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Bi-orthogonality of Resonance Wave Functions in NO_2[†]

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The overlap between nonorthogonal wave functions of resonance (Siegert) states is analyzed. Their asymptotic behavior, which controls the extent of nonorthogonality, is shown to be directly related to the residues of the energy **S** matrix. This allows one to estimate overlap integrals using solely positions and widths of resonance states, without the explicit calculation of the wave functions. This assessment, as applied to NO_2, suggests that resonances in the molecule are only slightly nonorthogonal and decay independently of one another.

I. Introduction

This paper substantiates the model used in our previous study for the analysis of the time-dependent decay of NO_2 molecules excited above the first dissociation threshold D_0 (see ref 1, to be referred to as paper I). Experimental time delay curves were successfully simulated by computing the survival probability,[1]

$$P(t) = \sum_\nu |p_\nu|^2 \tag{1}$$

where p_ν is the probability amplitude of finding a molecule in a resonance state ν at time t. The key assumption of the model was that the survival probability could be expressed in a simple multiexponential form:

$$P(t) = \sum_\nu |A_\nu|^2 \mathrm{e}^{-\Gamma_\nu t} \tag{2}$$

Here, Γ_ν denotes the width of the νth resonance state, known from the numerical solution of the Schrödinger equation; $|A_\nu|^2$ measures the probability for exciting this resonance state with laser light. For a chaotic molecule, such as NO_2, the coefficients $|A_\nu|^2$ are determined by the form of the pump pulse,[1] and the summation in eq 2 runs over those states that fall within the spectral bandwidth of the laser. The chief value of eq 2 is that it uses a limited amount of information for transforming a resonance spectrum into a time-dependent decay: only the positions and the widths of resonances are required, but not the corresponding wave functions. This was of importance to the previous study[1] since the wave functions of the resonance states have not been calculated. At the same time, such a "diagonal approximation", in which states decay independently of one another, requires justification, at least in the case of NO_2 where resonances are known to overlap. For the spectrum, calculated in paper I, the overlap parameter ξ, composed of the average resonance width $\langle\Gamma\rangle$ and the density of states ρ,

$$\xi = \langle\Gamma\rangle\rho \tag{3}$$

varies between 1 and 3. Is it permissible to neglect *this* overlap in $P(t)$?

In the present paper we shall explain why the "diagonal approximation", eq 2, provides a reliable estimation of the survival probability $P(t)$. The problem will be tackled by considering the asymptotic properties of resonance eigenfunctions: exact solutions of the Schrödinger equation. In this respect, our approach is different from the more familiar one, in which the decay of overlapping resonances is studied after statistical averaging over the energy window containing many states.[2−6]

The accuracy of the approximation depends on the extent to which resonance wave functions are orthogonal. Let $\Phi(t = 0; \mathbf{R})$ be the initial wave packet describing the molecule above the dissociation threshold (vector $\mathbf{R}$ denotes a set of internal coordinates; Jacobi coordinates R, r, and γ defined in section III of paper I are used throughout this work). Assume further that $\Phi(t = 0; \mathbf{R})$ can be expanded over a set of resonance wave functions ψ_ν:[7]

$$\Phi(t = 0; \mathbf{R}) = \sum_\nu A_\nu \psi_\nu(\mathbf{R})$$

The probability amplitude p_μ in eq 1 is a projection of the wave packet at time t, $\Phi(t)$, onto state μ. In the most general form, this projection can be written as

$$p_\mu = \int \tilde{\psi}_\mu^* \Phi(t)\, \mathrm{d}\Omega = \sum_\nu A_\nu \mathrm{e}^{-\mathrm{i}E_\nu t} \int \tilde{\psi}_\mu^* \psi_\nu\, \mathrm{d}\Omega$$

Here, $\mathrm{d}\Omega$ is a volume element; $E_\nu = E_\nu^0 - \mathrm{i}\Gamma_\nu/2$ is a complex resonance energy; $\tilde{\psi}_\mu$ is a function of the *dual* space[9] (in Dirac notation, $\tilde{\psi}_\mu^*$ is nothing but a *bra*-vector). The dual function $\tilde{\psi}_\mu$ coincides with ψ_μ if the eigenvalue is real; otherwise, $\tilde{\psi}_\mu$ and ψ_μ are two distinct functions (see discussion below). If the overlap between $\tilde{\psi}_\nu^*$ and ψ_μ is zero, the two states are said to be bi-orthogonal. Were all states ν and μ bi-orthogonal, the amplitude p_μ would be equal to $A_\mu \mathrm{e}^{-\mathrm{i}E_\mu t}$ and the survival probability $P(t)$ would take on a "diagonal" form, as in eq 2. If, however, ν and μ are not bi-orthogonal, both p_μ and $P(t)$ depend on the elements of the overlap matrix $\mathbf{N}$:

$$N_{\mu\nu} = \int \tilde{\psi}_\mu^* \psi_\nu\, \mathrm{d}\Omega \tag{4}$$

and $P(t)$ contains not only exponential decays but also oscillating cosine terms describing interference between pairs of resonance states.

The chief cause of nonorthogonality of resonance wave functions is the following. Since E_ν has a negative imaginary

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part, the amplitude of $\psi_\nu(\mathbf{R})$ exponentially grows in the asymptotic region ($R \to \infty$).[10] In fact, the integrals in eq 4 do not exist! They are only meaningful if taken over a "bounded interaction region", $R \le R_{\max}$ (see, for example, ref 8). When defined in this way, the overlap integrals do not diverge but are not zero either; by the same token, the normalization integrals, i.e., the diagonal elements $N_{\nu\nu}$, differ from unity. It is these matrix elements $N_{\mu\nu}$ that we are going to estimate for NO_2 from first principles, using only calculated positions and widths of the resonance states. Of crucial importance is the fact that we can express $N_{\mu\nu}$ through the residues of the **S** matrix at energies E_μ and E_ν (cf. eq 25 below). The residues, in turn, can be estimated without reference to the resonance wave functions.

The plan of the paper is the following. In section II we outline the most important features of Siegert states. The asymptotic behavior of resonance eigenfunctions is analyzed in section III. Finally, the results of section III are further used in section IV for estimating the overlap matrix **N** for NO_2.

II. Siegert States

Let us briefly review what is known about the resonance wave functions. Since several in-depth introductory texts are available (see, for example, refs 8, 10, and 11) and, additionally, the subject was recently addressed by a number of research groups,[12−14] we have restricted the consideration to the properties essential for our model.

Resonance states ψ_ν (also called Siegert states, ref 15) are solutions of the Schrödinger equation with "radiation" boundary conditions:

$$\hat{H}\psi_\nu \equiv [\hat{T} + V(R,r,\gamma)]\,\psi_\nu = E_\nu\psi_\nu \tag{5a}$$

$$\left[\frac{\partial\psi_\nu}{\partial R}\right]_{R=R_{\max}} = \mathrm{i}k_\nu\psi_\nu \tag{5b}$$

Here, $\hat{H}$ is the molecular Hamiltonian; the (complex) wave vector is given by $k_\nu = (2E_\nu)^{1/2}$ and the resonance energy is measured from the first dissociation threshold (in what follows we assume $\hbar = \mu_R = 1$, where μ_R is the mass associated with the coordinate R). The boundary condition (5b) is imposed in the asymptotic region of the potential V, where rotation and vibration of NO are already separated from the (free) translational motion along the dissociation coordinate R. Siegert functions are the residues of the energy Green's function $\mathsf{G}\,(E)$, which is written as

$$\mathsf{G}\,(E) = \sum_\nu \frac{\tilde{\psi}_\nu^*\psi_\nu}{E - E_\nu} \tag{6}$$

The eigenfunctions defined in eqs 5a, 5b, or 6 form a suitable basis for expanding wave packets and studying their temporal evolution. The simplicity of the energy dependence of the Green's function guarantees that the evolution operator [energy Fourier transform of $\mathsf{G}\,(E)$] is diagonal in the ψ_ν representation. It is these states that we shall use for calculating the overlap matrix **N**. In the strict sense, the Schrödinger equation, which we solved numerically in paper I, *approximates* the problem (5a) and (5b) but is different from it. Recall that the resonance spectrum was calculated using the optical model[16] with the Hamiltonian

$$\hat{H}_{\mathrm{opt}}(E) = \hat{H} - \mathrm{i}V_{\mathrm{opt}}(E) \tag{7}$$

Boundary condition (5b) was not imposed individually on every resonance state; instead, an energy-dependent imaginary potential $-\mathrm{i}V_{\mathrm{opt}}(E)$ was introduced. This potential was meant for absorption of incoming waves and simulation of the correct asymptotic behavior. The eigenvalues and eigenfunctions of the problem solved in paper I and the problem defined in eqs 5a and 5b are known to be closely related if V_{opt} depends weakly on energy.[2,8,17] For NO_2 this is indeed the case. The change in $V_{\mathrm{opt}}(E)$ over a given energy interval δE is roughly proportional to $\sim\delta E/\Delta H$, where ΔH is the spectral range of the Hamiltonian $\hat{H}$. Since ΔH is about 30 eV for the spatial grid used in the calculations, while the considered energy range is $\delta E \approx 2000$ cm^{-1}, the relation $\delta E/\Delta H \ll 1$ and, hence, $|\partial V_{\mathrm{opt}}/\partial E| \ll 1$ is satisfied. This means that the optical potential is almost independent of energy within the entire energy range studied. Consequently, the choice between the Schrödinger equation with a real Hamiltonian and complex boundary conditions (as in eqs 5a and 5b) and the Schrödinger equation with a complex Hamiltonian (as in the optical model, eq 7) becomes a matter of convenience: for numerical computations, the absorbing potential appears to be a sound alternative today, while the analysis of properties of resonance wave functions can be performed with eq 5a.

A remark is in order concerning Green's function, eq 6, and the boundary condition in eq 5b. Representation of $\mathsf{G}\,(E)$ as a meromorphic function (i.e., as a sum over simple poles) is appropriate only if the decay proceeds via a single product channel.[11,18] If the number of channels is larger than one (as happens with NO_2 roughly 3.5 cm^{-1} above the dissociation threshold), $\mathsf{G}\,(E)$ contains branch points, and the Riemann surface can no longer be mapped onto the complex k plane (examples of multichannel Green's functions and **S** matrices are discussed in chapter 17 of ref 18). At the same time, we remind the reader, that the "single-channel" eq 6 is at the heart of the harmonic inversion algorithm employed in paper I for solving the Schrödinger equation. Moreover, when quantum results obtained with different methods are compared, it is apparent that eq 6 works well for multichannel decay: the spectrum behaves as if there were only one threshold in the reaction — the first dissociation threshold D_0. Therefore, in what follows we shall use the single-channel approximation. Consistent with this, the boundary condition, eq 5b, is also written for one channel only. Generalization to the multichannel case will be given elsewhere.[19]

The functional space of solutions of eq 5a is non-Hermitian, because the boundary condition is complex. The scalar product in this space is also non-Hermitian,[8,20] so that integrals involving resonance states contain unusual *bra*-functions, as in eq 4. This formal mathematical definition is physically significant: for example, combinations $\tilde{\psi}_\nu^*\psi_\nu$ are shown to enter perturbation series for resonance states.[11,17] The function $\tilde{\psi}_\nu$ satisfies the same Schrödinger equation as ψ_ν, but with a boundary condition corresponding to a purely incoming wave:[8,21]

$$\left[\frac{\partial\tilde{\psi}_\nu}{\partial R}\right]_{R=R_{\max}} = -\mathrm{i}k_\nu^*\tilde{\psi}_\nu \tag{8}$$

Thus, $\tilde{\psi}_\nu$ corresponds to the eigenvalue E_ν^*. It can be easily shown that $\tilde{\psi}_\nu$ and ψ_ν are related through

$$\tilde{\psi}_\nu = \psi_\nu^* \tag{9}$$

Therefore, the overlap matrix, eq 4, can be rewritten as

$$N_{\mu\nu} = \int_{R\le R_{\max}} \psi_\mu\psi_\nu\,\mathrm{d}\Omega \tag{10}$$

Resonance wave functions enter the integral without complex conjugation, as do the bound eigenfunctions. This shows, by the way, that all matrix elements $N_{\mu\nu}$, including the normalization constants $N_{\nu\nu}$ are complex (the significance of the complex norm is discussed in ref 17). The time dependence of the dual state vectors is given by

$$\tilde{\Psi}_\nu(t;\mathbf{R}) = \tilde{\psi}_\nu \mathrm{e}^{-\mathrm{i}E_\nu^* t} \tag{11}$$

Note that eq 9 holds only for the coordinate part $\tilde{\psi}_\nu$ of the time-dependent function $\tilde{\Psi}_\nu(t;\mathbf{R})$. By means of the dual functions one can define the norm of a state, expectation values of operators, and the probability current density. For example, an analogue of the continuity equation reads as

$$\frac{\partial}{\partial t}\int_{R\le R_{\max}} \tilde{\Psi}_\mu^* \Psi_\nu \,\mathrm{d}\Omega = -\frac{\mathrm{i}}{2}\oint_{R=R_{\max}} [\Psi_\nu \nabla \tilde{\Psi}_\mu^* - \tilde{\Psi}_\mu^* \nabla \Psi_\nu]\,\mathrm{d}s \tag{12}$$

The integral on the right-hand side (rhs) is evaluated along Jacobi coordinates r and γ over the surface s defined by the condition $R = R_{\max}$.

The overlap matrix, eq 10 can be cast in a different form.[8] Just as in the one-dimensional case,[8] one considers two wave equations for $\tilde{\psi}_\mu$ and ψ_ν, multiplies them with (respective) dual functions and applies Green's formula to their difference. The result of these transformations is the following convenient expression for $\mathbf{N}$:

$$N_{\mu\nu} = \delta_{\mu\nu} - \frac{\mathrm{i}}{k_\mu + k_\nu}\oint_{R=R_{\max}} \psi_\mu \psi_\nu \,\mathrm{d}s \tag{13}$$

Equation 13 shows that the overlap is sensitive to the "tails" of resonance wave functions on the surface $R = R_{\max}$ where the boundary condition, eq 5b, is imposed. Thus, to calculate $\mathbf{N}$ one has to exactly know ψ_ν at large interfragment distances.

III. Asymptotic Behavior of Resonance Wave Functions and Residues of the S Matrix

The interaction between the decay products vanishes on the surface $R = R_{\max}$. Therefore, at large distances R the function ψ_ν has the following form consistent with the boundary condition (5b):

$$[\psi_\nu(R,r,\gamma)]_{R\ge R_{\max}} = C_\nu(k_\nu)\mathrm{e}^{\mathrm{i}k_\nu R}\phi_n(r,\gamma) \tag{14}$$

Here, $C_\nu(k_\nu)$ is a complex number [$C_\nu(k_\nu) = C_\nu^*(-k_\nu^*)$, because of the symmetry property (9)]; $\phi_n(r,\gamma)$ is a wave function of the NO fragment, and n denotes its vibrational and rotational quantum numbers. Since $\phi_n(r,\gamma)$ is a real and quadratically integrable function, the surface integral in $N_{\mu\nu}$ (eq 13) is unity, and the overlap matrix reduces to

$$N_{\mu\nu} = \delta_{\mu\nu} - \frac{\mathrm{i}}{k_\mu + k_\nu} C_\mu(k_\mu)\, C_\nu(k_\nu)\mathrm{e}^{\mathrm{i}(k_\mu + k_\nu)R_{\max}} \tag{15}$$

The coefficients C_ν control the norm, as well as the overlap. We show now that C_ν is related to the residue of the $\mathbf{S}$ matrix at the pole k_ν. Explicitly: If the $\mathbf{S}$ matrix near the pole is written as[22]

$$S(k) = \frac{g_\nu}{k - k_\nu} \tag{16}$$

then C_ν is given by

$$C_\nu^{\,2} = \mathrm{i}g_\nu \tag{17}$$

This is one of the main results of this paper. It generalizes an analogous relation obtained earlier in ref 11 for wave functions of bound states.[23] Equation 17 implies that the information about the asymptotic behavior of resonance wave functions lurks in scattering phases.

Here is the proof of eq 17. Let us consider a regular solution of the wave equation above the dissociation threshold. At large interfragment distances it can be written as

$$\chi(R,r,\gamma) = \mathrm{const}\,[\mathrm{e}^{-\mathrm{i}kR} - S(k)\,\mathrm{e}^{\mathrm{i}kR}]\,\phi_n(r,\gamma) \tag{18}$$

At $k = k_\nu$ this solution goes over into the eigenfunction ψ_ν. Therefore, in a small vicinity of the complex pole k_ν,

$$k = k_\nu + \epsilon, \qquad |\epsilon| \to 0$$

where the pole expansion, eq 16, is valid, the function χ must assume the following form:

$$\chi(R,r,\gamma) \approx C_\nu\left[\mathrm{e}^{\mathrm{i}kR} - \frac{\epsilon}{g_\nu}\mathrm{e}^{-\mathrm{i}kR}\right]\phi_n(r,\gamma) \tag{19}$$

This form can be enforced upon χ by adjusting the constant factor in eq 18. Now we use the "continuity equation" (12) near the pole k_ν. Let one of the functions, on which the current density is built, be the function χ. Another one can be chosen to be the dual function $\tilde{\psi}_\nu$. Since it corresponds to a distant pole $-k_\nu^*$, its asymptotic behavior remains unchanged as $k \to k_\nu$:

$$\tilde{\psi}_\nu(R,r,\gamma) = C_\nu(-k_\nu^*)\mathrm{e}^{-\mathrm{i}k_\nu^* R}\phi_n(r,\gamma) = C_\nu(-k_\nu^*)\mathrm{e}^{-\mathrm{i}(k^* - \epsilon^*)R}\phi_n(r,\gamma)$$

Then, the continuity equation for χ and $\tilde{\psi}_\nu$ reads as

$$\frac{\partial}{\partial t}\int_{R\le R_{\max}} \tilde{\psi}_\nu^*\,\chi\,\mathrm{e}^{\mathrm{i}E_\nu t}\mathrm{e}^{-\mathrm{i}E_\epsilon t}\,\mathrm{d}\Omega = -\frac{\mathrm{i}}{2}\mathrm{e}^{\mathrm{i}E_\nu t}\mathrm{e}^{-\mathrm{i}E_\epsilon t}\oint_{R=R_{\max}} [\chi\nabla\tilde{\psi}_\nu^* - \tilde{\psi}_\nu^*\nabla\chi]\,\mathrm{d}s \tag{20}$$

Here E_ϵ is the energy associated with the wave vector k:

$$E_\epsilon = \frac{1}{2}(k_\nu + \epsilon)^2 \approx E_\nu + k_\nu\,\epsilon + O(|\epsilon|^2)$$

Let us estimate both sides of eq 20 to first order in ϵ. On the left-hand side (lhs) we find:

$$\frac{\partial}{\partial t}\int_{R\le R_{\max}} \tilde{\psi}_\nu^*\,\chi\mathrm{e}^{-\mathrm{i}k_\nu\epsilon t}\,\mathrm{d}\Omega \xrightarrow{\epsilon\to 0} (-\mathrm{i}k_\nu\epsilon)\int_{R\le R_{\max}} \tilde{\psi}_\nu^*\psi_\nu\,\mathrm{d}\Omega = (-\mathrm{i}k_\nu\epsilon)\left[1 - \frac{\mathrm{i}C_\nu^{\,2}}{2k_\nu}\mathrm{e}^{2\mathrm{i}k_\nu R_{\max}}\right] \tag{21}$$

In the last equality we take into account that the norm of ψ_ν is given by eq 15 with $\mu = \nu$. Estimating the rhs of eq 20, one has to keep in mind that $\oint \phi_n^{\,2}\,\mathrm{d}s = 1$ and the normal derivative to the surface s coincides with $\partial/\partial R$. Then, after simple transformations one gets

$$(-\mathrm{i}k_\nu\epsilon)\left[-\frac{\mathrm{i}C_\nu^{\,2}}{g_\nu} - \frac{\mathrm{i}C_\nu^{\,2}}{2k_\nu}\,\mathrm{e}^{2\mathrm{i}k_\nu R_{\max}}\right] \tag{22}$$

Comparing eqs 21 and 22, we see that

$$-\mathrm{i}C_\nu^{\,2}/g_\nu = 1$$

which coincides with eq 17.

A related expression for the asymptotic form of a resonance wave function was previously obtained for radial *s*-wave scattering in ref 24. However, the final result was expressed through a combination of Jost functions, and this limited its applicability to one-dimensional problems for which the Schrödinger equation is an ordinary differential equation. Moreover, the derivation was based on specific properties of 1D Green's functions. The asset of eq 17 is that it is valid for any number of dimensions and, as such, is based on the most general properties of the wave equation.

IV. Estimation of the Overlap Matrix in NO_2.

The theorem we just proved can be utilized to estimate the matrix elements $N_{\mu\nu}$ for the resonances of NO_2 employed in calculation of the decay curves (they are shown in Figure 3 of paper I). The pole expansion of the **S** matrix (we return back to the energy representation) reads as[10,11,18]

$$S(E) = B(E) - \mathrm{i}\sum_\nu \frac{G_\nu}{E - E_\nu} \tag{23}$$

where $B(E)$ is a smooth background and G_ν is the residue at energy E_ν, related to the residue g_ν of the previous section through

$$\mathrm{i}g_\nu = G_\nu/2k_\nu \tag{24}$$

The matrix **N**, eq 15, is, therefore

$$N_{\mu\nu} = \delta_{\mu\nu} - \frac{i(G_\mu G_\nu)^{1/2}}{2(k_\mu + k_\nu)(k_\mu k_\nu)^{1/2}} \mathrm{e}^{\mathrm{i}(k_\mu + k_\nu)R_{\max}} \tag{25}$$

Let us first consider the diagonal elements. For the absolute value of the "norm defect" one gets

$$|N_{\nu\nu} - 1| = \left|\frac{G_\nu}{4E_\nu}\right| \mathrm{e}^{2\mathrm{Im}k_\nu R_{\max}} \approx \left|\frac{G_\nu}{4E_\nu}\right| \tag{26}$$

This follows from the limitation on the maximum width of resonances, $\Gamma_{\max}$, in our quantum mechanical calculations (cf. eq 4 in paper I): the condition $\Gamma \le \Gamma_{\max}$, which holds for all states, means exactly $2\mathrm{Im}k_\nu R_{\max} \le 1$.

Care is required in the estimation of G_ν. If, as is customary,[10] this residue is assumed to be equal to the product of the resonance width and the nonresonant phase, $\Gamma_\nu \exp[2\mathrm{i}\delta_0(E_\nu)]$, the "norm defect" amounts to $\Gamma_\nu/4E_\nu^0$. For all converged resonances of NO_2 this ratio never exceeds 0.01. The same is also true for the overlap integrals: deviations from bi-orthogonality are less than 0.02. Thus, the set of resonance wave functions appears to be bi-orthogonal with a high degree of precision.

This result, however, is not exactly correct. The fact is that $|G_\nu|$ coincides with Γ_ν only if the resonances are completely isolated. Nearby states can change both the phase δ_0 and the absolute value of G_ν. We make this clear by representing the single channel **S** matrix $S(E)$ as a unitary product expansion,[2,3]

$$S(E) = \mathrm{e}^{2\mathrm{i}\delta_0(E_\nu)} \prod_\mu \frac{E - E_\mu^*}{E - E_\mu} \tag{27}$$

and taking the residue:

$$\begin{aligned} G_\nu &= \Gamma_\nu\, \mathrm{e}^{2\mathrm{i}\delta_0(E_\nu)} \prod_{\mu \neq \nu} \frac{E_\nu - E_\mu^*}{E_\nu - E_\mu} \\ &= \Gamma_\nu\, \mathrm{e}^{2\mathrm{i}\delta_0(E_\nu)} \prod_{\mu \neq \nu} \left(1 + \frac{\xi_\mu^{\,2}\kappa_\mu - \mathrm{i}\xi_\mu}{1 + \xi_\mu^{\,2}\,\kappa_\mu^{\,2}}\right) \end{aligned} \tag{28}$$

Here, we introduced two parameters that characterize the resonance spectrum: $\xi_\mu = \Gamma_\mu/(E_\mu^0 - E_\nu^0)$ is analogous to the overlap parameter ξ, eq 3; $\kappa_\mu = (\Gamma_\nu - \Gamma_\mu)/2\Gamma_\mu$ is governed by the amplitude of fluctuations of resonance widths. If all $\xi_\mu \ll 1$ (the resonances do not overlap), $|G_\nu|$ is indeed equal to Γ_ν. With growing ξ_μ, $|G_\nu|$ rises and becomes larger than the resonance width. It is remarkable, however, that the condition $\xi_\mu \gg 1$ alone does not yield large residues. For example, if the overlapped resonances are broadly distributed, $\kappa_\mu \gg 1$, $|G_\nu|$ turns out to be of the order of Γ_ν again. It could be beneficial to analyze the bi-orthogonality of resonance wave functions by averaging eq 28 over a statistical distribution function of widths *and* positions of resonances.

In NO_2, both ξ_μ and κ_μ vary over wide limits, and we estimate $|G_\nu|$ numerically. For every ν, only those resonances are included in the product in eq 28, which lie within the window of ~200 cm^{-1} around E_ν (this coincides with the average spectral width of laser pulses used in the time-resolved experiment). We find that the overlap of resonances causes $|G_\nu|$ to increase by about an order of magnitude with respect to Γ_ν. As a result, the maximum "norm defect" for the absolute majority of resonance states rises to 0.1. This is still a tolerable deviation, and the "diagonal" equation (2) provides a decent approximation to the survival probability. The overall decay of the molecule is very close to a sum of independent exponential decays.

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