Studies of Rydberg-valence mixed autoionizing states in NO

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Interference between overlapping Rydberg- and valence-level autoionizing states can have dramatic effects on photoionization dynamics. Our calculations demonstrate this type of interference in NO, where we predict that the autoionizing structure is of a mixed Rydberg-valence character and dominates the cross sections, obscuring the underlying shape resonance. Such studies have important implications for understanding autoionization mechanisms in molecular systems as well as other areas of physics.

INTRODUCTION

Resonances play a major role in many areas of physics, such as nuclear-resonance theories, defects in solid-state structure, electron-molecule scattering, as well as in understanding photoionization dynamics. In appropriate energy regions, resonance phenomena will often dominate the process under study. Typically these resonances are of two types, classified by their nature, being either single-particle (shape) or multielectron (autoionizing) transitions. The former arise from the temporary trapping of the photoelectron in a potential barrier while the latter evolve through the formation and decay of a compound state of the target and projectile. Autoionizing states are often described by their valencelike or Rydberg-like character, implying either "molecular" excited states or "atomic" states which correspond to a loosely bound-electron external to the molecular-ion core. In many cases these single and multiparticle resonances may overlap and can hence be expected to interfere, producing dramatic effects in the photoionization dynamics. Earlier multichannel quantum defect (MCQD) studies[1] have demonstrated that overlapping, separate Rydberg series can alter the widths of the individual members. In addition the interaction of sharp Rydberg series with shape or giant resonances has been considered by Connerade and Lane.[2]

Shape resonances are now well understood for many small molecular systems;[3] however, autoionization, being a final-state correlation effect, is usually neglected in *ab initio* molecular-photoionization studies. The theoretical basis for the understanding of autoionization has been developed and understood for many years in the context of Feshbach resonance theory[4] as well as configuration interaction in the continuum.[5] In fact, only recently have *ab initio* treatments been developed to investigate these resonances in electron-molecule collisions.[6−10] MCQD calculations require the input of electronic parameters, e.g., quantum defects, which are usually, although not necessarily, obtained from experimental data. In this paper we report the first fully *ab initio* results for Rydberg-valence mixed autoionizing states in 2π photoionization of NO. This system is of particular interest due to the underlying shape-resonance feature which is in the same spectral region as the overlapping Rydberg-valence structure. Therefore, one has the common interaction of a

sharp Rydberg series, a broad molecular valence state, and a much broader shape-resonance feature.

Recent experimental studies of molecular photoionization have illustrated the dramatic effects that shape and autoionizing resonances produce in the ionization dynamics.[11,12] Through the resonance region, pronounced structure in the cross sections and photoelectron asymmetry parameters are observed. Indeed the experimental situation is quite advanced with the use of synchrotron radiation as a photon source.[12] These sources can provide the intense tunable radiation necessary to study the continuous, and in resonance regions, the rapid variation of molecular photoionization cross sections with energy. When coupled with photoelectron kinetic-energy analysis, measurements can provide information on the production of different vibrational levels of the molecular ion. Such studies have demonstrated that strong non-Franck-Condon effects are induced by the resonant states. Non-Franck-Condon behavior results from dependence of the electronic transition matrix elements on R, the internuclear distance. Examples are vibrational-state-dependent asymmetry parameters and vibrational branching ratios that deviate from ratios of the appropriate Franck-Condon factors.

Southworth, Parr, Hardis, and Dehmer[13] have reported vibrationally resolved data for the photoionization of the 2π level of NO using synchrotron radiation in the 11−26 eV energy range. The results of these measurements indicate sharp features superimposed upon broad structure in the 11−18 eV region for both the vibrational branching ratios and vibrational-state resolved asymmetry parameters. They also observed the production of very high ionic vibrational levels $(v > 5)$ of the $X\,^1\Sigma^+$ state of NO^+, which are not predicted by a Franck-Condon analysis.

The underlying mechanism for producing the observed non-Franck-Condon behavior has not been established, although theoretical studies[14] have demonstrated that the influence of the $k\sigma$ shape resonance centered at 14 eV produces some non-Franck-Condon effects. However, these calculations clearly indicate that the presence of the shape resonance *does not account* for all the observed structure and that another mechanism, possibly autoionization, may be dominating the photoionization process in this energy range.

We have developed and applied a Feshbach partitioning

scheme, including an effective optical potential[6,15] to describe the quasibound states, in order to investigate autoionization in molecular systems. This method has been successfully applied to the study of valence and Rydberg levels in electron-H_2^+ scattering.[6,7] In this paper we report our results for the study of Rydberg-valence mixed autoionizing states in the 2π photoionization of NO with overall $^2\Sigma^+$ symmetry. Our results demonstrate that Rydberg-valence autoionization dominates the ionization process, as was suggested in our preliminary study[16] for NO photoionization, as well as the model calculations of Sobolewski.[17] In fact, the underlying shape resonance is completely obscured by these states. In addition, we observe a dramatic configuration mixing between the individual Rydberg and valence autoionizing states. The $5\sigma \rightarrow n\pi$ Rydberg levels interfere strongly with a broad valencelike autoionizing state, identified as a $4\sigma \rightarrow 2\pi$ excitation. Indeed the interference of these states is central in understanding the nature of the resonance structure observed in the 11–17 eV energy range and indicates that independent-resonance models would be invalid in these regions.

METHOD

The linear-algebraic effective-optical-potential method has been applied to study resonance effects in electron-molecular scattering processes. In this method the wave function is expanded as

$$|\Psi\rangle = \sum_c A [\phi_c(1\ldots N)F_c(N+1) + \sum_q c_q \psi_q(1\ldots N+1) ,$$

(1)

where ϕ_c is an N-electron target wave function for channel c, F_c is the single-particle scattering function, and A is the antisymmetrization operator. Correlation effects are included in the second sum of Eq. (1), which is present to ensure completeness, where ψ_q is an $(N+1)$ antisymmetrized function. For example, energetically closed channels, used to describe polarization effects in electron–neutral-species collision processes, or autoionizing states can be included in this portion of the total wave function. To cast the Schrödinger equation

$$(H-E)|\Psi\rangle = 0$$

(2)

into standard Feshbach form we introduce the projection operators P and Q,[6,15] partition the Schrödinger equation as

$$(H_{PP} + L_b + V_{opt} - E)P|\Psi\rangle = L_b P|\Psi\rangle ,$$

(3a)

$$(E - H_{QQ})Q|\Psi\rangle = H_{QP}P|\Psi\rangle ,$$

(3b)

with

$$V_{opt} = H_{PQ}(E - H_{QQ})^{-1}H_{QP} ,$$

(3c)

where L_b is the Bloch operator, which forces logarithmic boundary conditions on the scattering wave function at the boundary $(r = a)$. The optical potential is approximated by placing it on an L^2 basis and calculated using standard configuration-interaction bound-state methods. As

opposed to electron-scattering phenomena, in photoionization processes, the total wave function $(P+Q)|\Psi\rangle$ is necessary to compute the dipole transition-matrix elements. Thus, with the solution of Eq. (3a), the $Q|\Psi\rangle$ portion is obtained with Eq. (3b), and the photoionization cross section in the length form is calculated;[18]

$$\sigma = \frac{4\pi^2 E}{3c} |\langle \Psi_i | \mu | \Psi_f \rangle|^2 ,$$

where Ψ_i is the initial wave function describing the neutral molecular system, Ψ_f is the energy-normalized final-state wave function corresponding to the molecular-ion core plus photoelectron, and μ is the length form of the dipole moment operator.

RESULTS AND DISCUSSION

We have performed a series of scattering calculations in order to access the influence of (1) the valence autoionizing state, (2) the autoionizing $5\sigma \rightarrow n\pi$ Rydberg series, and (3) the mixture of the valence and Rydberg series. The calculations were performed by selectively including the various autoionizing states in an optical potential. These transitions are represented schematically as

(1) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4 2\pi^2 (NO^*) ,$

(2) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^4 2\pi n\pi (NO^*) ,$

(a) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi (X^2\Pi, NO) + h\nu ,$

$$2e^- \text{ decay} ,$$

(b) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 (X^1\Sigma^+, NO^+) + e^- (k\sigma) .$

The neutral NO absorbs a photon sufficiently energetic to cause direct ionization (b) or excitation of the quasibound valence and/or Rydberg states (a). These processes interfere as the autoionizing states decay via a two-electron transition into the underlying shape-resonant continuum. The ionic configuration, $1\sigma^2 2\sigma^2 3\sigma^3 4\sigma^2 5\sigma 1\pi^4 2\pi$, has two spin states corresponding to the $b\,^3\Pi$ and $A\,^1\Pi$ levels of NO^+; thus process (2) is actually two separate Rydberg series leading to these different ion cores. We have not included the Rydberg series leading to other ion cores (i.e., $a\,^3\Pi$) in this calculation or the δ-symmetry final states. Their inclusion would certainly effect the quantitative aspects of the calculation but not the qualitative interactions of Rydberg and valence levels.

The initial state was taken as the self-consistent-field (SCF) wave function for NO $(R = 2.175$ a.u.). The valence basis $(N; 9s\,5p\,2d/5s\,3p\,2d, O; 9s\,5p\,2d/5s\,3p\,2d)$ (Ref. 19) was augmented, with two s- and p-type Gaussian orbitals at each nucleus and four- s-, p_x-, and p_y-type Gaussians at the center of mass in order to describe the $^2\Sigma^+ 5\sigma \rightarrow n\pi$ Rydberg series $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma 1\pi^4 2\pi n\pi)$ as well as the $2\pi \rightarrow k\sigma$ continuum in the separable approximation to the exchange and optical potentials. The final-state wave function is overall $^2\Sigma^+$ symmetry corresponding to the $2\pi \rightarrow k\sigma$ partial channel, and we have taken the experimental value 9.26 eV for the 2π ionization potential. In this basis the excitation energies and oscillator strengths for the Rydberg series leading to the $b\,^3\Pi$

and $A\,^1\Pi$ states have been calculated and are in good agreement with available experimental[20] and theoretical[21] results. The valence $4\sigma\rightarrow 2\pi$ ($^2\Sigma^+$) transition occurs at approximately 15.8 eV with a large dipole transition matrix element (0.565 a.u.). The calculation was performed in the impulse approximation at the equilibrium internuclear separation of the neutral NO. The effects of vibrational averaging will be included in a later paper.

In Fig. 1 we compare the photoionization cross sections leading to the $X\,^1\Sigma^+$ state of NO$^+$, in overall $^2\Sigma^+$ symmetry, calculated (1) using the static-exchange approximation and (2) using an optical potential with only the $Q=1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 5\sigma^2 1\pi^4 2\pi^2$ valence level included. The static-exchange results are in good agreement with previous calculations[14,19,22] and contain the $k\sigma$ shape resonance, peaking at 1.5 Mb near 14 eV. The inclusion of the valence-level transition significantly alters the photoionization cross section and appears as a broad feature centered at 15.8 eV with a peak cross section of 14.2 Mb. This results from the strong $4\sigma\rightarrow 2\pi$ intravalence transition.

An analogous set of calculations is reported in Fig. 2 where the optical potential contains only the $5\sigma\rightarrow n\pi$ Rydberg series leading to the $b\,^3\Pi$ and $A\,^1\Pi$ states of the ion. In this case very intense, sharp structure is superimposed upon the $k\sigma$ shape-resonant background continuum. The asymmetric Fano profile can be clearly seen in the vicinity of each resonance. The lowest (energetically) four peaks correspond to the Rydberg series leading to the $b\,^3\Pi$ state while the last resonance is the first member of the Rydberg series leading to the $A\,^1\Pi$ state. These calculations were not performed past 15.97 eV where the $b\,^3\Pi$ state becomes an open channel and pseudoresonances may be introduced by the optical potential.[23]

Lastly, we have included the two Rydberg series and the valence excitation in the optical potential. The interaction of these excitations is striking, as seen in Fig. 3. The broad valence level excitation is raked into several peaks, via interaction with the Rydberg series, or alterna-
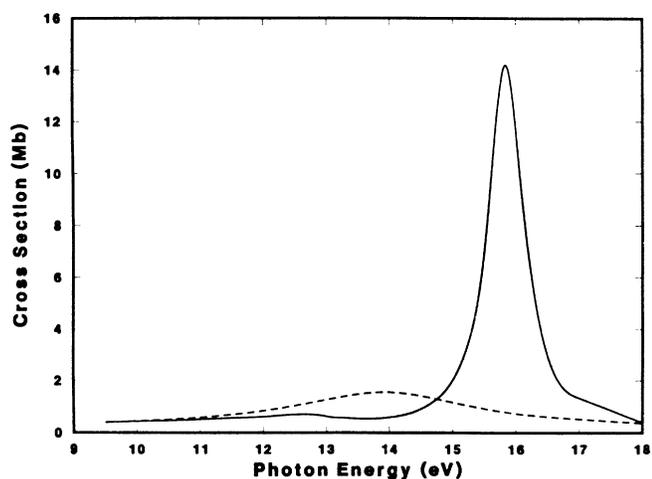

FIG. 2. $2\pi\rightarrow k\sigma$ photoionization cross sections in the static exchange approximation (dashed line), including the $5\sigma\rightarrow n\pi$ Rydberg series (solid line).

tively the sharp Rydberg features are broadened by their coupling with the valence state. The peak cross sections of the lowest member of both the $b\,^3\Pi$ and $A\,^1\Pi$ series are reduced in magnitude but essentially unshifted. The composition of the resonant features can be roughly determined by diagonalizing the H_{QQ} Hamiltonian matrix. The feature at 14.4 eV is primarily the valence state although it is spread through all the roots by configuration mixing. This interaction shifts the valence transition from 15.8 to 14.4 eV and reduces its intensity by nearly a factor of 2.

These calculations do not include all possible Rydberg series present in this energy range; for example, the series leading to the $a\,^3\Pi$ state of the ion ($1\pi^{-1}$, ionization potential 15.67 eV) has members between 12.61 and 15.06 eV.[20,23] However, the underlying mixture of the Rydberg-valence levels should persist with the inclusion of

FIG. 1. $2\pi\rightarrow k\sigma$ photoionization cross sections in the static exchange approximation (dashed line), including the $4\sigma\rightarrow 2\pi$ valence autoionizing state (solid line).
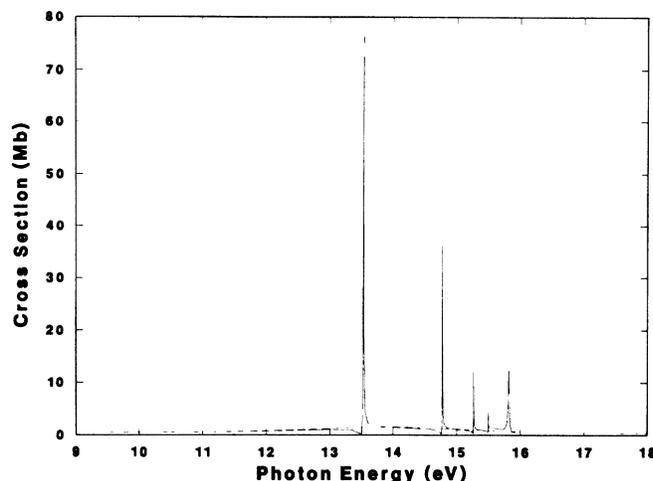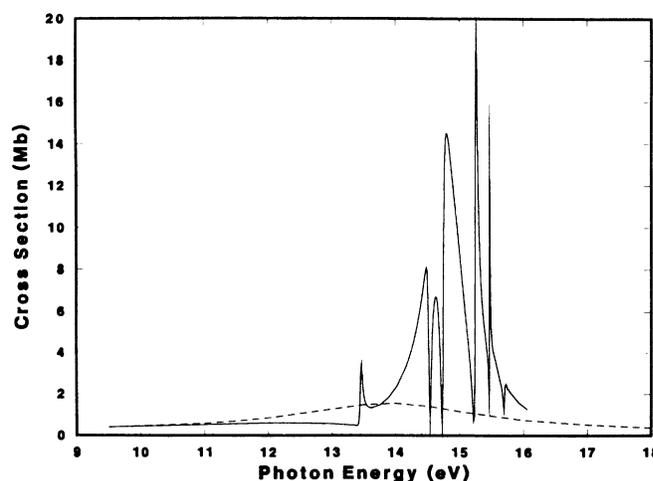

FIG. 3. $2\pi\rightarrow k\sigma$ photoionization cross sections in the static exchange approximation (dashed line), including the Rydberg-valence mixed autoionizing states (solid line).

this Rydberg series. The effect of additional Rydberg members is to introduce more sharp structure in this energy region.[23] Indeed, high-resolution measurements have been made for NO photoionization showing many features in the 11–17 eV (Ref. 24) range. In addition, dissociation, which may interfere with the ionization processes, is an open channel in this energy range[20] and has not been included. Since we are only examining $^2\Sigma$ symmetry in order to access the qualitative influence of Rydberg-valence mixing of these autoionizing states, total cross sections and β parameters are as yet unavailable to compare directly to these experiments.[13,24]

Based on the present calculations we can suggest that the sharp features superimposed on a broad background, observed in both the vibrational branching ratios and vibrationally resolved asymmetry parameters, arise from narrow Rydberg structure interacting with the broad valence transition, which essentially swamp the weak shape-resonance feature. Our results demonstrate that these complicated interchannel interactions can be treated at an *ab initio* level and that including autoionizing levels is essential for the detailed understanding of photoionization processes.

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