Vibronic coupling in the superoxide anion: The vibrational dependence of the photoelectron angular distribution

Matthew Van Duzor, Foster Mbiawa, Jie Wei, Tulsi Singh, Richard Mabbs, Andrei Sanov, Steven J. Cavanagh, Stephen T. Gibson, Brenton R. Lewis, and Jason R. Gascooke

Citation: The Journal of Chemical Physics 133, 174311 (2010); doi: 10.1063/1.3493349
View online: http://dx.doi.org/10.1063/1.3493349
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/133/17?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
High-resolution photoelectron imaging of cold C 60 − anions and accurate determination of the electron affinity of C60

Slow photoelectron velocity-map imaging spectroscopy of the C9H7 (indenyl) and C13H9 (fluorenyl) anions

Low-lying electronic states of CH 3 NO 2 via photoelectron imaging of the nitromethane anion

Slow electron velocity-map imaging photoelectron spectra of the methoxide anion

Spectroscopic characterization of the ground and low-lying electronic states of Ga 2 N via anion photoelectron spectroscopy
Vibronic coupling in the superoxide anion: The vibrational dependence of the photoelectron angular distribution

Matthew Van Duzor,1 Foster Mbaia,1 Jie Wei,1 Tulsi Singh,1 Richard Mabbs,1,a Andrei Sanov,2 Steven J. Cavanagh,3 Stephen T. Gibson,3 Brenton R. Lewis,3 and Jason R. Gascooke4

1Department of Chemistry, Washington University, One Brookings Dr., Campus Box 1134 Saint Louis, Missouri 63130, USA
2Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85721-0041, USA
3Research School of Physics and Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia
4School of Chemical and Physical Sciences, Flinders University, G.P.O. Box 2100, Adelaide, South Australia 5001, Australia

(Received 20 April 2010; accepted 3 September 2010; published online 3 November 2010)

We present a comprehensive photoelectron imaging study of the $\text{O}_2(3\Sigma^-_g,v'=0\rightarrow6)$ and $\text{O}_2(1\Delta_g,v'=0\rightarrow4)$ photodetachment bands at wavelengths between 900 and 455 nm, examining the effect of vibronic coupling on the photoelectron angular distribution (PAD). This work extends the $v'=1\rightarrow4$ data for detachment into the ground electronic state, presented in a recent communication [R. Mabbs, F. Mbaia, J. Wei, M. Van Duzor, S. T. Gibson, S. J. Cavanagh, and B. R. Lewis, Phys. Rev. A 82, 011401(R) (2010)]. Measured vibronic intensities are compared to Franck–Condon predictions and used as supporting evidence of vibronic coupling. The results are analyzed within the context of the one-electron, zero core contribution (ZCC) model [R. M. Stehman and S. B. Woo, Phys. Rev. A 23, 2866 (1981)]. For both bands, the photoelectron anisotropy parameter variation with electron kinetic energy, $\beta(E)$, displays the characteristics of photodetachment from a $d$-like orbital, consistent with the $\pi^*_2 2p$ highest occupied molecular orbital of $\text{O}_2^-$. However, differences exist between the $\beta(E)$ trends for detachment into different vibrational levels of the $3\Sigma^-_g$ and $1\Delta_g$ electronic states of $\text{O}_2$. The ZCC model invokes vibrational channel specific “detachment orbitals” and attributes this behavior to coupling of the electronic and nuclear motion in the parent anion. The spatial extent of the model detachment orbital is dependent on the final state of $\text{O}_2$: the higher the neutral vibrational excitation, the larger the electron binding energy. Although vibronic coupling is ignored in most theoretical treatments of PADs in the direct photodetachment of molecular anions, the present findings clearly show that it can be important. These results represent a benchmark data set for a relatively simple system, upon which to base rigorous tests of more sophisticated models. © 2010 American Institute of Physics. [doi:10.1063/1.3493349]

I. INTRODUCTION

The coupling between electronic and vibrational degrees of freedom often affects the spectroscopic and structural properties of molecules. However, experimental evidence of vibrational influence on the photoelectron angular distributions (PADs) in negative-ion photodetachment has so far been sparse, and little attention has been paid to such effects in theoretical treatments of direct detachment processes. In a recent communication,1 we reported a strong dependence of the PADs in $\text{O}_2(3\Sigma^-_g,v'=0)$ photodetachment on the final vibrational state of the neutral, $\text{O}_2(3\Sigma^-_g,v'=1\rightarrow4)$. These results provided experimental evidence of vibronic coupling in the anion ground electronic state, supplying essential data for the evaluation and refinement of existing theoretical models.

In the present work, we extend the above measurements to include the additional $v'=0, 5$, and 6 transitions of the $\text{O}_2(3\Sigma^-_g)\rightarrow\text{O}_2^-(3\Pi_g^\circ)$ band and the $v'=0\rightarrow4$ transitions of the excited-state $\text{O}_2(1\Delta_g)\rightarrow\text{O}_2^-(3\Pi_g^\circ)$ band. We present a new, detailed discussion of these results in the context of the zero core contribution (ZCC) model,2 complementing our previous analysis.1 In addition, the observed trend in vibronic transition intensities in the $\text{O}_2(3\Sigma^-_g)\rightarrow\text{O}_2^-(3\Pi_g^\circ)$ band is evaluated.

The dominant long range interaction in anion photodetachment is associated with the centrifugal term in the effective potential.3 The nature of the long range potential significantly affects the energy dependence of the total4 and differential detachment cross sections.5 In fact, the application of orbital angular momentum conservation and consideration of the influence of the centrifugal barrier in principle allows the characterization of the parent orbital from the photoelectron angular distribution.5,6 Within the one-electron and electric-dipole approximations, the PAD of an atomic anion detachment can be thought of as a signature of the parent orbital.5

---

1Electronic mail: mabbs@wustl.edu.
The relationship between the parent orbital and the PAD is in principle more complex for molecular anions.\textsuperscript{9,10} Orbital angular momentum ($\ell$) is no longer a good quantum number, and the vibrational excitation often accompanies the change in electronic state. The application of symmetry arguments can still act as a guide to the nature of the parent molecular orbital.\textsuperscript{11–18} More subtle effects, such as the influence of the final, neutral molecular state are often difficult to extract. There are, however, a few small molecular anions that might allow detailed experimental studies into these effects.

In the case of superoxide, O$_2^-$, the highest occupied molecular orbital ($\pi_g$) has a strong similarity to an atomic $d$ orbital. There is only one vibrational degree of freedom, and photoelectron-spectroscopic techniques are capable of resolving the vibrational structure in the low electron kinetic energy region of the spectrum. A comparison of O$_2^-$ photodetachment results with atomic anion model predictions yields considerable insight into the effect of vibrational excitation on the photodetachment properties, in particular the PAD.\textsuperscript{1}

Several detachment studies of this species have probed the photon energy dependence of the total detachment cross section\textsuperscript{19–26} or reported the photoelectron spectrum of O$_2^-$.\textsuperscript{1,27–38} Until very recently, much less data were reported regarding the PAD.\textsuperscript{1,28,35} Among other anions, the prominent dependence of photoelectron anisotropy on the final vibrational state of the neutral was reported in the photodetachment of NO$^-$.\textsuperscript{39} In the case of neutral diatomic molecules, dramatic changes in the PAD have been observed between different vibronic photoionization bands of N$_2$, CO, and O$_2$.\textsuperscript{40–42} Such effects are associated with strong coupling of the electronic and vibrational motion and usually a breakdown of the Born–Oppenheimer approximation as a consequence of excitation of intermediate, autoionizing Rydberg states or shape resonances.\textsuperscript{42}

It is well known that the PAD is dependent on electron kinetic energy ($E$).\textsuperscript{31} To separate the effect of vibrational excitation from the $E$ dependence, one must, ideally, compare transitions that terminate in different vibrational states but correspond to the same $E$. This approach requires experiments at multiple, carefully selected photoexcitation wavelengths. Studies of this type are rarely performed, particularly for molecular anions. Despite the work reported in Ref. 44 for photoionization, the prevalent view seems to have been that in the absence of vibrationally resolved data in direct photodetachment processes, vibrational effects on the PAD can be ignored.

A comparison of near-threshold PADS of O$_2^-$ recorded at different excitation wavelengths shows that this view is shortsighted.\textsuperscript{1,35} Figure 1 compares anisotropy parameter ($\beta$) data for the O$_2$(X $^3\Sigma_g^-$)←O$_2^-(X ^3\Pi_g)$ vibronic band at detachment wavelengths 780 nm (open circles), 396 nm (closed circles),\textsuperscript{35} and 488 nm (open squares).\textsuperscript{28} $\beta$ characterizes the PAD, and a change is clearly seen in the 780 nm data. However, if the PAD were dependent only on the parent ($\pi_g$) orbital and $E$, one would expect $\beta$ to be constant within the $X←X$ band for a given $E$, regardless of the detachment wavelength and, therefore, the final vibrational state of the neutral. Nonetheless, distinctly different $\beta$ values are observed for comparable $E$ but different final vibrational states.

FIG. 1. Comparison of anisotropy parameters associated with detachment from the $\pi_g$ orbital of O$_2^-$ at 780 nm (open circles), 396 nm (filled circles) from Ref. 35, and 488 nm (open squares) from Ref. 28 via the O$_2$(X $^3\Sigma_g^-$)←O$_2^-(X ^3\Pi_g)$ transition. Numeric labels represent $v''$.

The more recent study of the $E$ evolution of the angular distributions associated with photodetachment via the O$_2$(X $^3\Sigma_g^-$)←O$_2^-(X ^3\Pi_g)$ band has clearly shown that the level of vibrational excitation of the neutral molecule influences the angular distributions associated with direct detachment from the superoxide anion.\textsuperscript{1}

While several theoretical treatments have been developed to treat photoelectron angular distributions from diatomic molecules, the effect of accompanying vibrational excitation is almost completely ignored (with the notable exception of Ref. 44), presumably in part due to a lack of experimental data. Anion detachment studies have tended to focus either on the nature of the parent orbital itself or on the effects of momentum transfer in rare cases of rotationally resolved detachment spectra. Momentum transfer formalisms\textsuperscript{45–50} have been used to explain the differential cross section (angular distribution) for photoelectrons produced in rotationally resolved\textsuperscript{51} and nonrotationally resolved\textsuperscript{52,53} H$_2$ spectra. The effect of spin polarization of the photoelectrons has also been taken into account in rotationally resolved molecular photoelectron spectra.\textsuperscript{54} More recent treatments of O$_2^-$ photodetachment include single and multichannel scattering calculations using Schwinger variational methods\textsuperscript{55} and calculation of the radial matrix elements for the central-potential model of Cooper and Zare using Dyson orbitals computed via coupled-cluster equation of motion methods.\textsuperscript{56} Only in the application of the ZCC model\textsuperscript{57} to diatomic anion photodetachment has the effect of vibrational excitation on the angular distribution been quantified.\textsuperscript{2} The systematic test of the predicted $\beta(E)$ trends for each vibronic transition associated with the O$_2$(X $^3\Sigma_g^-$)←O$_2^-(X ^3\Pi_g)$ band, begun in Ref. 1 and extended and discussed in greater depth here, is hoped to stimulate further theoretical interest in this phenomenon.

II. EXPERIMENTAL METHODS

O$_2^-$ photoelectron images were recorded over a range of detachment wavelengths between 900 and 455 nm in small intervals. The precise determination of $\beta$ requires care. The extracted value is sensitive to a variety of possible experimental artifacts.\textsuperscript{58,59} To minimize the influence of such effects and to verify the repeatability of our observations, in-
dependent measurements were recently reported from two different laboratories in St. Louis (USA) and Canberra (Australia).

The results presented here were recorded on the Canberra instrument and extend the data set to the \( \text{O}_2(X \Sigma_g^+, v') - \text{O}_2(X \Pi_g, v''=0) \), \( v'=0,5,6 \) transitions, and \( \text{O}_2(a^1 \Delta_g, v') - \text{O}_2(X \Pi_g, v''=0) \), \( v'=0-4 \) band. The instrumentation has been described previously, and only brief details will be provided. Essentially, the apparatus produces a collimated beam of mass-selected negative ions, which can then be interrogated by a laser beam, subsequently producing photoelectrons. The photodetached electrons are imaged onto a multichannel-plate (MCP) phosphor detector using a modified velocity-map imaging lens.

Molecular oxygen anions are produced by passing pure oxygen gas through a pulsed nozzle (General Valve Series 9) at a stagnation pressure of 2.7 atm and then supersonically expanding it through a pulsed discharge. All negative ions are extracted, accelerated to 500 eV, focused into an ion-gating, bunching, and potential referencing unit, and allowed to propagate along a ground-referenced 2 m time-of-flight (TOF) tube. The ion-beam and imaging lens axes are arranged coaxially. A fast potential switch rereferences the ion packet to the imaging assembly repeller-plate potential. A potential barrier is placed between the second potential switch and the repeller plate of the imaging lens. This acts, when switched together with the potential switch, as a mass discriminator, allowing only the mass of interest to enter the imaging lens.

The mass-selected ion packet intersects the detachment laser beam, generated by a Continuum Sunlite EX optical parametric oscillator, which is pumped by a Powerlite 9010 Nd:yttrium aluminum garnet laser, operated at its third harmonic, 355 nm. The laser operates between 1 and 3 mJ per pulse and at 10 Hz. To ensure a very high degree of polarization parallel to the MCP detector face, the laser beam was passed through a 1/2-waveplate and a high-quality broad bandwidth Glan-Laser polarizer. A Galilean telescope arrangement is used to produce a parallel beam of 2 mm diameter, reduced from the laser diameter of 8 mm. The wavelength of the laser is measured using a high-quality wavemeter (High Finesse WS7 UV).

The high resolution velocity-map imaging lens is a substantially modified version of Eppink and Parker’s arrangement. It was designed to accommodate fast ion-beam energies of \( 10^2 - 10^3 \) eV and an increased interaction region volume size (at least 2 mm³), achieving electron kinetic energy resolutions of \( \Delta E/E = 0.3\% \) or better. Photoelectrons are imaged onto a position sensitive detector consisting of a pair of high dynamic range, imaging quality 10 μm-pore MCPs, a P47 phosphor screen, and a 2048 × 2048-pixel monochrome charge coupled device camera (PCO2000). The imaging detector is situated at the end of the TOF tube, 800 mm from the interaction region, and is shielded from magnetic fields through a combination of μ-metal and three orthogonal Helmholtz coils. The MCP gain is gated using a purpose-built fast high-voltage pulser to coincide with the arrival of the photoelectrons. This ensures that unwanted events from ions or neutral species are not detected. Each camera frame is transferred to a PC at the 10 Hz repetition rate and is processed in real time to identify events, centroiding to subpixel accuracy, with the \( x, y \)-coordinates written to a file, for subsequent analysis.

III. RESULTS AND ANALYSIS

The photoelectron images obtained in this study were recorded at detachment wavelengths of 454.57, 489.56, 531.79, 629.89, 679.72, 750.90, 800.87, 850.88, and 901.22 nm. A typical image is shown in Fig. 2 (454.57 nm). Lighter colored areas of the image indicate higher photoelectron intensity.

The use of linearly polarized photons confers cylindrical symmetry upon the laboratory frame (LF) photoelectron momentum distribution. The raw image in Fig. 2 is an Abel transform of the three-dimensional LF distribution, a two-dimensional projection onto the plane of the detector. The LF distribution can be mathematically reconstructed by applying the inverse transform. The inverse transformation is performed using the Hansen and Law algorithm, and photoelectron spectra are then extracted.

A. Photoelectron spectra

The momentum domain spectrum is obtained from the reconstructed image by integration over \( \theta = 0 - 2\pi \) at all radii, where \( \theta \) is defined as the angle between the laser polarization axis (\( \vec{E}_p \), vertical in the plane of the image) and the momentum vector of the electron. The conversion to the energy domain is effected using the appropriate Jacobian transformation.

The spectrum in Fig. 2 is displayed as a function of electron binding energy, \( eBE = h\nu - E \). A detachment from the superoxide anion (at the photon energies employed here) removes an electron from the antibonding \( \pi^* \) orbital. Consequently, the equilibrium bond length is shorter in the neutral \( \text{O}_2(X \Sigma_g^+: \text{R}_{c'} = 1.2075 \text{ Å}) \) compared to the anion \( (X \Pi_g, \text{R}_{\text{c''}} = 1.348 \text{ Å}) \) (Ref. 27) and vibrational excitation accompanies the detachment process, resulting in significant population of up to six vibrational quanta, as seen in the
vibrational progression in the \( \text{O}_2(X^3\Sigma_g^-) \rightarrow \text{O}_2^-(X^2\Pi_g, \nu''=0) \) band. The vibronic transitions are clearly seen in the image as a series of concentric rings, with the larger rings corresponding to lower levels of internal excitation in the neutral \( \text{O}_2 \). These features are clear in the spectrum, which also resolves transitions from the two spin-orbit states (\( ^2\Pi_{g,\Omega=3/2,1/2} \)) of the anion.

The spectral intensities are normalized relative to the \( \text{O}_2(X^3\Sigma_g^-, \nu'=0) \rightarrow \text{O}_2^-(X^2\Pi_g, \nu''=0) \) transition. Three vibronic bands are visible in the portion of the spectrum shown in Fig. 2, which correspond to detachment via the ground \( (X^3\Sigma_g^-) \) and first two excited (\( a^1\Delta_g, b^1\Sigma_g^+ \)) electronic states of \( \text{O}_2 \).

### B. The photoelectron angular distributions

It is clear in the image in Fig. 2 that the photoelectron intensity is not necessarily constant about a ring of given radius. This is particularly obvious in the outer rings in the image in Fig. 2, where the intensity is greatest at \( \theta=\pi/2 \). The intensity distribution, \( I(E, \theta) \) is a measure of the differential cross section for detachment and is described by

\[
I(E, \theta) = \frac{\sigma(E)}{4\pi} [1 + \beta(E)P_2(\cos \theta)],
\]

where \( \sigma \) is the integrated cross section and \( P_2 \) is the second Legendre polynomial. The anisotropy parameter \( \beta \) is determined by the details of the detachment process and characterizes the angular distribution. Any effects of the detachment process on the angular distribution can therefore be conveniently discussed in terms of changes in the anisotropy parameter.

In this work, we focus on the PADs accompanying the \( \text{O}_2(X^3\Sigma_g^-) \rightarrow \text{O}_2^-(X^2\Pi_g) \) vibronic transitions of \( \text{O}_2^- \) detachment. However, Fig. 4 shows that the \( \text{O}_2(a^1\Delta_g) \rightarrow \text{O}_2^-(X^2\Pi_g) \) vibronic transitions display a similar behavior. The apparent changes in \( \beta(E) \) trends have significant implications for theoretical treatments of the detachment process. The anisotropy parameter is extracted by plotting \( I(E, \theta) \) against \( P_2(\cos \theta) \) at a given \( E \). We note that the \( \beta \) values reported in this work differ slightly from those previously reported.\(^{58,35}\) This is not too surprising, considering that \( \beta \) values are very sensitive to image distortion (imparted by external fields or imperfect focusing) and detector saturation. In the present work, extreme care has been applied to minimize such adverse effects. The images are circularized to eliminate distortion effects.\(^{58} \) Additionally, saturation effects are easily identified as deviations from linearity at the extremes of the angular range in a plot of \( I(E, \theta) \) versus \( P_2(\cos \theta) \), and we note that none of the images reported here display any evidence of saturation. Furthermore, the results have been verified independently in the different laboratories of the authors, with each set of measurements being in excellent agreement.\(^{1} \)

For the remainder of this work, we focus on the relationship between \( \beta \) and \( E \) in particular the effect that the level of vibrational excitation of the neutral residue seems to exert. In Fig. 3, we show the variation of \( \beta \) with \( E \) for the \( \text{O}_2(X^3\Sigma_g^-) \rightarrow \text{O}_2^-(X^2\Pi_g) \) band. All data shown are for transitions originating in the \( \text{O}_2^-(X^2\Pi_g, \Omega=3/2) \) spin-orbit state. The neutral \( \text{O}_2 \) vibrational levels accessed are (a) \( \nu'=0 \), (b) \( \nu'=1 \), (c) \( \nu'=2 \), (d) \( \nu'=3 \), (e) \( \nu'=4 \), (f) \( \nu'=5 \), and (g) \( \nu'=6 \). A change in \( \beta \) with \( E \) is not unexpected. More surprising, at least in the light of the expectation that the PAD depends on the parent \( \pi \) orbital only, is the difference in \( \beta \) seen in Fig. 3(h) for different vibronic transitions at comparable \( E \). Figure 4 shows similar behavior in the \( \text{O}_2(a^1\Delta_g, \nu') \rightarrow \text{O}_2^-(X^2\Pi_g, \nu''=0) \) band for \( \nu'=0-4 \).

There is an initial shift toward increasingly negative values until a minimum is reached (at least for the \( \nu'=0 \) \( \nu'=1 \) series) before becoming less negative. However, the rate of change of \( \beta \) in each case is different. For \( E \) between 0 and 1.5 eV, lower \( \nu' \) correspond to more negative \( \beta \). Clearly, accessing different terminal neutral states has a profound influence on the photoelectron angular distribution.

### IV. DISCUSSION

The \( E \) dependence of \( \beta \) when \( \ell > 0 \) has been previously demonstrated in atomic anion detachment experiments.\(^{58,63-68} \) In these cases, the change in \( \beta \) can be explained through consideration of the dominant long range term in the potential, the centrifugal term. The free electron wave can be represented as a superposition of partial angular momentum waves for which we will use the symbol \( \ell' = (\ell \pm 1) \) to allow distinction from the parent orbital angular momentum quantum number \( \ell \). The centrifugal barrier increases with \( \ell' \) and decreases with distance. In the asymptotic limit, the barrier is therefore zero, but in the near-field limit, the barrier leads to different contributions of the partial waves to the overall superposition. According to the Wigner law,\(^{4} \) at the detachment threshold the cross section of each partial wave varies as \( \sigma = E(\ell+1/2) \). The angular distribution, and hence \( \beta \), is the result of interference between these partial waves, and so changing the composition of the superposition changes the angular distribution. For atomic anions, this behavior is encapsulated in the equation

\[
\beta(E) = \frac{\ell (\ell - 1) + (\ell + 1)(\ell + 2)A^2 \cdot E^2 - 6\ell (\ell + 1)A \cdot E \cos \delta_{(\ell+1)-(\ell-1)}}{(2\ell + 1)[ \ell + (\ell + 1)A^2 \cdot E^2 ]},
\]
This is a simplification of the result of an approach initially outlined by Bethe for single-electron atoms, later generalized to multielectron atoms and with the approximation that the relative partial wave cross sections obey the Wigner threshold behavior within a few eV of threshold, so that $\sigma_{\ell+1}/\sigma_{\ell-1} = A \cdot E$. The physical picture behind Eq. (2) is the interference of the two partial electron waves, which of course depends on the relative cross sections (carried through the $A \cdot E$ term) and their relative phase shift, $\delta_{\ell+1} - \delta_{\ell-1}$. 

FIG. 3. Variation in $\beta$ with $E$ for $\text{O}_2(X^3\Sigma_g^+, \nu') \rightarrow \text{O}_2(X^2\Pi_g, \nu''=0)$ transitions, [(a)–(g)] $\nu''=0$–6, respectively. Experimental data are indicated by symbols, and, where absent, error bars are smaller than the symbols. Solid curves represent the fit of an atomic model to these data. Dashed curves represent the predictions of the ZCC model. (h) Direct comparison of $\nu''=0$–6.
This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to 130.56.106.27 On: Thu, 10 Dec 2015 02:36:24
produce the neutral curve. The increase in binding energy at
dependence, while et the vibrational overlaps integral occur at different
extent of the detachment orbital changes throughout the
wave functions is
where is the distance from the center of mass of
transition from the anion is vertical
is a direct consequence of Born–Oppenheimer behavior. The
reason for the phase changes extracted by application of Eq. (2)
in Table I is not transparent in this approach. However, it
does offer a rationalization for the behavior of the parameter in the application of the atomic model of Eq. (2). The A
coefficient represents a measure of anion size. "The “contra-
diction” arises from a lack of clarity in the meaning of size in
the molecular picture we have outlined, where preferential
detachment from larger corresponds to smaller .
Rather than internuclear separation, size here refers to the
spatial extent of the detachment orbital.

The above discussion identifies the vibrational level depen-
dence of to be a direct result of variation in the
electronic matrix element with .
As supporting evidence, a further manifestation of this behavior is found in the variation in transition intensities across the band. In the absence of vibronic coupling, the
relative intensities should be reproduced by .

Figure 6 compares with the band of our nm spectrum.
The Franck–Condon factors were calculated using
Morse oscillator wave functions employing the spectro-
scopic constants in Ref. and evaluating the vibrational
overlap integral numerically using a 600 point Simpson’s
method calculation. It is clear that these Franck Condon factors (FCFs) are a poor representation of the spectral intensi-
ties, particularly at higher , showing the influence of vib-
ronic coupling.

It is instructive to compare this finding with the Franck–Condon (FC) treatment of the spectrum given in Ref. .
The latter work shows that the intensity variation in the band recorded at nm is very well described by the
Franck–Condon factors alone. The key difference is the
increased photon energy. The vibrational transition intensities can be calculated using the same ZCC approach applied above, integrating Eq. (3) over all angles,
FIG. 7. ZCC total cross sections (symbols) and Franck–Condon factors (solid lines) for \( \text{O}_2(\Sigma^+ \Gamma, v' = 0) \rightarrow \text{O}_2(\Pi_g, v'' = 0) \) transitions to \( \text{O}_2(\Pi_g, v' = 2) \rightarrow \text{O}_2(\Pi_g, v'' = 0) \).

\[
\sigma(v',v'') = F(v',v'')k\omega \int |M|^2 d\Omega_{in}d\Omega.
\]

The variation in relative transition intensities [effectively \( \sigma(v',0)/\sigma(2,0) \)] is shown in Fig. 7. At photon energies close to threshold, there is considerable deviation from the Franck–Condon prediction (the horizontal lines). However, as the photon energy increases the values converge, a result of the dependence of the cross section (and \( M^\ast \)) on \( k \). The trends in \( E \) and the vibrational dependence of the overall cross sections for \( \text{O}_2^- \) detachment will be dealt with thoroughly in a forthcoming publication.

Agreement between the ZCC calculation of \( \beta(E) \) and experiment is not particularly good. A comparison of the united-atom orbital and a more realistic linear combination of atomic \( p \) orbitals as the detachment orbital reveals that the atomic \( d \) orbital approximation makes little difference to the result of the calculation. However, more significant errors are introduced in the nature of the ZCC model itself. As \( E \) increases, the de Broglie wavelength becomes comparable with the dimensions of the core region, in which case zero core contribution will no longer be a good approximation. Additionally, the employment of the one-electron approximation and assumption of no interaction between the detachment and core electrons implicitly neglects electron correlation effects that are known to be strongly influential in anionic species. Nevertheless, as a means of illustrating the effect of the changing spatial extent of \( \phi_{in} \) on the vibrational dependence of \( \beta(E) \), the model is enlightening. It should also be pointed out that more sophisticated models that include many-body effects have so far neglected the influence of product vibration on the photoelectron angular distributions. Furthermore, recent multi-configuration single excited configuration interaction (MCSCI) (Ref. 55) and equation of motion-coupled cluster (EOM-CC) (Ref. 56) calculations consistently underestimate the magnitude of the \( \beta \) parameter from the \( \text{O}_2(X^2 \Sigma_g^-, v' = 0) \rightarrow \text{O}_2(\Pi_g, v'' = 0) \) transition. The results presented here extend the previous systematic experimental study of the vibrational dependence of photodetachment angular distributions from \( \text{O}_2^- \).

V. CONCLUSION

To summarize, we have experimentally demonstrated that the variation of \( \beta \) with \( E \) for molecular anion detachment depends on the level of neutral molecule vibrational excitation. While the quantitative agreement with the experimental data is not perfect, the simple one-electron ZCC model allows us to interpret this behavior in terms of the changes in the electronic transition matrix element. There is significant coupling of the electronic and nuclear motion in the ground state of the anion, and the experimentally determined \( \beta(E) \) values are significantly different to those predicted by the latest quantum chemical treatments.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support by the National Science Foundation (Grant No. CHE-0748738) and ANU ARC Discovery Projects under Grant Nos. DP0666267 and DP0880850. We also thank Professor B. J. Orr for discussions regarding treatment of diatomic anion angular distributions.
