

## Supporting information for Time-Energy Mapping of Photoelectron Angular Distribution: Application to Photoionization Stereodynamics of Nitric Oxide

Yoshi-Ichi Suzuki, Ying Tang<sup>1</sup>, Takuya Horio and Toshinori Suzuki<sup>2</sup>

*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*

*Advanced Science Institute, RIKEN, Wako, Saitama 351-0198 Japan*

### Continuum multiple scattering $X\alpha$ calculations for NO

Continuum multiple scattering  $X\alpha$  (CMSX $\alpha$ )<sup>1</sup> is a simple model of photoionization that approximates the interaction between an electron and an ion core by one-electron muffin-tin potential. Despite of its limited accuracy, CMSX $\alpha$  has been serving as a useful tool for experimental studies of photoionization dynamics. The muffin-tin potential consists of three regions, *i.e.* the atomic, outer, and Coulombic regions. In our CMSX $\alpha$  calculations on NO, the muffin-tin radii of the nitrogen and oxygen atoms were assumed to be a half of the internuclear distance in the  $A$  state ( $R = 2.011$  a.u.) that is slightly longer than the distance of  $\text{NO}^+$  ( $R = 2.009$  a.u.). We used the touching sphere model with  $\alpha = 1$ .<sup>2</sup> The potential in the outer region was determined to be  $-36.81$  eV from Hartree-Fock calculation of the  $A$  state. The boundary between the outer sphere and a pure Coulomb region was set at  $R = 2.0780$  a.u. Because of the Rydberg nature of the  $A(3s)$  state, we employed a large basis set used by Rudolph and McKoy.<sup>3</sup> The angular momentum was included up to  $l = 3$  and  $5$  for the continuum states in the atomic region and the outer region, respectively.

Previous theory<sup>4,5</sup> and experiment<sup>4</sup> have identified a shape resonance at around  $\text{PKE} = 6\text{--}9$  eV in the  $\sigma$  channel of photoionization of NO from the ground state. Wallace *et al.* have reproduced the resonance energy (c.a. 8 eV) by CMSX $\alpha$  calculations using an overlapping sphere model with  $\alpha = 0.744 - 0.751$ . Our calculations predict the same resonance state at  $\text{PKE} = 4.5$  eV. The shift of the resonance energy is ascribed to the  $\alpha$  value of 1, which is a typical choice for a touching sphere model.<sup>2,6</sup> A larger  $\alpha$  value makes the potential more attractive and lowers the resonance energy: when we employ  $\alpha = 0.7$ , the muffin tin potential energy of the outer region rose to  $-31.41$  eV and the resonance energy became c.a. 10 eV. The quantum defects and scattering phase shifts were only slightly affected by this change: for instance, the energy of the  $3s$  Rydberg state increased by only 0.4 eV. Therefore, the estimation of the phase shift is relatively insensitive to the choice of  $\alpha$ . In any case, no shape-resonance is anticipated in the energy range we discuss in the present work.

The quality of the continuum states obtained by CMSX $\alpha$  calculations was examined by

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<sup>1</sup> Present address: Wuhan institute of physics and mathematics, Chinese Academy of Sciences.

<sup>2</sup> Author to whom correspondence should be addressed. Electronic mail: [suzuki@kuchem.kyoto-u.ac.jp](mailto:suzuki@kuchem.kyoto-u.ac.jp).

comparing the calculated quantum defects of the Rydberg states and corresponding experimental values. The quantum defects  $\delta$  is obtained from the energy ( $E$ ) of the Rydberg state using the following relation,

$$E = -\frac{1}{2(n-\delta)^2}, \quad (1)$$

in atomic unit. The Rydberg state energies were calculated by solving eigenvalue equation with the boundary condition that the wave functions vanish asymptotically. As shown in Fig. S1, the calculated quantum defects agree reasonably well with the experimental values.<sup>7</sup> The quantum defects of the Rydberg states have the same physical meaning with the eigenphase shifts of the continuum state wave functions in the positive energy region: Fig. S1 shows smooth connection of the quantum defects to the eigenphase shifts. For NO molecule, it is well-known that the s and d waves are strongly mixed (s-d super complex).<sup>8</sup> The mixed states are termed as sd1 and sd2 in the present work following the previous notation.<sup>9</sup> Our CMSX $\alpha$  calculations show that the mixing angle of the s and d states is weakly energy-dependent:  $\theta_{sd} = \sin^{-1} U_{d,sd1}^{(\sigma)} = 0.55 + 0.03E$  (eV) rad, which is in qualitative agreement with  $0.675 + 0.01E$  (eV) rad, estimated by Rydberg state spectroscopy [Fig. 8 of Reference<sup>8</sup>]. Because the mixing matrix varies only slightly in the narrow energy range of our experiment, we assumed that the mixing matrix is independent of energy, when using it in the analysis of  $t$ - $E$  maps.

Figure 8 of our paper shows the relative magnitudes and relative phases of TDMs for various partial waves calculated by CMSX $\alpha$ . It is seen that the relative magnitudes of the transition dipole moments vary only slightly with energy; therefore, in the zeroth order approximation, they can be assumed energy-independent in the analysis. The results also show that the p and f waves are important both in  $\sigma$  and  $\pi$  channels in accordance with previous theory<sup>10</sup> and experiment<sup>11</sup>. Slight increases of  $r_{f\sigma}$  and  $r_{p\sigma}$  may be the influence from a resonance state in the  $\sigma$  channel at higher energy.

We evaluated the relative phases and relative quantum defects using CMSX $\alpha$  (Table SI). The calculated relative phase of  $\chi_{s\sigma} - \chi_{p\pi} = 1.8$  rad agrees well with 1.85 rad obtained by more accurate Schwinger variational method.<sup>10</sup> The nonzero value in the fourth row means the partial wave mixing. These values agree with our experimental results<sup>12</sup> in signs but the magnitudes are smaller (Table IV of the manuscript).

In summary, the CMSX $\alpha$  calculations were able to suggest which dynamical factor, including energy dependence, is important. The CMSX $\alpha$  method can also be used predict the difference between the scattering phases and the quantum defects, because it takes into account hybridization of partial waves.

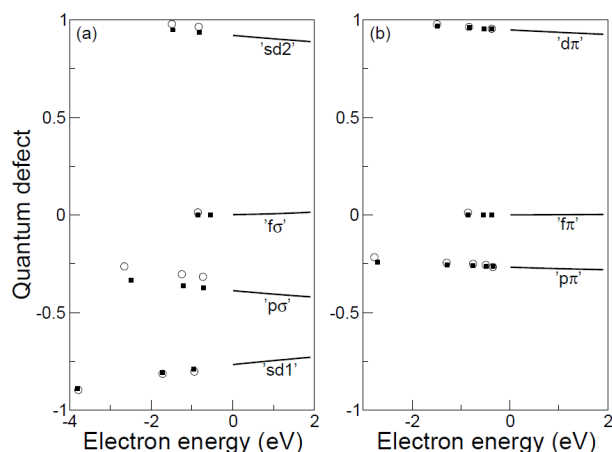


FIG. S1. Quantum defects and eigenphases of NO obtained by CMSX $\alpha$  calculations (solid squares and lines) and by Rydberg state spectroscopy of Reference <sup>7</sup> (circles).

TABLE SI. Differences between scattering phase shifts ( $\chi_{l\lambda-p\pi}$ ) and quantum defects ( $\pi\delta_{l\lambda-p\pi}$ ) in radian units obtained by CMSX $\alpha$ .

$l\lambda$	$p\sigma$	$f\sigma$	$f\pi$
$\chi_{l\lambda-p\pi}$	-0.32	0.90	0.75
$\pi\delta_{l\lambda-p\pi}$	-0.40	0.88	0.86
difference	0.08	0.02	-0.11

## Reference

- 1 D. Dill and J. L. Dehmer, J. Chem. Phys. **61**, 692 (1974).
- 2 W. Thiel, Chem. Phys. **57**, 227 (1981).
- 3 H. Rudolph and V. McKoy, J. Chem. Phys. **93**, 7054 (1990).
- 4 S. Wallace, D. Dill, and J. L. Dehmer, J. Chem. Phys. **76**, 1217 (1982).
- 5 R. E. Stratmann, R. W. Zurales, and R. R. Lucchese, J. Chem. Phys. **104**, 8989 (1996).
- 6 Y.-I. Suzuki and T. Suzuki, J. Phys. Chem. A **112**, 402 (2008).
- 7 E. Miescher and F. Alberti, J. Phys. Chem. Ref. Data **2**, 309 (1976).
- 8 S. Fredin, D. Gauyacq, M. Horani, C. Jungen, G. Lefevre, and F. Masnou-Seeuws, Mol. Phys. **60**, 825 (1987).
- 9 H. Park and R. N. Zare, J. Chem. Phys. **104**, 4568 (1996).
- 10 H. Rudolph and V. McKoy, J. Chem. Phys. **91**, 2235 (1989).
- 11 D. J. Leahy, K. L. Reid, H. Park, and R. N. Zare, J. Chem. Phys. **97**, 4948 (1992).
- 12 Y. Tang, Y.-I. Suzuki, T. Horio, and T. Suzuki, Phys. Rev. Lett. **104**, 073002 (2010).