# Symmetry-Forbidden Electronic State Interference Observed in Angularly Resolved NO$^+$($A\,^1\Pi$) Deexcitation Spectra of the N$^*$O($2\sigma^{-1}2\pi^2$) Resonance

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Quantum mechanical interference between different pathways in inner-shell resonance excitation-deexcitation spectra is a realization of a double-slit experiment on the atomic scale. If the intermediate inner-shell resonances are of different symmetries, this interference is symmetry forbidden in the solid-angle-averaged or magic-angle-recorded deexcitation spectra. It has, however, been suggested that interference may by observable in off-magic-angle-recorded spectra. Here, we prove this interference in angularly resolved deexcitation spectra of the $2\sigma^{-1}2\pi^2(^2\Delta, {}^2\Sigma^\pm)$ resonances of N$^*$O by a quantitative comparison between *ab initio* calculations and experiment.

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Quantum mechanical interference is an effect fundamental to a wide range of processes and applications in different branches of science. For many processes occurring in nature it causes dramatic counterintuitive observations, requiring detailed understanding of this effect.

Interference between excitation-deexcitation pathways via different intermediate electronic resonances overlapping within their natural widths is known as electronic state interference (ESI) [1], and is a prototype for an atomic double-slit experiment [2]. In case the intermediate electronic resonances have equal symmetries, the total (magic-angle-recorded) cross section for the production of a particular final state of "ion + photoelectron" is given by the square of the coherent sum of amplitudes $D_i$ for photoionization via different intermediate resonances $i$: $\sigma = |\sum_i D_i|^2 = \sum_{i,j} D_i^* D_j$. This case is well studied for rare gas atoms by means of photoelectron spectroscopy (PES) (see, e.g., [3,4]) and photon-induced fluorescence spectroscopy (PIFS) (see, e.g., [5,6]), showing that ESI can be observed even for well separated intermediate resonances in the corresponding angular distributions. Total cross sections and fluorescence angular distributions do not include the phase difference between outgoing partial photoelectron waves. This fact reduces the "visibility" of ESI in fluorescence experiments. The same fact, however, allows us to perform a partial wave analysis [6] based on PIFS measurements *only*, providing very important information on the dynamics of resonant photoionization.

If the intermediate states have different symmetries, the total solid-angle-averaged cross section is given by the incoherent sum of the transition amplitudes, $\sigma = \sum_i |D_i|^2$, displaying no interference terms $D_i^* D_{j\neq i}$. However, if angular averaging is reduced, then ESI becomes possible [7]. This effect has been suggested to be responsible for a large disagreement between non-angular-averaged experimental and theoretical resonant Auger decay spectra of the core-excited N$^*$O molecule [7], where three overlapping electronic states with different symmetries $1s^{-1}2\pi^2$ ($^2\Delta$, $^2\Sigma^-$, and $^2\Sigma^+$) are accessible by one-photon absorption from its ground state $X\,^2\Pi$. By qualitative symmetry arguments it has been concluded in [7] that the amplitude for excitation and decay of the $^2\Delta$ resonance for *oriented* NO molecules may interfere with those for the $^2\Sigma^\pm$ resonances. In this case symmetry-different final states of the system are not any more orthogonal and they mix, allowing the corresponding amplitudes to interfere. Even for randomly oriented molecules excited by *polarized* photons, ESI may be observed by measuring decay spectra off the magic angle or by determining corresponding angular distribution parameters [7]. However, there was no quantitative proof of this idea in [7]. The main aim of the present letter is the experimental and theoretical prove of the symmetry-forbidden ESI in photon-induced fluorescence spectra. We demonstrate, that the ESI is sufficiently "visible" in fluorescence spectra, and that PIFS experiments may be the base for a new area of research: partial wave analysis of the resonant photoionization of molecules.

Different deexcitation spectra of the N$^*$O resonance have been studied in [7–15] both experimentally and theoretically. Here, the participator Auger decay of the core-excited states into the NO$^+$($A\,^1\Pi$) valence-ionized state, and the subsequent NO$^+$($A\,^1\Pi \rightarrow X\,^1\Sigma^+$) fluorescence are investigated. The processes relevant to the present study can be schematically represented as follows:

$$\begin{array}{cc}
(G) & \text{NO } 2\sigma^2 5\sigma^2 1\pi^4 2\pi^1 (X\,^2\Pi, \Omega_0 v_0 = 0) + \hbar\omega \\
\downarrow & \text{Resonant core excitation} \\
(R) & \text{NO}^* \; 2\sigma^1 5\sigma^2 1\pi^4 2\pi^2 (\Lambda_r \Sigma_r, \Omega_r v_r) \\
\Downarrow & \text{Autoionization or Direct ionization} \\
(D) & \text{NO}^+ \; 2\sigma^2 5\sigma^1 1\pi^4 2\pi^1 (A\,^1\Pi, \Omega_1 v_1) + \varepsilon\ell m\mu \\
\downarrow & \text{Fluorescence decay} \\
(F) & \text{NO}^+ \; 2\sigma^2 5\sigma^2 1\pi^4 2\pi^0 (X\,^1\Sigma^+, \Omega_2 v_2) + hc/\lambda
\end{array} \qquad (1)$$

The following notation is used throughout this Letter: $\Omega$ is the projection of the total electronic angular momentum along the molecular axis; $v$ is the vibrational quantum number; $\varepsilon\ell m\mu$ stands for a photoelectron in a continuum, which can be expanded in the asymptotical region via partial waves [16] with fixed projections $m$ and $\mu$ of the orbital angular momentum $\ell$ and spin $s$, respectively, on the molecular axis, and a given phase shift $\delta_{\ell m}$.

Linearly polarized synchrotron radiation with photon energies $\omega$ of around 400 eV excites the ground state ($G$) of NO into the $2\sigma^{-1}2\pi^2({}^2\Sigma^-, {}^2\Delta, \text{ or } {}^2\Sigma^+)\Omega_r v_r$ vibronic resonances ($R$) of N*O, which subsequently autoionize via a participator Auger decay into the $\mathrm{NO}^+(A\,{}^1\Pi, \Omega_1 v_1)\varepsilon\ell\pi\mu\,{}^2\Delta/{}^2\Sigma^\pm$ continua ($D$). In addition, the direct population of the $\mathrm{NO}^+(A\,{}^1\Pi, \Omega_1 v_1)$ ionic states via a $(G) \to (D)$ dipole transition with emission of $\varepsilon\ell\sigma\mu$ or $\varepsilon\ell\pi\mu$ electrons takes place (the symmetries of the ion + photoelectron are ${}^2\Pi$ or ${}^2\Delta/{}^2\Sigma^\pm$, respectively). The $A\,{}^1\Pi$, $\Omega_1 v_1$ states of the $\mathrm{NO}^+$ ion decay further via emission of a fluorescence photon $hc/\lambda$ into the $X\,{}^1\Sigma^+$, $\Omega_2 v_2$ states ($F$). In order to describe the angular distributions of the photoelectrons and fluorescence photons, we used the previously developed *ab initio* theoretical approach [17], which has been successfully applied there to study a similar problem in core-excited CO.

The angular distribution of photoelectrons after excitation of randomly oriented diatomic molecules by linearly polarized light is given by the well-known formula [16]:

$$\frac{d\sigma_{\Omega_1 v_1}(\omega)}{d\Omega} = \frac{\sigma_{\Omega_1 v_1}(\omega)}{4\pi}[1 + \beta^e_{\Omega_1 v_1}(\omega)P_2(\cos\theta)], \qquad (2)$$

where $\theta$ is the angle between the electric field vector of the exciting radiation and the direction of propagation of the outgoing electron. The total photoionization cross section, $\sigma_{\Omega_1 v_1}(\omega)$, can be computed as [17]

$$\sigma_{\Omega_1 v_1}(\omega) = \sum_{\Omega_0 \Omega_1} \sum_{\ell m} \sum_{\mu k} |D_k(\Omega_0, \Omega_1 v_1 \varepsilon\ell m\mu)|^2. \qquad (3)$$

The amplitude for the population of the $|\Omega_1 v_1\rangle$ ionic state from the initial state $|\Omega_0 v_0\rangle$ in the vicinity of the $|\Omega_r v_r\rangle$ resonances is the sum of the direct and all resonant amplitudes [17]

$$\begin{aligned} &D_k(\Omega_0, \Omega_1 v_1 \varepsilon\ell m\mu) \\ &\propto \langle \Omega_1 v_1 \varepsilon\ell m\mu | \mathbf{D}_k | \Omega_0 v_0 \rangle \\ &\quad + \sum_{\Omega_r v_r} \frac{\langle \Omega_1 v_1 \varepsilon\ell m\mu | \mathbf{H}^{\mathbf{ee}} | \Omega_r v_r \rangle \langle \Omega_r v_r | \mathbf{D}_k | \Omega_0 v_0 \rangle}{\omega - E_{\Omega_r v_r} + i\Gamma_{\Omega_r v_r}/2}, \end{aligned} \qquad (4)$$

where $E_{\Omega_r v_r}$ and $\Gamma_{\Omega_r v_r} = 124$ meV [13] are the energies and natural widths of the vibronic resonances $|\Omega_r v_r\rangle$, respectively. One should note that the amplitude (4) accounts for the lifetime vibrational interference (LVI, [18]) only, but—not the ESI. Owing to symmetry reasons, only the electronic substates with $\pm|\Omega_r|$ (but not with different $|\Omega_r|$) enter its resonant part. Thus, the ESI does not influence the total cross section (3).

The complete equation for the electron angular distribution parameter, $\beta^e_{\Omega_1 v_1}(\omega)$, can be found, e.g., in [16,17]. It contains the interference between the photoionization amplitudes corresponding to the emission of different partial electron waves $\varepsilon\ell m\mu$

$$\begin{aligned} \beta^e_{\Omega_1 v_1}(\omega) \propto &\sum_{\Omega_0 \Omega_1} \sum_{\ell m} \sum_{\ell' m'} \sum_{kk'} \sum_{\mu} b^{\ell' m' k'}_{\ell m k} e^{-i(\delta_{\ell m} - \delta_{\ell' m'})} \\ &\times D^*_{k'}(\Omega_0, \Omega_1 v_1 \varepsilon\ell' m'\mu) D_k(\Omega_0, \Omega_1 v_1 \varepsilon\ell m\mu), \end{aligned} \qquad (5)$$

where $b^{\ell' m' k'}_{\ell m k}$ are kinematic coefficients. If $\theta \neq 54.7°$ (i.e., not the magic angle), the cross terms with different amplitudes, corresponding to the excitation and decay of different electronic resonances, enter the *differential* cross sections (2) via the angular distribution parameter (5), and are responsible for the ESI in the angularly resolved Auger electron spectra.

For randomly oriented diatomic molecules excited by linearly polarized light, the angular distribution of fluorescence emitted via the subsequent $|\Omega_1 v_1\rangle \to |\Omega_2 v_2\rangle$ radiative transition is given by [17]

$$\frac{dI^{\Omega_2 v_2}_{\Omega_1 v_1}(\omega)}{d\Omega} = \frac{I^{\Omega_2 v_2}_{\Omega_1 v_1}(\omega)}{4\pi}[1 + \beta 2^{\Omega_2 v_2}_{\Omega_1 v_1}(\omega) P_2(\cos\theta)], \qquad (6)$$

where $\theta$ is the angle between the electric field vector of the exciting radiation and the direction of detection of the fluorescence. The total fluorescence intensity, $I^{\Omega_2 v_2}_{\Omega_1 v_1}(\omega)$, is proportional to the total cross section (3) and, thus, contains no interference. The complete equation for the fluorescence angular distribution parameter, $\beta 2^{\Omega_2 v_2}_{\Omega_1 v_1}(\omega)$, can be found in [17]. It includes the interference between the amplitudes for the population and radiative decay of different degenerate electronic substates with $\Omega_1 \neq \Omega_1'$,

$$\begin{aligned} \beta 2^{\Omega_2 v_2}_{\Omega_1 v_1}(\omega) \propto &\sum_{\Omega_0 \Omega_2} \sum_{qq'} \sum_{\Omega_1 \Omega_1'} \sum_{\ell m\mu} \sum_{kk'} b2^{k'q'}_{kq} \\ &\times \langle \Omega_2 v_2 | \mathbf{D}_{q'} | \Omega_1' v_1 \rangle^* D^*_{k'}(\Omega_0, \Omega_1' v_1 \varepsilon\ell m\mu) \\ &\times \langle \Omega_2 v_2 | \mathbf{D}_q | \Omega_1 v_1 \rangle D_k(\Omega_0, \Omega_1 v_1 \varepsilon\ell m\mu). \end{aligned} \qquad (7)$$

One should note that in the case of closed shell molecules, e.g., CO, the cross terms in the fluorescence angular distribution parameter (7) are forbidden [17], similar to the fluorescence angular distribution parameter of the closed shell atoms [2,6,19]. For the open shell NO molecule, the cross terms are allowed and enter the *differential* fluorescence intensities (6) via the angular distribution parameter (7). Thus, ESI can also be observed by measuring the angularly resolved fluorescence spectra of N*O. We emphasize that the absence of the phase difference between partial waves in Eq. (7) vs Eq. (5) provide a hint for a future partial wave analysis in molecules.

Electronic and vibrational parts of the amplitudes (4) were computed in the present work as described in [15,17], respectively. In order to test the theoretical approach we

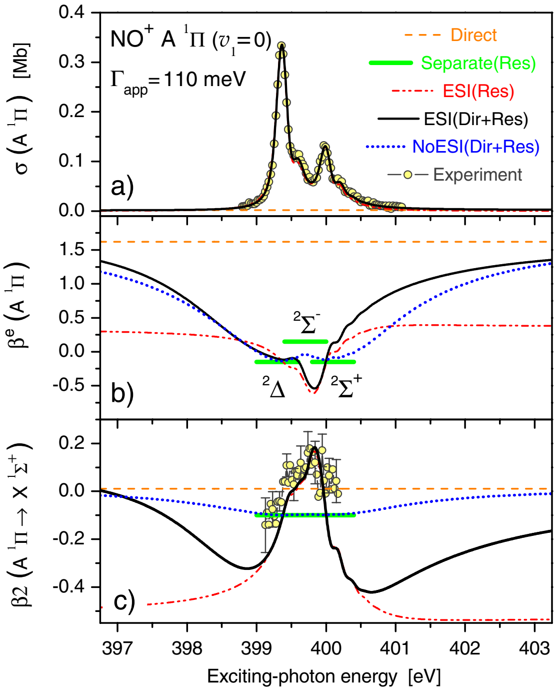

FIG. 1 (color online). Results of the present calculations performed in different approximations (see text) together with the present experimental results. Computed parameters were convolved with a Gaussian of 110 meV FWHM. Panel (a): cross section for the population of the NO$^+A\,^1\Pi(v_1 = 0)$ vibronic state across the N$^*$O resonance. Experimental data are normalized to the theory at the maximum. Panel (b): angular distribution parameter for the NO$^+$ $A\,^1\Pi(v_1 = 0)$ photoelectrons. Panel (c): angular distribution parameter for the $A\,^1\Pi(v_1 = 0) \rightarrow X\,^1\Sigma^+(v_2)$ fluorescence bands progression. No normalization for experimental $\beta2$ values is required.

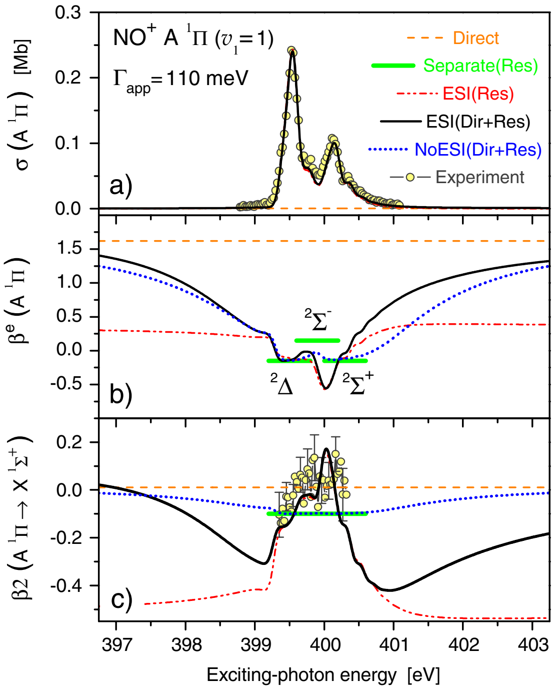

FIG. 2 (color online). Parameters computed and measured for the NO$^+$ $A\,^1\Pi$ ($v_1 = 1$) state (see notations in Fig. 1).

have reproduced the experimental results of [7] (will be published elsewhere). Present theoretical results are summarized in Figs. 1 and 2 for the final states NO$^+A^1\Pi$ ($v_1 =$ 0 and 1) with the highest population probabilities. Calculations were performed within several approximations to illustrate the influence of the ESI:

(i) *Direct*: only direct photoionization channels were accounted for;

(ii) *Separate(Res)*: only resonant photoionization channels were accounted for separately for each intermediate electronic resonance;

(iii) *NoESI(Dir+Res)*: the direct and all electronic resonant amplitudes were incorporated incoherently;

(iv) *ESI(Res)*: interference between all resonant electronic amplitudes was taken into account;

(v) *ESI(Dir+Res)*: interference between the direct and all resonant amplitudes was taken into account.

Cross sections and angular distribution parameters computed within the most accurate approximation *ESI (Dir+Res)* are depicted in Figs. 1 and 2 by solid lines. The two maxima in the computed cross sections $\sigma_{Av_1}(\omega)$ at lower and higher exciting-photon energies correspond to the decay of the $^2\Delta$ and $^2\Sigma^+$ resonances, respectively [15]. Weak contributions from the $^2\Sigma^-$ resonance are located between the two maxima but blended. This is due to the "filtering effect" [13] in the core excitation spectra of NO based on the cancellation of the direct and exchange Coulomb integrals in the Auger decay matrix element [15]. The relative electronic probabilities for the excitation and decay of the $^2\Sigma^+$, $^2\Delta$ and $^2\Sigma^-$ states computed in the present work are equal to 1:2:0.1, respectively.

One can see that the weak direct photoionization influences the computed $\sigma_{Av_1}(\omega)$ negligibly (solid and dash-dot-dotted curves in panels (a) are practically indistinguishable). The same holds for the computed parameters $\beta^e_{Av_1}(\omega)$ and $\beta2^{Xv_2}_{Av_1}(\omega)$ close to the resonance. The weak direct photoionization influences the angular distribution parameters noticeably only for large energy detunings from the resonance [cf. solid and dash-dot-dotted curves in panels (b) and (c)]. Far away from the resonance, the $\beta^e_{Av_1}(\omega)$ and $\beta2^{Xv_2}_{Av_1}(\omega)$ parameters are almost entirely determined by the direct photoionization channels, as is also intuitively clear.

In order to reveal the ESI between the multiplet components of the N$^*$O resonance we performed calculations in the *NoESI(Dir+Res)* approximation and compared these results with those for the *ESI(Dir+Res)* approximation. For this purpose we first computed the angular distribution parameters for the direct (*Direct*) and for each electronic resonant photoionization channel separately [*Separate (Res)*]. Results of these calculations are depicted in panels (b) and (c) of Figs. 1 and 2 (note, that the $\beta2^{Xv_2}_{Av_1}$ values for the fluorescence angular distribution parameter are equal to $-0.1$ for all electronic resonances). The obtained angular distribution parameters were then weighted by the corresponding cross sections $\sigma_{Av_1}(\omega)$. As expected, neglecting the ESI does not change the computed cross sections (not shown in the figures). The angular distribution parameters computed in the *NoESI(Dir+Res)* approximation are depicted in Figs. 1 and 2 by dotted curves. One can see that neglecting the ESI changes the computed $\beta^{e}_{Av_1}(\omega)$ and $\beta 2^{Xv_2}_{Av_1}(\omega)$ dispersions drastically. The ESI is responsible for the curvature changes of the dispersions between the $^2\Delta$ and $^2\Sigma^+$ resonances from concave to convex and vice versa. Moreover, for the $\beta 2^{Xv_2}_{Av_1}$ parameter, ESI also changes its sign twice across the resonance.

In the present case, cross terms in Eqs. (5) and (7) are allowed between the $^2\Delta$ and $^2\Sigma^\pm$ resonant amplitudes (corresponding kinematic coefficients $b^{\ell' m' k'}_{\ell m k}$ and $b2^{k'q'}_{kq}$ [17] are non equal to zero). Since the amplitude for the population and decay of the $^2\Sigma^-$ resonance is small, the main ESI effect stems from the interplay between the $^2\Delta$ and $^2\Sigma^+$ resonant amplitudes. Because of the energy denominator, the resonant amplitude in Eq. (4) changes its sign across the resonance. At exciting-photon energies below the $^2\Delta$ resonance, both amplitudes have the same signs. At energies above the $^2\Sigma^+$ resonance, they again have the same signs (but opposite to the previous one). Thus, in these energy ranges, the cross terms are positive. In between the $^2\Delta$ and $^2\Sigma^+$ resonances, the amplitudes have opposite signs, and the cross terms are negative. The change of the signs of the cross terms in Eqs. (5) and (7) across the N*O resonance from positive to negative and again to positive is responsible for the change of the ESI from constructive to destructive and again to constructive.

As a first experimental test of the ESI we measured the fluorescence angular distribution parameters $\beta 2^{Xv_2}_{Av_1}(\omega)$. The experiment was carried out at the planar elliptical undulator beam line UE56/2-PGM-2 at BESSY II, Berlin using photon-induced fluorescence spectroscopy. The present experiment is very similar to that performed in [15]. The angular distribution parameter has been determined by the setup geometry and procedure described in [19]. The energy of the linearly polarized synchrotron radiation was varied in steps of 25 meV covering the energy range from 398.8 to 401.1 eV. The band width of the exciting radiation was 110 meV which, in view of the natural width of the N*O resonances of 124 meV [13], is still in the Raman regime of excitation. Dispersed fluorescence intensities were measured in the directions perpendicular to the exciting-photon beam, and parallel and perpendicular to the electric field vector of the incoming radiation with a fluorescence resolution of 0.2 nm.

The total fluorescence intensities $I^{Xv_2}_{Av_1}(\omega)$ and angular distribution parameters $\beta 2^{Xv_2}_{Av_1}(\omega)$ measured for the 0–2 ($\lambda \approx 146.2$ nm) and 1–2 ($\lambda \approx 143.0$ nm) fluorescence bands are depicted in Figs. 1 and 2, respectively. From panels (a) it is evident that the measured fluorescence intensities are in very good agreement with the computed cross sections for the population of the initial fluorescence states. The measured $\beta 2^{Xv_2}_{Av_1}(\omega)$ parameters are shown in panels (c) only at those energies where the present count rate (signal-to-noise ratio) was reliable (error bars $\Delta\beta 2$ within $\pm 0.1$). One can see that the measured absolute values and dispersions of the $\beta 2^{Xv_2}_{Av_1}(\omega)$ parameters are also in good agreement with those computed by including ESI between three intermediate resonances (solid curves). Although the experimental error bars are still large, the present measurement proves the ESI, illustrated by the theory, unambiguously [the experimental uncertainties are less than the difference between the $\beta 2^{Xv_2}_{Av_1}(\omega)$ parameters computed in the *NoESI(Dir+Res)* and *ESI(Dir+Res)* approximations].

In conclusion, we have demonstrated that the interference between the amplitudes for excitation and decay of neighboring core-excited N*O resonances of different symmetries plays a crucial role in the formation of their angularly resolved deexcitation spectra, although it is symmetry forbidden in the solid-angle-averaged spectra. Symmetry-forbidden interference is necessarily appearing when open shell atoms and molecules or initially polarized targets are probed with polarized radiation, and is important for interpretation of polarizability of matter. For the future studies of NO it is also important to verify the impact of the weak direct photoionization illustrated theoretically by measuring the angular distribution parameters in the off-resonance excitation regime with considerably improved experimental count rate.

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