Shape resonance behavior in $1\pi_g$ photoionization of $O_2$

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We report calculations of vibrationally resolved cross sections and photoelectron angular distributions for photoionization of $O_2$ leading to the $X^2\Pi_g$ ($\nu^+ = 0$–4) states of $O_2^+$ using Hartree–Fock continuum photoelectron orbitals. These studies were motivated by recent results which show that a $\sigma_u$ shape resonance plays a dominant role in producing non-Franck–Condon vibrational distributions in resonant multiphoton ionization of $O_2$ via the $C^3\Pi_g$ ($1\pi_g\ 3\sigma_g^-$) Rydberg state. In the present study, we investigate how this shape resonance influences photoionization dynamics in single-photon ionization. Below 21 eV photon energy, we find significant non-Franck–Condon effects in the vibrational branching ratios as well as in the vibrationally resolved photoelectron angular distributions. Substantial autoionization hinders a direct comparison between theory and experiment.

I. INTRODUCTION

Recent resonant multiphoton ionization studies via the $C^3\Pi_g$ ($1\pi_g\ 3\sigma_g^-$) state of $O_2$ have shown that a shape resonance has a substantial influence on the vibrational distribution of the ground state $X^2\Pi_g$ ion.\(^1\) For single-photon ionization leading to the same ion, however, experimental evidence of any corresponding shape-resonant feature is inconclusive. Experimental studies of $O_2$ in the near-threshold region by single-photon ionization is complicated by the internuclear distance which, to date, has hindered assessment of the possible role of a low-energy shape resonance in the photoionization dynamics. To some extent this complication was avoided in the resonant multiphoton ionization studies\(^1\) through specific and limited selection of the photon wavelength.

To further elucidate the role of the $\sigma_u$ shape resonance in single-photon ionization, we have calculated vibrationally resolved cross sections and photoelectron angular distributions for photoionization leading to the $X^2\Pi_g$ state of $O_2^+$ using frozen-core Hartree–Fock photoelectron orbitals.\(^7\)\(^8\) These results show that a $\sigma_u$ shape resonance becomes evident in the cross section near the ionization threshold as the internuclear distance $R$ is decreased. This dependence of the transition moment on $R$, particularly for $R$ values less than $R_e$ of $O_2$ in this case, leads to significant deviations in the calculated branching ratios from Franck–Condon values for energies from threshold to $\sim21$ eV. The non-Franck–Condon effects are also apparent in our photoelectron asymmetry parameters. Comparison and subsequent interpretation of existing measured branching ratios (obtained from line-source measurements) is inconclusive, giving impetus for measurements that employ tunable radiation and extend to the ionization threshold.

An outline of the paper is as follows. In Sec. II we briefly discuss the Schrödinger variational method used to obtain the Hartree–Fock photoelectron orbitals and the procedures with which we obtain our vibrationally resolved cross sections and photoelectron angular distributions. In Sec. III our results are discussed and compared with available experimental data, and in Sec. IV concluding remarks are given.

II. METHOD AND CALCULATIONS

The continuum wave functions were obtained using the iterative Schrödinger variational method\(^7\)\(^8\) to solve the one-electron Schrödinger equation which the photoelectron orbitals satisfy in the frozen-core Hartree–Fock approximation. In this procedure, the $(lm)$ partial-wave component of the continuum orbital is given by the equation\(^8\)

$$\psi_{klm}^{(0)}(r) = \phi_{km}(r) + \sum_{\alpha} \langle \alpha | G^{-1} | \alpha \rangle \times \left[ D^{-1} \right]_\alpha \langle \alpha | U | \phi_{km} \rangle,$$ \hspace{1cm} (1)

where

$$D_\alpha = \langle \alpha | U - U G^{-1} | \alpha \rangle,$$ \hspace{1cm} (2)

$U$ is twice the static-exchange interaction potential of the ion core with the Coulomb potential removed, $G^{-1}$ is the Coulomb Green’s function, $\phi_{km}$ is the $(lm)$ component of the Coulomb scattering function, and the $\alpha$’s are discrete basis functions, the same as those used in Ref. 9. This large basis was sufficient to obtain well-converged results without resorting to an iterative procedure for improving $\psi_{klm}^{(0)}$. All integrations were carried out via partial-wave expansions with the resulting radial integrals evaluated by Simpson’s rule. The parameters used in the expansion of the static-exchange potential were the same as those in our previous studies of $O_2$ (Ref. 9) except that the maximum $l$ included in the expansion of the occupied orbitals in the exchange terms were made slightly larger so that $l_e = 24 (1\sigma_g)$, 24 (1$\pi_g$), 14 (2$\sigma_g$), 14 (2$\pi_g$), 12 (3$\sigma_g$), 12 (1$\pi_g$). The grid used to compute the radial integrals consisted of 900 points and extended out to 96.0 a.u. The continuum solutions are constrained to be orthogonal to the bound orbitals of the same symmetry. More details can be found in earlier studies.\(^7\)

The Hartree–Fock wave function for $O_2$ was constructed from a $[9s5p]/[4s3p]$ contracted Gaussian basis set\(^{10}\) and two $d$-type polarization functions with exponents of 2.7040 and 0.5350.\(^11\) The Hartree–Fock energy with this basis at the equilibrium internuclear distance of 2.282 a.u. is $-149.634$ 130 a.u.
We have obtained the photoionization transition matrix elements in both the dipole-length form
\[ I_{L_{\text{im}}}(R) = k^{1/2} \langle \Psi_i(r, R)|\hat{r}_n|\Psi_{J_{\text{km}}}(r, R) \rangle, \tag{3} \]
and the dipole-velocity form
\[ I_{V_{\text{im}}}(R) = (k^{1/2}/E) \langle \Psi_i(r, R)|\nabla_n|\Psi_{J_{\text{km}}}(r, R) \rangle \] \tag{4}

at the internuclear distances listed in Table I. In Eqs. (3) and (4), \( \Psi_i \) represents the initial \( N \)-electron wave function and \( \Psi_j \) is the wave function for the final ionized state, i.e., an \( N-1 \) molecular ion plus photoelectron, \( R \) specifies the nuclear coordinates, and \( n \) stands collectively for all electronic coordinates. These matrix elements were then interpolated with a cubic spline function. The length and velocity forms of the cross section for ionization of the \( v = 0 \) level of \( \text{O}_2 \) to the \( n \)th vibrational state of \( \text{O}_2^+ \) are then given by
\[ \sigma_{L_{\text{im}}}^n = \frac{4\pi^2}{3c} E \sum_{\text{im}_\mu} |\langle \chi_{\text{im}_\mu}^n |\hat{r}_n| \chi_{\text{im}} \rangle |^2, \tag{5} \]
where \( \chi \) are appropriate vibrational wave functions, \( E \) is the photon energy, and \( c \) is the speed of light. The vibrationally resolved photoelectron asymmetry parameter \( \beta_k \) is defined from the photoelectron differential cross section by
\[ \frac{d\sigma_{L_{\text{im}}}^n}{d\Omega_k} = \frac{\sigma_{L_{\text{im}}}^n}{4\pi} \times [1 + \beta_k \cos \theta], \tag{6} \]
where \( \theta \) is the angle between the direction of polarization of the light and the photoelectron momentum.

The vibrational wave functions were obtained by numerical integration of the Schrödinger equation using the Rydberg–Klein–Rees potentials of Krupenie. The Franck–Condon factors thus obtained agreed with those of Ref. 12, i.e., \( v = 0, v^+ = 0 \) = 0.1884, \( v = 0, v^+ = 1 \) = 0.3645, \( v = 0, v^+ = 2 \) = 0.2901, \( v = 0, v^+ = 3 \) = 0.1227, \( v = 0, v^+ = 4 \) = 0.0298.

**III. RESULTS AND DISCUSSION**

In previous studies of \( \text{O}_2 \), a \( \sigma_u \) shape resonance has been assigned experimentally \(^{13,14}\) and investigated theoretically in near-threshold \( 3\sigma_g \) photoionization.\(^{9,15-18}\) For \( 1\pi_g \) photoionization, an earlier fixed-nuclei Stieltjes moment theory (SMT) study showed an apparently weak set of \( n\sigma_u \) transitions converging to the first ionization threshold.\(^{17}\) From consideration of the energy dependence of the quantum de

![FIG. 1. Oscillator strength distribution in the discrete and continuous spectra for the \( 1\pi_g \rightarrow \sigma_u \) transition at \( R_s \). The energy scale is relative to the ionization threshold at 12.07 eV. Calculations of Ref. 17 were used to construct the discrete part and the present results (dipole length) are shown above threshold.](image1)

![FIG. 2. Photoionization cross sections (dipole length) for the \( 1\pi_g \rightarrow k\sigma_u \) channel in \( \text{O}_2 \) at several values of the internuclear distance.](image2)
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![Graph showing vibrationally resolved cross sections leading to the $X^2\Pi_g$ state of $\text{O}_2^+$](image1)

**FIG. 3.** Vibrationally resolved cross sections leading to the $X^2\Pi_g$ state of $\text{O}_2^+$: —, present results (dipole length); ---, present results (dipole velocity).

shape resonance partially obscured by the nonresonant $k\sigma_u$ and $k\delta_u$ channels, appears as a weak feature in the total cross section at low energy. These variations are sufficient to cause significant deviations from Franck-Condon values in the branching ratios, $\sigma(v = 0 - v^+ = n)/\sigma(v = 0 - v^+ = 0)$, at energies below 21 eV photon energy. We use the notation $n:0$ to denote the branching ratio for the $n$th vibrational level. As seen in Fig. 4 the non-Franck-Condon behavior is quite substantial near threshold but by 21 eV the branching ratios reach their Franck-Condon values. For the

![Graph showing vibrational branching ratios for photoionization leading to the $X^2\Pi_g$ state of $\text{O}_2^+$](image2)

**FIG. 4.** Vibrational branching ratios for photoionization leading to the $X^2\Pi_g$ state of $\text{O}_2^+$: —, present results (dipole length); ---, present results (dipole velocity). The horizontal lines are the Franck-Condon values.

![Graph showing vibrationally resolved photoionization cross sections for the $1\pi_u \rightarrow k\sigma_u$ transition (dipole length).](image3)

**FIG. 5.** Vibrationally resolved photoionization cross sections for the $1\pi_u \rightarrow k\sigma_u$ transition (dipole length).

old, obscuring its presence.

For purposes of illustration, in Fig. 2 we show the $k\sigma_u$ partial cross sections for photoionization out of the $1\pi_u$ orbital of $\text{O}_2$ at eight internuclear distances. The photon energy scale in this figure assumes an ionization potential of 12.07 eV. The dependence of the shape-resonant cross section on internuclear distance is as expected, becoming broader and shifting to higher energy as the internuclear distance is decreased. This dependence leads to non-Franck-Condon behavior in the calculated ionic vibrational distributions. In Fig. 3 we show the vibrationally resolved photoionization cross sections for the $v^+ = 0-4$ states of the $X^2\Pi_g$ ion. The

![Graph showing photoionization cross section for the $X^2\Pi_g$ state of $\text{O}_2^+$](image4)

**FIG. 6.** Photoionization cross section for the $X^2\Pi_g$ state of $\text{O}_2^+$: —, present results (dipole length) obtained by summing contributions from $v^+ = 0-4$ vibrational levels; --- (short dash), fixed-nuclei results of Ref. 15 at $R_r$ (MSM); --- (long dash), vibrationally averaged results of Ref. 15 (MSM); --- (medium dash), fixed-nuclei results of Ref. 17 at $R_r$ (SMT); □ experimental $(e, 2e)$ results of Brion et al. (Ref. 6); Δ, experimental linesource results of Samson et al. (Ref. 5). Our fixed-nuclei results at $R_r$ are nearly identical to our vibrationally summed results and are not shown.

lower vibrational levels \((v^+ = 0-2)\), the behavior of the branching ratios can be understood by examining the dependence of the integrand in Eq. (5) on internuclear distance for the shape-resonant \(\sigma_u\) channel. For these levels the integrand is strongly peaked around one value of the internuclear distance \(R\) for the energy range studied. As the vibrational level increases, the largest contribution to the integrand comes from increasing values of \(R\). The resulting shape-resonant \(\sigma_u\) cross sections peak at successively lower values of the photoelectron kinetic energy for increasing vibrational excitation. This behavior is best illustrated in Fig. 5 by showing vibrationally resolved \(k\sigma_u\) partial cross sections. The ratios of the total cross sections therefore give rise to the sharp increase at threshold and dip at \(-15.0\) eV photon energy for the 1:0 and 2:0 branching ratios. For the higher ionic vibrational levels, larger internuclear distances are sampled, but the behavior of the integrands is more complex and cannot be as straightforwardly interpreted.

In Fig. 6 we show the vibrationally summed cross sections for \(v^+ = 0-4\). Our results calculated at equilibrium geometry are nearly identical to the vibrationally summed results and are not shown. We also show both the fixed-nuclei results at \(R_n\) and the vibrationally averaged cross sections of the multiple scattering model (MSM) study of Dittman \textit{et al.},\textsuperscript{15} and the fixed-nuclei results at equilibrium of the SMT study of Gerwer \textit{et al.}\textsuperscript{17} We find that vibrational averaging hardly affects the present cross sections, in contrast to what is seen in the MSM study. This exaggeration of the effects of vibrational averaging in the MSM treatment has also been noted in earlier studies on \(N_2\).\textsuperscript{21} Moreover, the shape resonance is much more pronounced and at higher energy than in the present study. Figure 6 also shows the experimental results of Samson \textit{et al.}\textsuperscript{5} and Brion \textit{et al.}\textsuperscript{6} The prominent structure in the experimental data indicates that autoionization may play a significant role in the low-energy cross section for the \(X^2\Pi_u^+\) state of \(O_2^+_\). Holmes \textit{et al.}\textsuperscript{24} suggest that Rydberg states leading to the \(b^4\Sigma_u^-\) ion (ionization potential equal to 18.17 eV) are responsible for some of the autoionization in the vibrationally unresolved angular distributions. Moreover, the high-resolution photoionization efficiency study of Dehmer \textit{et al.}\textsuperscript{25} identifies several other Rydberg states which may contribute to autoionization features in the vibrationally resolved photoionization cross sections. Clearly, the autoionization structure is rich and com-
complex, and warrants further detailed experimental and theoretical study, as has been done on $3\sigma_g$ photoionization.

In Fig. 7 we compare our calculated branching ratios to the line source data of Gardner et al.\textsuperscript{26} As discussed above, autoionization structure complicates a comparison of the branching ratios with experimental data. Experiments employing a synchrotron source are needed to investigate the role of autoionization on these spectra. Finally, in Fig. 8 we show our calculated vibrationally resolved photoelectron asymmetry parameters. These $\beta$'s are strongly state dependent, particularly near threshold. This non-Franck-Condon behavior should be observable experimentally, barring additional complicating structure due to autoionization.

IV. CONCLUDING REMARKS

We have studied the vibrationally resolved cross sections and photoelectron angular distributions for photoionization leading to the $X^2\Pi_g$ ($\nu^+ = 0-4$) states of $\text{O}_2^+$. These studies were motivated by recent work showing the prominent role of a shape resonance in producing non-Franck-Condon effects in resonant multiphoton ionization of $\text{O}_2$ via the $C^2\Pi_u$ Rydberg state.\textsuperscript{14} A $\sigma_n$ shape resonance strongly influences these cross sections near the ionization threshold. This $\sigma_n$ shape resonance leads to significant non-Franck-Condon behavior in ionization of the $1\sigma_g^+$ level, and is evident in both the branching ratios and a vibrational state dependence of the photoelectron angular distributions below 21 eV photon energy. Comparison of our vibrationally resolved cross sections with available line-source data is seriously hindered by autoionization. Continuum source experiments are needed to further understand this structure, and to elucidate the shape-resonant continuum.

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