Multiplet-specific shape resonant features in vibrationally resolved 3σg photoionization of O₂

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We report multiplet-specific vibrationally resolved photoionization cross sections and photoelectron angular distributions for the 3σg orbital of O₂ leading to the v⁺ = 0–3 levels of the b¹Σg⁻ and B¹Σg⁺ states of O⁺²⁺. These studies were motivated by recent work which shows significant nonstatistical behavior in the vibrationally unresolved spectrum at low photoelectron energies arising from the sensitivity of the kσu resonance to the multiplet-specific exchange potentials. In addition to the anticipated non-Franck-Condon vibrational distributions arising from the kσu shape resonance, we also find substantial nonstatistical effects in our vibrationally resolved cross sections and particularly in our photoelectron angular distributions over a broad energy range. Extensive electronic autoionization due to Rydberg levels leading to the c 4Σu⁻(2σu⁻¹) ion makes it difficult to assess these effects in the available experimental data.

INTRODUCTION

Previous theoretical studies of vibrationally unresolved 3σg photoionization of O₂ leading to the B¹Σg⁺ and b¹Σg⁻ ions have shown significant nonstatistical behavior in the spectral region of the well known σu shape resonance.¹² The sensitivity of this shape resonance to the multiplet-specific exchange potentials of these molecular ions gives rise to shifts in the oscillator strength distributions near threshold. In fact, the b¹Σg⁻ cross section peaks around 4 eV above threshold, while the oscillator strength associated with the σu shape resonance in the B¹Σg⁺ cross section shifts closer to threshold, perturbing the spectral distribution of the σu Rydberg states leading to the B¹Σg⁺ ion.² This shift in oscillator strength associated with the σu shape resonance is also reflected in large differences in the multiplet-specific photoelectron angular distributions.² These differences are difficult to assess in the experimental spectra due to extensive electronic autoionization of Rydberg states leading to the c 4Σu⁻(2σu⁻¹) ion.³−⁶ However, recent high-resolution measurements do show a relatively broad maximum in the B¹Σg⁺ cross section at considerably lower photoelectron energies than the shape-resonant maximum seen in the b¹Σg⁻ cross section.⁷⁻⁸ Similar multiplet-specific behavior has also been observed in the 5σ resonance of NO leading to the A¹Π² and b¹Π₁ ions, where a difference of as much as 3 eV is seen in the positions of the shape resonance.⁹−¹¹ In (2 + 1) resonance-enhanced multiphoton ionization (REMPI) of O₂ via the C¹Π₂(π 3σg) and d¹Π₁(π 3σg) states, significant multiplet-specific effects were also seen in the vibrationally resolved ion cross sections and photoelectron angular distributions.¹²,¹³

In the present work we extend our previous vibrationally unresolved studies of multiplet-specific 3σg photoionization in O₂ (Ref. 2) by obtaining vibrationally resolved cross sections and photoelectron angular distributions for v⁺ = 0–3 to further assess multiplet-specific effects. Our vibrationally resolved cross sections show the expected large non-Franck-Condon effects in the region of the σu shape resonance as well as significant multiplet-specific behavior in the cross sections. Comparison with experimental measurements is again made difficult by the role of electronic autoionization in the region of these shape resonances. The photoelectron angular distributions also show both non-Franck-Condon behavior and multiplet-specific differences well beyond the energy range of autoionizing features in the measured cross sections. Measurements of these photoelectron angular distributions using tunable radiation would be of considerable importance in understanding these multiplet-specific effects.

THEORY

Our procedure for obtaining vibrationally resolved photoionization cross sections and photoelectron angular distributions has been described extensively elsewhere.²,¹⁴−¹⁷ Briefly, we include full kinetic energy and internuclear dependence in the bound–free transition moment,

\[ M_{0→v'} = \int dR \chi_0 \mu_d(k,R) \chi_{v'}. \] (1)

Here \( \mu_d(k,R) \) is the transition moment between the initial bound state of O₂ (X³Σg⁻) and final continuum state (ionic core + photoelectron). In Table I we give the internuclear distances at which the transition moments are determined. For the ground state of O₂ we used a Hartree–Fock SCF wave function obtained with a [4s3p2d] Cartesian Gaussian basis set.¹⁴ For the final state we used the frozen-core approximation with Hartree–Fock photoelectron orbitals for the dipole-allowed ³Σu⁻(kσu) and ³Πu(kπu) channels obtained with the interactive Schrödinger variational technique and multiplet-specific static-exchange potentials.⁶ All integrations associated with obtaining the transition moments were carried out via partial-wave expansions with the resulting radial integrals evaluated by Simpson's rule. The partial-wave expansion parameters and radial grid are the same as those of Ref. 14.

The vibrational wave functions \( \chi \) of Eq. (1) were ob-
tained by numerical integration. For the ground and \( b^4\Sigma_g^- \) ion states, we used the Rydberg–Klein–Rees (RKR) potentials of Krupenie.\(^{18}\) A Morse potential was used for the \( B^2\Sigma_g^- \) ion potential with spectroscopic constants given by Huber and Herzberg.\(^{19}\) Franck–Condon factors obtained with these potentials are given in Table II along with other calculated values\(^{20}\) and measured vibrational intensities at high energy,\(^{21,22}\) well away from the influence of the \( k\sigma_u \) shape resonance.

RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b) we show our calculated multiplet-specific photoionization cross sections for the \( 3\sigma_g \rightarrow k\sigma_u \) transition in \( O_2 \) at various internuclear distances for the \( b^4\Sigma_g^- \) and \( B^2\Sigma_g^- \) ions, respectively. The most prominent feature here is the large maximum in the cross section caused by the well known \( k\sigma_u \) shape resonance.\(^{1-8,23-26}\) These resonant cross sections show the expected dependence on internuclear distance, becoming broader and peaking at higher energy with decreasing internuclear distance (\( R \)). This dependence leads to deviations from Franck–Condon behavior.\(^{27-29}\) For a particular \( R \), the peak of the shape resonance for each multiplet is at considerably different photoelectron energies. At \( R_g \), the ground state (2.282 a.u.) shape resonance is seen \( \sim 4 \) eV above threshold for the \( b^4\Sigma_g^- \) ion, while the oscillator strength associated with the \( B^2\Sigma_g^- \) cross section is shifted toward threshold,\(^{12}\) and, in fact, significantly perturbs the discrete spectral distribution.\(^2\) This shift arises from the sensitivity of the \( \sigma_u \) shape resonance to differences in the exchange component of the multiplet potentials and is not seen in studies using multiplet-averaged potentials.\(^{23-26}\) This behavior leads to large differences in the cross sections and photoelectron angular distributions for these multiplets.

TABLE I. Internuclear distances of \( O_2 \) at which photoionization transition moments were evaluated.

<table>
<thead>
<tr>
<th>Continuum symmetry</th>
<th>Internuclear distance*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k\sigma_u )</td>
<td>2.0, 2.1, 2.182, 2.232, 2.282</td>
</tr>
<tr>
<td></td>
<td>2.332, 2.382, 2.482, 2.6, 2.8, 3.0</td>
</tr>
<tr>
<td>( k\pi_u )</td>
<td>2.0, 2.1, 2.282, 2.382, 3.0</td>
</tr>
</tbody>
</table>

* In atomic units.

\(^b\) Resonant channel.

TABLE II. Franck–Condon factors for transitions from the ground state of \( O_2 \) (\( R = 2.282 \) a.u.) to vibrational levels of the \( b^4\Sigma_g^- \) (3\( \sigma_g^- \)) and \( B^2\Sigma_g^- \) (3\( \sigma_g^- \)) states of \( O_2^+ \).

\[ b^4\Sigma_g^- (R_g = 2.418 \text{ a.u.}) \]

<table>
<thead>
<tr>
<th>( v^+ )</th>
<th>Present work</th>
<th>Ref. 20 (theory)</th>
<th>Ref. 21 (experiment)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.408</td>
<td>0.411</td>
<td>0.452</td>
</tr>
<tr>
<td>1</td>
<td>0.336</td>
<td>0.337</td>
<td>0.319</td>
</tr>
<tr>
<td>2</td>
<td>0.164</td>
<td>0.163</td>
<td>0.154</td>
</tr>
<tr>
<td>3</td>
<td>0.062</td>
<td>0.062</td>
<td>0.057</td>
</tr>
</tbody>
</table>

\[ B^2\Sigma_g^- (R_g = 2.453 \text{ a.u.}) \]

<table>
<thead>
<tr>
<th>( v^+ )</th>
<th>Present work</th>
<th>Ref. 22 (experiment)</th>
<th>Ref. 21 (experiment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.245</td>
<td>0.247</td>
<td>0.265</td>
</tr>
<tr>
<td>1</td>
<td>0.293</td>
<td>0.316</td>
<td>0.307</td>
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<tr>
<td>2</td>
<td>0.213</td>
<td>0.211</td>
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<tr>
<td>3</td>
<td>0.125</td>
<td>0.130</td>
<td>0.135</td>
</tr>
</tbody>
</table>

* Experimental quantities are obtained at the He II resonance line (40.8 eV) and have been normalized by taking the total relative intensities to be unity. This energy is far enough away from any shape and/or autoionizing resonances so that Franck–Condon behavior is expected.

Figures 2(a) and 2(b) show our vibrationally resolved photoionization cross sections for the \( b^4\Sigma_g^- \) and \( B^2\Sigma_g^- \) ion states, respectively. These multiplet-specific cross sections for the \( b^4\Sigma_g^- \) ion agree with the static-exchange multiplet-averaged calculations of Raseev et al.,\(^{26}\) but are consistently...
slightly larger. The vibrationally resolved cross sections of both studies peak at successively higher photon energies with increasing vibrational excitation. For the vibrationally resolved $B^2\Sigma_g^-$ cross sections, however, there are significant differences between the multiplet-averaged calculations of Raseev et al.,$^{26}$ which are expectedly similar to the $b^4\Sigma_g^-$ cross sections, and the present multiplet-specific results. These differences reflect the strong multiplet-specific behavior seen in the fixed-nuclei cross sections. Shape-resonant behavior appears closer to threshold in the vibrationally resolved $B^2\Sigma_g^-$ cross sections than in the $b^4\Sigma_g^-$ cross sections. The $B^2\Sigma_g^-$ cross sections also show a strong minimum around a photoelectron energy of 5 eV. This is due to cancellation between partial-wave contributions to the transition moment in the $k\sigma_u$ channel and can be understood by examining the partial-wave composition of the initial bound $3\sigma_g^-$ and final continuum $k\sigma_u$ orbitals. The $3\sigma_g^-$ orbital is $\sim 50\%$ $s$ wave and $\sim 50\%$ $d$ wave for the internuclear distances of interest here. These $s$ and $d$ waves both show a radial node at $\sim 1.2$ a.u. from the molecular center. The principle-value transition moments for the $\zeta_s = 1$ and $\zeta_s = 3$ continuum partial waves—made up of mostly $p$ and $f$ waves—go through zero at this energy producing a minimum in the $k\sigma_u$ cross section. This is akin to the so-called Cooper minimum$^{30,31}$ seen in atoms, except that the anisotropic molecular potential induces partial-wave mixing. The dominant contribution to the total cross sections arises from the $k\sigma_u$ partial channel in this region. This cancellation also occurs in the $b^4\Sigma_g^-$ channel at a higher energy (15 eV photoelectron kinetic energy) where the $k\sigma_u$ cross section is larger thus obscuring the effect in the total cross section. Studies of fluorescence polarization for the $b^4\Sigma_g^-$ ion do show the $\pi_u:\sigma_u$ cross section ratio growing rapidly from threshold to $\sim 30$ eV photon energy.$^{32,33}$ Measurements of the fluores-

FIG. 2. (a) and (b) Vibrationally resolved photoionization cross sections (dipole length) for the $b^4\Sigma_g^-$ and $B^2\Sigma_g^-$ ions, respectively. Dipole-velocity results are nearly the same but are sometimes slightly less in magnitude. See Ref. 2 for more details.

FIG. 3. (a) and (b) Vibrational branching ratios for photoionization (dipole length) for the $b^4\Sigma_g^-$ and $B^2\Sigma_g^-$ ions, respectively. Horizontal lines show the Franck–Condon ratios.
cidence polarization at slightly higher energy should show this behavior clearly as the $\kappa \sigma_\nu$ cross section goes through a minimum there.

High resolution vibrationally resolved photoionization measurements from threshold up to $\sim 24$ eV photon energy show differences between the vibrationally resolved multiplet cross sections. However, electronic autoionization from Rydberg levels leading to the $c^4 \Sigma_g^-$ ion ($IP = 24.5$ eV) in the energy region of the shape resonance makes comparisons difficult. Experiments over a broader energy range and theoretical studies which include these autoionizing states are needed to better understand these multiplet-specific effects.

Ion vibrational branching ratios for the $b^4 \Sigma_g^-$ and $B^2 \Sigma_g^-$ ions are shown in Figs. 3(a) and 3(b), respectively, where we use the notation $n:0$ to denote the branching ratio, $\sigma(v = 0 \rightarrow b^+ = n)/\sigma(v = 0 \rightarrow b^+ = 0)$. Dramatic deviations from Franck-Condon behavior are seen in these branching ratios. For the $b^4 \Sigma_g^-$ ion this behavior extends over a large energy range similar to that seen in $3\sigma_g$ photoionization of $N_2$. While the $B^2 \Sigma_g^-$ branching ratios show non-Franck-Condon behavior only in a limited energy range near threshold. These features reflect differences seen in the vibrationally resolved multiplet-specific cross sections of Figs. 2(a) and 2(b).

Vibrationally resolved photoelectron angular distributions for these two multiplets of $O_2^+$ ($3\sigma_g^-$) are shown in Figs. 4(a) and 4(b). These photoelectron asymmetry parameters are vibrational-state dependent. This non-Franck-Condon behavior extends over a broader energy range than in the vibrational branching ratios. The vibrationally resolved $\beta$'s also show strong multiplet-specific effects. In particular, there is a shoulder in the $B^2 \Sigma_g^-$ $\beta$'s at around 25 eV photon energy, the same energy where the $\sigma_\nu$ cross section goes through a minimum, which is not seen in the $\beta$'s for the $b^4 \Sigma_g^-$ ion. These multiplet-specific differences extend over a broad range, well beyond the complicating effects of autoionization due to states leading to the $c^4 \Sigma_g^-$ ion. Measured photoelectron asymmetry parameters of Katsumata et al. at 21.2 and 40.8 eV are also shown in Figs. 4(a) and 4(b). At low energy there is a significant difference between the measured multiplet $\beta$'s, while at higher energy, away from the shape resonance, this difference is considerably less. Continuum source measurements are needed to fully assess the accuracy of these calculations.

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12P. J. Miller and W. A. Chupka (private communication).
13J. A. Stephens, M. Braunstein, and V. McKoy (to be published).

![Diagram](https://example.com/diagram.png)

**FIG. 4.** (a) and (b) Vibrationally resolved photoelectron asymmetry parameters (dipole length) for the $b^4 \Sigma_g^-$ and $B^2 \Sigma_g^-$ ions, respectively. The open circles are experimental data from Ref. 34 for the $v^+ = 0$ level ($b^4 \Sigma_g^-$ ion) and $v^+ = 1$ level ($B^2 \Sigma_g^-$ ion).