABLE II. Calculated and Experimental Spectroscopic Data in the Two Step Indirect Model Photodissociation NOCl $\rightarrow$ NO($X^2\Pi_{3/2}$) + Cl($^2P_{3/2}$)

Vibrational State	$\Gamma^a_{r\,exp}$ (cm^{-1})	$\Gamma^b_{r\,calc}$ (cm^{-1})	$E^c_{r\,calc}$ (cm^{-1})	E^d_{av} (eV)	$E^{calc\,e}_{peak}$ (cm^{-1})	$E^{exp\,f}_{peak}$ (cm^{-1})
			$n_4 = 0$			
(0,0,0)	264.41	195.44	16,207	0.3823	16,162	16,206
(0,0,1)	331.00	152.18	16,588	0.4324	16,580	16,611
(0,0,2)	—	122.61	16,967	0.4849	16,981	17,035
			$n_4 = 1$			
(1,0,0)	188.00	290.23	17,713	0.3385	17,723	17,730
(1,0,1)	251.00	422.14	18,093	0.3864	17,895	18,115
(1,0,2)	374.00	371.33	18,473	0.4364	18,332	18,519
			$n_4 = 2$			
(2,0,0)	93.00	100.45	19,219	0.3053	19,223	19,306
(2,0,1)	116.00	182.60	19,599	0.3470	19,617	19,646
(2,0,2)	261.00	298.58	19,979	0.3900	–	20,000

[a] Calculated from Ref.[43]

[b] Calculated from Eq. (2.9) ommiting the sum over n_4.

[c] Calculated from Eq. (2.11).

[d] Calculated from $E_{av} = \hbar\omega$ - D_0 - E_v(NO) - E_{el}(NO) where $\hbar\omega$ is the photon energy, D_0 is the dissociation threshold (13,000 cm $^{-1}$) (see Ref.[50]), E_v(NO) is the energy of the NO vibration, and E_{el}(NO) is the NO spin-orbit electronic energy (123 cm^{-1}) (see Ref.[43]).

[e] Calculated from Figs. (2-4).

[f] Calculated from Ref.[43]

FIGURE CAPTIONS

Fig. 1: Variation of the anisotropic part of the repulsive portion of the $T_1(1^3A'')$ state potential for the two step indirect model photodissociation NOCl $\rightarrow$ NO($X^2\Pi_{3/2}$)+Cl($^2P_{3/2}$)

Fig. 2: Calculated absorption and photofragment yield spectrum of NOCl in the region of the $T_1 \leftarrow S_0$ transition for $n_{NO} = 0$, $J = 0$, $J' = 1$. The solid and dashed curves are, respectively, the spectra calculated from 523 intermediate state vibrational states and from only the three resonances in the bending progression [(0,0,0), (0,0,1), (0,0,2)]. The transition dipole moment is taken to lie along the Cl-NO bond. The experimental spectrum is displayed in the inset.

Fig. 3: Calculated absorption and photofragment yield spectrum of NOCl in the region of the $T_1 \leftarrow S_0$ transition for $n_{NO} = 1$, $J = 0$, $J' = 1$. The transition dipole moment is taken to lie along the Cl-NO bond. The experimental spectrum is displayed in the inset.

Fig. 4: Calculated absorption and photofragment yield spectrum of NOCl in the region of the $T_1 \leftarrow S_0$ transtion for $n_{NO} = 2$, $J = 0$, $J' = 1$. The solid and dashed curves are, respectively, the spectra calculated from 523 intermediate state vibrational states and from only the three resonances in the bending progression [(2,0,0), (2,0,1), (2,0,2)]. The transition dipole moment is taken to lie along the Cl-NO bond. The experimental spectrum is displayed in the inset.

Fig. 5: Normalized IOS quantum-mechanical rotational fragment distributions for the two step indirect model photodissociation NOCl $\rightarrow$ NO($X^2\Pi_{3/2}$) + Cl($^2P_{3/2}$) in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transition for $n_4 = 0$. The transition dipole moment is taken to lie along the Cl-NO bond. (a) $J = 0$; (—) $E_{ph} = 15,800\ cm^{-1}$; (- - -) $E_{ph} = 16,162$ cm^{-1}. (b) $J = K = 3$; (—) $E_{ph} = 15,800$ cm^{-1}; (- - -) $E_{ph} = 16,162$ cm^{-1}. (c) $J = 0$; (—) $E_{ph} = 16,418$ cm^{-1}; (- - -) $E_{ph} = 16,580$ cm^{-1}. (d) $J = K = 3$; (—) $E_{ph} = 16,418$ cm^{-1}; (- - -) $E_{ph} = 16,580$ cm^{-1}.

Fig. 6: Normalized thermally averaged IOS quantum-mechanical rotational fragment distributions for the two step indirect model photodissociation NOCl $\rightarrow$ NO($X^2\Pi_{3/2}$) + Cl($^2P_{3/2}$) in the region of the $T_1(1^3A'') \leftarrow S_0(1^1A')$ transtion for $n_4 = 0$. The transition dipole moment is taken to lie along the Cl-NO bond. (a) $T = 1\ K$, $J_{max} = 7$; (—) $E_{ph} = 15,800$ cm^{-1}; (- - -) $E_{ph} = 16,162$ cm^{-1}. (b) $T = 5\ K$, $J_{max} = 7$; (—) $E_{ph} = 15,800$ cm^{-1}; (- - -) $E_{ph} = 16,162$ cm^{-1}. (c) $T = 1\ K$, $J_{max} = 9$; (—) $E_{ph} = 16,580$ cm^{-1}; (- - -) $E_{ph} = 16,162$ cm^{-1}. (d) $T = 5\ K$, $J_{max} = 9$; (—) $E_{ph} = 16,580$ cm^{-1}; (- - -) $E_{ph} = 16,162$ cm^{-1}.