Rotationally resolved photoionization of molecular oxygen
M. Braunstein, V. McKoy, and S. N. Dixit

Citation: The Journal of Chemical Physics 96, 5726 (1992); doi: 10.1063/1.462671
View online: http://dx.doi.org/10.1063/1.462671
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/96/8?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Rotationally resolved photoionization dynamics of hot CO fragmented from OCS

Rotationally resolved fluorescence as a probe of molecular photoionization dynamics

Rotationally resolved photoionization of H2O
J. Chem. Phys. 95, 7033 (1991); 10.1063/1.461431

Rotational distributions of molecular photoions following resonant excitation
J. Chem. Phys. 85, 6232 (1986); 10.1063/1.451492

Soft-x-ray photoionization cross sections of molecular oxygen
J. Appl. Phys. 47, 4911 (1976); 10.1063/1.322493
Rotationally resolved photoionization of molecular oxygen

M. Braunstein and V. McKoy
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125
S. N. Dixit
Theoretical Atomic and Molecular Physics Group, Lawrence Livermore National Laboratory, L-493, Livermore, California 94550

(Received 14 August 1991; accepted 7 January 1992)

We report the results of theoretical studies of the rotationally resolved photoelectron spectra of ground state O$_2$ leading to the $X^3\Sigma_g^-$ state of O$_2^+$ via the absorption of a single vacuum ultraviolet photon. These studies elaborate on a recent report [M. Braunstein et al., J. Chem. Phys. 93, 5345 (1990)] where we showed that a shape resonance near threshold creates a significant dependence of the rotational branching ratios on the ion vibrational level. We also showed that analysis of the rotational branches yields detailed information on the angular momentum composition of the shape resonance. We continue this analysis giving a comprehensive derivation of the rotationally resolved cross sections and photoelectron angular distributions. We discuss the selection rules implied by these expressions and present very high resolution cross sections ($J \rightarrow J'$) obtained using static-exchange photoelectron orbitals and explicitly taking into account the internuclear distance dependence of the electronic transition moment. These cross sections illustrate the selection rules and show more explicitly the angular momentum composition of the shape resonance. We also present rotationally resolved photoelectron angular distributions which would be expected at low energy.

I. INTRODUCTION

Rotationally resolved photoelectron spectra of molecules can provide much insight into both the properties and dynamics of excited electronic states, and the angular momentum composition of the electronic continuum. Recently, very high resolution threshold photoelectron spectroscopy has been used to obtain rotationally resolved photoelectron spectra of molecules. With cooling in a supersonic nozzle, rotationally resolved spectra were obtained for photoionization of the ground state of O$_2$ ($X^3\Sigma_g^-$) leading to the ground state ($X^3\Pi_g$) of O$_2^+$ via a single vacuum ultraviolet (VUV) photon. The spectral transitions of interest here are illustrated schematically in Fig. 1. Figure 2 shows the measured rotational transition amplitudes for these transitions, including a full description of the vibrational level dependence of the rotational branching ratios.

II. THEORY

We extend the formulation given previously to treat transitions from a Hund’s case (b) resonant state to a mixed Hund’s case (a)–(b) ion which is especially appropriate for the $\Sigma^+ \rightarrow \Pi$ transition of interest in the photoionization of O$_2$. The development closely follows the work of Buck-
ingham et al.,27 but includes the effects of mixing of the Hund’s cases (a) and (b) in the final ionic state.

The differential cross section for photoionization of a rotational state \( J \) leading to an ion in an angular momentum state \( J^+ \) is given by

\[
\sigma_{J \rightarrow J'}(\theta, \phi) = \frac{4\pi^2}{c} E \sum_{m_J, m_J', m_i(c,d)} |\langle J|D_{m_J'}|J'\rangle|^2,
\]

where \( E \) is the photon energy, \( c \) is the speed of light, \( m_J \) is the projection of \( J \) on the laboratory \( z \) axis, \( m_J^+ \) is the projection of \( J^+ \) on the laboratory \( z \) axis, and \( m_i \) is the projection of the photoelectron spin on the laboratory \( z \) axis. The notation \( (c,d) \) implies a sum over the \( c \) and \( d \) parity states of the ion.\(^{28}\) \( P_m \) is the statistical weight of the initial \( m_i \) states, which for an isotropic distribution is given by \( e^{-E/V_{kT}}/Z \), where \( Z = \Sigma_{J'}(2J' + 1) e^{-E/V_{kT}} \). In Eq. (1), \( \Psi_{J'}^+ \) is the final state.

FIG. 1. Diagram illustrating the rotationally resolved photoelectron spectra for photoionization of \( \text{O}_2 \) \( (X^3\Sigma_g^-) \) by a single VUV photon. The left side of the figure shows the potential curves of the ground and ion states, while the right side shows some of the rotational states of an ion vibrational level and the first few rotational states of the ground vibrational level of the \( X^3\Sigma_g^- \) electronic ground state.

FIG. 2. Threshold rotationally resolved photoelectron spectra for single-photon ionization of \( \text{O}_2 \) \( (X^3\Sigma_g^-) \) leading to \( v^* = 0, 1, \) and 2 levels of \( \text{O}_2^+ \) \( (X^1\Pi_u^-) \): measured spectra at about 10 K (top frame); calculated spectra at 10 K (center frame); calculated spectra at 5 K (bottom frame). These spectra are taken from Ref. 13. The branch designations refer to \( \Delta N = (N^+ - N) \) transitions. For example, an \( S \) branch under \( F_1 \) on the bottom row of letters refers to a transition from the \( N = 1 \) rotational level of the ground state to the \( N^+ = 3 \) level of the \( F_1 \) spin–orbit manifold of the ion. (We have switched to the more modern notation for the total angular momentum excluding spin, replacing \( K \) of Ref. 13 with \( N^+ \).) The calculated spectra have an assumed linewidth of 2 cm\(^{-1}\). The experimental spectra have arbitrary intensity units. The base lines of the 10\(^v\) spectra have been shifted upward by a constant amount.
wave function (ion plus photoelectron), \( |\Psi_f^+\rangle \) is the initial target state, and \( D_\infty \) is the dipole moment operator where \( \mu_0 \) characterizes the polarization of the radiation. For the initial state case (b) wave function, we use the Born–Oppenheimer approximation so that

\[
|\gamma_{\nu}\Lambda N \Sigma M_J_f\rangle = \sum_{M_s M_J} \langle N SM_s | M_J_f \rangle |SM_s\rangle \psi_{A}^{\nu} (\{r_i^f\}; R) \chi_{\nu} (R)
\]

\[
\times (-1)^{M - \Lambda} D_{A}^{\nu} (\hat{R}) \sqrt{\frac{2N + 1}{8\pi^2}}, \tag{2}
\]

where \( \psi_{A}^{\nu} (\{r_i^f\}; R) \) is the electronic wave function, \( \chi_{\nu} \) is the wave function for the vibrational state \( \nu \), and \( D_{A}^{\nu} (\hat{R}) \) is a symmetric top rotational wave function with total angular momentum (excluding spin) of \( N. M \) and \( \Lambda \) are the projections of \( N \) along the laboratory \( z \) axis and the molecular \( z \) axis (\( \Lambda = 0 \) for \( \Sigma \) states, \( \Lambda = \pm 1 \) for \( \Pi \) states), respectively, \( J \) is the total angular momentum including spin (\( J = N + S \)), and \( M_f \) its projection along the laboratory \( z \) axis. \( S \) is the total spin with a projection \( M_s \) on the laboratory \( z \) axis, and \( \gamma \) contains all other subscripts needed for an unambiguous designation of the state. Due to the many-particle nature of the wave function, and for reasons which will be made clear later, it is convenient to transform the spin in Eq. (2) into the molecular frame. We then have

\[
|\gamma_{\nu}\Lambda N \Sigma M_J_f\rangle = \sum_{M_s M_J} \langle N SM_s | M_J_f \rangle |SM_s\rangle \psi_{A}^{\nu} (\{r_i^f\}; R) \chi_{\nu} (R)
\]

\[
\times (-1)^{M - \Lambda} D_{A}^{\nu} (\hat{R}) \sqrt{\frac{2N + 1}{8\pi^2}}, \tag{3}
\]

where \( \Sigma \) is the projection of \( S \) on the molecular \( z \) axis.

It is well known that the rotational states of the \( X^2 \Pi_g \) ion of \( O_2 \) do not belong to a pure Hund’s case coupling. In the low \( J^+ \) limit, they can be best described by Hund’s case (a), while for high \( J^+ \) the rotational levels are best described using Hund’s case (b). By our wish to describe a wide range of \( J^+ \) here, we use a mixed rotational basis. This is done by expanding the rotational wave function in Hund’s case (a) basis functions with \( \Omega^+ = 1/2 \) and \( \Omega^+ = 3/2 \) and diagonalizing the rotational Hamiltonian, as discussed by Hougen. The energy levels and rotational wave functions with this mixed basis are given in Appendix A. The wave function for the final state can therefore be written as

\[
|\Psi_f^+\rangle = \frac{c_1 (J^+)}{\sqrt{2}} (|\gamma^+ \Lambda^+ S^+ + \Omega_{1/2}^+ J^+ M_J^+\rangle
\]

\[
\pm |\gamma^+ - \Lambda^+ S^+ - \Omega_{3/2}^+ J^+ M_J^+\rangle
\]

\[
+ \frac{c_2 (J^+)}{\sqrt{2}} (|\gamma^+ \Lambda^+ S^+ + \Omega_{3/2}^+ J^+ M_J^+\rangle
\]

\[
\pm |\gamma^+ - \Lambda^+ S^+ - \Omega_{1/2}^+ J^+ M_J^+\rangle \right) |\phi_k\rangle, \tag{4}
\]

where \( c_1 \) and \( c_2 \) are coefficients which depend on \( J^+ \) and are given in Appendix A, the \( + \) and \( - \) combinations describe \( c \) and \( d \) parity states of the ion, respectively, and \( \Omega^+ = \Omega^+ + \Sigma^+ \) and \( \Omega^+ = |\Lambda^+| \) (see Ref. 28). Here \( |\phi_k\rangle \) is the photoelectron wave function. The final-state wave function therefore consists of linear combinations of four “primitive” wave functions of the form,

\[
|\gamma^+ \nu^+ \Lambda^+ S^+ + \Omega^+ J^+ M_J^+\rangle |\phi_k\rangle
\]

\[
= \sqrt{\frac{2J^+ + 1}{8\pi^2}} \psi_{A}^{\nu^+ \Lambda^+} (\{r_i^f\}; R) |S^+ \Omega^+\rangle
\]

\[
\times \chi_{\nu^+} (R) (-1)^{M^+ - \Lambda^+} D_{A}^{\nu^+ \Lambda^+} (\hat{R}) |m_f\rangle. \tag{5}
\]

The photoelectron wave function \( |\phi_k\rangle \) can be expanded in partial waves,

\[
|\phi_k\rangle = \sum_{l m \mu \nu} \psi_{l m l}^{K} (r_i) \epsilon^\nu m \left(-1\right)^{\nu-\nu^+} Y_{m}^{\nu^+}(\hat{k}) D_{m \nu}^{l}
\]

\[
\times |m_f\rangle, \tag{6}
\]

where \( k \) denotes the momentum of the photoelectron and \( \hat{k} \) its direction in the laboratory frame. \( l m \lambda \) denote the angular momentum of the photoelectron and its projections along the laboratory and molecular frame \( z \) axes, respectively, \( \nu^+ \) is the electron spin and \( m_f \) its projection on the laboratory \( z \) axis. Again it is convenient to transform the spin into the molecular frame so that we have

\[
|\phi_k\rangle = \sum_{l m \mu \nu} \psi_{l m l}^{K} (r_i) \epsilon^\nu m \left(-1\right)^{\nu-\nu^+} Y_{m}^{\nu^+}(\hat{k}) D_{m \nu}^{l}
\]

\[
\times |m_f\rangle, \tag{7}
\]

where \( \mu_0 \) characterizes the polarization of the light; \( \mu_0 = 0 \) for light linearly polarized along the laboratory \( z \) axis, \( \mu_0 = \pm 1 \) for circularly polarized light propagating along the laboratory \( z \) axis. It is necessary to transform the dipole moment operator into the molecular frame so that

\[
D_{\mu_0} = \left(4\pi/3\right)^{1/2} \sum_{\ell} r_\ell Y_{\mu_0}^{\ell}(r_\ell), \tag{8}
\]

where \( \mu_{\ell} \) characterizes the polarization of the light; \( \mu_0 = 0 \) for light linearly polarized along the laboratory \( z \) axis, \( \mu_0 = \pm 1 \) for circularly polarized light propagating along the laboratory \( z \) axis.

Using Eqs. (1) and (4), we have

\[
\sigma_{J^+ \rightarrow J^+} (\theta, \phi) = \frac{4\pi^2 c}{c} P_{m_f} \sum_{m, m_\Omega} \left[ \frac{c_1}{\sqrt{2}} \left[ M_{\ell} (\Omega_{1/2}^+) \right.ight.
\]

\[
\pm M_{\ell} (\Omega_{3/2}^+) \left. \right] ^2 + \frac{c_2}{\sqrt{2}} \left[ M_{\ell} (\Omega_{3/2}^+) \pm M_{\ell} (\Omega_{1/2}^+) \right]^2, \tag{10}
\]

where the “primitive” matrix elements are given by

\[
M_{\ell} = \langle \gamma^+ \nu^+ \Lambda^+ S^+ + \Omega^+ J^+ M_J^+ | \phi_k \rangle D_{\mu_0} |\gamma_{\nu}\Lambda N \Sigma M_J_f\rangle. \tag{11}
\]

Using Eqs. (3), (5), (7), and (9) these primitive matrix elements can be written as
\[ M_R = \sqrt{\frac{4\pi}{3}} \sum_{m_j, m, \Omega, \lambda} (2j + 1)(2J, + 1)(2N + 1)(2J + 1)(2S + 1) \]
\[ \times (-1)^{M_j} (-\lambda + m - \lambda + \Omega - N - S) \]
\[ \times \left( S^+ \frac{1}{2} S \right) \left( \Lambda^+ \Sigma^+ - \Omega \right) \left( J^+ J, J \right) \left( -M_j + M_j M_j \right) \left( -\Omega^+ \Omega \Omega \right) \]
\[ \times \left( \frac{1}{2} \right) \left( J, -M_j - m_j - m_j \right) \left( -\Omega_j - \Omega_j - m_o \right) \]
\[ \times (-1)^m \lambda \mu \Omega_j \left( -m - m_o m_j \right) \right) \]

where \( J, \) denotes the angular momentum transferred to the ion, and \( M, \) and \( \Omega, \) denote the projection of \( J, \) along the laboratory and molecular \( z \) axes, respectively. The indices \( j, m_j, \) and \( \lambda_j \) are dummy indices. Here the vibrationally resolved amplitudes are

\[ I_{\alpha}^{\text{res}}(\Lambda^+ \Sigma^+ + \lambda \mu m_o) = \int dR \chi_{\alpha}^*(R) I_{\alpha}^{\text{res}} \times (R; \Lambda^+ \Sigma^+ + \lambda \mu m_o) \]

and

\[ I_{\phi}(R; \Lambda^+ \Sigma^+ + \lambda \mu m_o) = \sum_{\text{composite final states}} \langle \psi_{l\lambda}^* \mid (\Lambda^+ \Sigma^+ + \lambda \mu m_o) \rangle \]
\[ \times \langle \psi_{l\lambda} \mid \psi_{l\lambda} \rangle \]

where these wave functions are antisymmetrized and \( \psi_{l\lambda} \) are composite final states as given in Appendix B. The re-expansion of the composite \( I_{\phi} \) amplitudes in terms of \( I_{\phi} \) amplitudes therefore comes from the necessity of defining final state basis functions for the molecular ion which have a well-defined \( \Lambda^+ \) projection. This occurs in \( \Sigma^- \) composite states \( (k \pi, \pi \text{ photoelectron}) \), where the composite final state wave function is built on a linear combination of \( \Lambda^+ \) and \( -\Lambda^+ \) ion cores. The overlaps \( O_{l\lambda} \) are simply constants. The composite amplitudes \( I_{\phi} \) have been evaluated previously in the context of vibrationally resolved transitions. Details are given elsewhere.\(^{14,31,32}\) It is important to note, however, that these amplitudes are obtained in the static-exchange approximation and in the fully anisotropic potential of the molecular ion and include the effects of the internuclear dependence of the electronic transition amplitude via Eq. (13). We have now completely defined the quantities needed to obtain the rotationally resolved differential cross section.

An alternative way of expressing the differential cross section, which is sometimes more convenient, is in terms of expansion coefficients \( B_{LM} \),

\[ \sigma_j (-J_\phi) = \sum_{m_j, m, \phi} B_{LM} Y_{LM}(\phi, \phi), \]

where

\[ B_{LM} = \frac{4\pi^2 E}{c} P_m \sum_{l, m_l, m_o} \langle \Psi_{l+} \mid D_{m_l} \mid \Psi_{l} \rangle \langle \Psi_{l+} \mid D_{m_o} \mid \Psi_{l} \rangle \]
\[ \times \left[ \frac{(2l + 1)(2l'+ 1)(2L + 1)}{4\pi} \right]^{1/2} \]
\[ \times \left( \begin{array}{ccc} l & l' & L \\ m & m' & M \end{array} \right) \left( \begin{array}{c} 0 \\ 0 \end{array} \right) \]
\[ \times (-1)^{m_m - M}, \]

where we have taken out the sum over \( l, l', m, \) and \( m' \) in the matrix element and shown it explicitly. The angle-integrated cross section is

\[ \sigma_{\text{tot}} = \sqrt{4\pi B_{00}}, \]

and

\[ \beta = \frac{B_{00}}{B_{\infty}}, \]

where \( \beta \) is the familiar asymmetry parameter.\(^{33}\) It is important to note, however, that these amplitudes are obtained in the static-exchange approximation and in the fully anisotropic potential of the molecular ion and include the effects of the internuclear dependence of the electronic transition amplitude via Eq. (1). We have now completely defined the quantities needed to obtain the rotationally resolved differential cross section.

Expanding in terms of the “primitive” matrix elements we obtain,

\[ \sigma_{\text{tot}} = \frac{4\pi^2 E}{c} P_m \sum_{m_j, m, \phi} \int |\langle \Psi_{l+} \mid D_{m_l} \mid \Psi_{l} \rangle|^2 d\Omega (\hat{k}). \]

The primitive amplitudes can be separated into a laboratory frame part and molecular frame contributions so that
\[ \sigma_{\text{tot}} = \frac{4\pi^2 E}{c} P_{m_j} \sum_{m_{j'}} \left[ M_{\text{lab}}^{\text{ab}}(M_{\text{lab}}^{\text{ab}})^* d\Omega_k \right] e^{-\mu_j^0} \]

\[ \times \left| \frac{c_1}{\sqrt{2}} \left[ M_{\text{molecule}}^{\text{molecule}}(\Omega_{1/2}^+) \pm M_{\text{molecule}}^{\text{molecule}}(\Omega_{-1/2}^-) \right] \right|^2, \]

where

\[ M_{\text{lab}}^{\text{ab}} = \frac{\sqrt{4\pi}}{3} \left( \frac{2J + 1}{2J + 1} \right) (-1)^{m_j + \mu_j - m_i} \sum_{J_M, J_m, m_j} (2j + 1)(2J + 1)
\]

\[ \times \left( J^+ J J_i \right) \left( -M_j M_j M_i \right) \left( -M_i - m_j - m_i \right) \left( \begin{array}{ccc} 1 & j & \frac{1}{2} \\ -m & 0 & m_j \end{array} \right) \left( -i \frac{e^{i\epsilon_j} Y^*_{\ell m} (\hat{k})}{\Omega^+} \right) , \]

and

\[ M_{\text{molecule}}^{\text{molecule}} = \sum_{\Delta \mu \geq 0, \lambda \geq 0, \lambda_i \geq 0} (-1)^{J^+ - \lambda + 2\Omega - N + N - \Sigma} \times \left( J^+ J J_i \right) \left( -M_j M_j M_i \right) \left( -M_i - m_j - m_i \right) \left( \begin{array}{ccc} 1 & j & \frac{1}{2} \\ -m & 0 & m_j \end{array} \right) \left( -i \frac{e^{i\epsilon_j} Y^*_{\ell m} (\hat{k})}{\Omega^+} \right) \]

\[ \times \left( J^+ J J_i \right) \left( -M_j M_j M_i \right) \left( -M_i - m_j - m_i \right) \left( \begin{array}{ccc} 1 & j & \frac{1}{2} \\ -m & 0 & m_j \end{array} \right) \left( -i \frac{e^{i\epsilon_j} Y^*_{\ell m} (\hat{k})}{\Omega^+} \right) \]

Integration over \( \Omega_k \) and summation over \( m_j, m_j^+, \) and \( m_s, \)
lead to the compact expression,

\[ \sigma_{\text{tot}} = \frac{4\pi^2 E}{c} P_{m_j} \frac{4\pi}{9} (2N + 1)(2J^+_1 + 1)
\]

\[ \times \sum_{J_M, J_m, m_j} (2j + 1)(2J + 1)
\]

\[ \times \left| \frac{c_1}{\sqrt{2}} \left[ M_{\text{molecule}}^{\text{molecule}}(\Omega_{1/2}^+) \pm M_{\text{molecule}}^{\text{molecule}}(\Omega_{-1/2}^-) \right] \right|^2, \]

\[ \times \left| \frac{c_2}{\sqrt{2}} \left[ M_{\text{molecule}}^{\text{molecule}}(\Omega_{3/2}^+) \pm M_{\text{molecule}}^{\text{molecule}}(\Omega_{-3/2}^-) \right] \right|^2. \]

This expression for the total cross section is considerably more efficient computationally than Eq. (17).

III. HIGH RESOLUTION RESULTS: SELECTION RULES

In Fig. 3, we show our calculated high-resolution threshold spectrum for photoionization of the ground state of \( \text{O}_2 \) leading to the \( v^+ = 2 \) level of \( \text{O}_2^+ \) (\( \Pi_g \)) at a rotational temperature of 5 K and for the F1 spin–orbit manifold. The peaks have an assumed bandwidth of 0.25 cm\(^{-1}\). These peaks may, however, still be evident at a lower resolution. The peaks seen in Fig. 2 are now split into three components so that the individual \( J \) levels of the ground state are resolved. We can now see the spin splitting of the ground state and have a fully resolved \( J \rightarrow J^+ \) transition.

From Eqs. (24) and (25) the transition amplitude can be seen to depend on the product of 3 – \( J \) symbols,

\[ \left( J^+ J J_i \right) \left( J_i J j \frac{1}{2} \right) \left( -\Omega^+ \Omega \Omega_i \right) \left( -\lambda - \lambda_i \frac{1}{2} \right) \left( \begin{array}{ccc} 1 & j & \frac{1}{2} \\ -m & 0 & m_j \end{array} \right) \]

For certain \( J \rightarrow J^+ \) transitions, this dependence restricts the allowed partial waves of the photoelectron to a single component. For example, for the transition \( J = 0 \rightarrow J^+ = 0.5 \) (Q branch), only the \( l = 1 \) partial wave is allowed. The transitions \( J = 0 \rightarrow J^+ = 3.5 \) (S branch), \( J = 0 \rightarrow J^+ = 4.5 \) (T branch), and all the U branch transitions, do not allow the \( l = 1 \) wave. Being so close to threshold, the intensity due to these higher partial waves (really only \( l = 3 \) since \( l = 5 \) and higher are negligible) signal the presence of a shape resonance near threshold. Such “fully resolved” transitions are dynamically significant because they decompose the continuum into single partial waves and offer a “snapshot” of the photoelectron continuum. Furthermore, if we now monitor these same rotational transitions for different vibrational levels, some of these features may be more visible at higher vibrational levels.
levels, we can see the changing partial wave character of the continuum brought about by the internuclear distance dependence of the electronic transition moment induced by the shape resonance. These selection rules may also be important in understanding Hund's case (b) to mixed case (a) transitions in other molecules. Experiments are now underway on single-photon VUV ionization of ground state HCl to the ground state $X^2\Sigma^+$ ion. Here the absence of gerade-ungerade symmetry may make the selection rules weaker since most transitions will now be mixtures of even and odd partial waves.

IV. PHOTOELECTRON ANGULAR DISTRIBUTIONS

In Fig. 4 we show our calculated photoelectron angular distributions for near-threshold energies (50 meV) for $v^+ = 2$. The angular distributions for the other vibrational levels are similar and are not shown. In this figure, the light is propagating into the page and the direction of polarization is vertical. For ease of viewing, each transition is normalized to have the same integrated intensity. For low $\Delta N$ transitions, most of the photoelectron flux is ejected perpendicular to the plane of polarization, giving a value of $\beta$ close to $-1$. For higher $\Delta N$ transitions, the distribution appears more isotropic with a $\beta$ close to zero. These angular distributions dramatically show that there is a change in the partial wave character of the continuum with rotational branch, and mirror the dominance of the $l = 1$ waves for low $\Delta N$ and the $l = 3$ waves for high $\Delta N$. Such dependence of photoelectron angular distributions on the final rotational state has been observed before in resonance enhanced multiphoton ionization studies, but to our knowledge not in ground state photoionization.

For completeness, our calculated rotationally and vibrationally unresolved photoelectron asymmetry parameter $\beta$ along with the measured values are shown in Fig. 5. Near threshold, $\beta$ is close to $-1$, rises steeply with increasing photon energy, and reaches a plateau near $+1$ at high energy. The value of near $-1$ close to threshold is consistent with the rotationally resolved results, if we note that the low $\Delta N$ levels are indeed the most intense in each rotational band.

ACKNOWLEDGMENTS

Research at the California Institute of Technology was supported by grants from the National Science Foundation (Grant No. CHE-8512191), AFOSR (Grant No. 87-0039), and the Office of Health and Environmental Research of the DOE (Grant No. DEFG03-87ER60513). We also acknowledge use of the resources of the San Diego Supercomputer Center, which is supported by the National Science Foundation. Work done by S. N. D. was performed under the auspices of the U.S. Department of Energy by...

APPENDIX A

Following Hougen,30 we derive rotational wave functions for the mixed Hund’s (a)–(b) from a basis of pure Hund’s case (a) for a $^2\Pi$ ion. We write the total Hamiltonian as

$$H = H_{\text{ro}} + H_r,$$

where

$$H_{\text{ro}} = \text{electronic} - \text{vib} + AL_zS_z,$$

and

$$H_r = \text{rotational}$$

$$= B(R^2_\lambda + R^2_{\lambda'})$$

$$= B \left[ (J^2 - J_\lambda^2 + L^2 - L_\lambda^2 + S^2 - S_\lambda^2) + (S_+ L_- + S_- L_+) - (J_+ S_- + J_- S_+) - (J_+ L_- + J_- L_+) \right].$$

(A3)

Here $A$ is the spin–orbit constant and $B$ is the rotational constant. For an isolated $2n$ state, we have,

$$H = -\frac{\hbar^2}{2\mu} \left[ \frac{\partial^2}{\partial \mathbf{r}^2} + \frac{1}{4\mu} \mathbf{r}^2 \right],$$

(A4)

Using the pure Hund’s case (a) basis, $\{\mathcal{A}\mathcal{S}\mathcal{E} \Omega \mathcal{J} \mathcal{M}\}$, we have for the Hamiltonian matrix, $\langle H \rangle$,

$$\begin{bmatrix}
-A + B(J + 1/2)^2 & -B \left[ (J + 1)^2 - 1 \right]^{1/2} \\
-B \left[ (J + 1)^2 - 1 \right]^{1/2} & 4A + B \left[ (J + 1/2)^2 - 2 \right]
\end{bmatrix}.$$

(A5)

This leads to a secular equation for the rotational energy with roots

$$E_{\pm} = B \left[ (J + 1/2)^2 - 1 \right] \pm 1/2BX,$$

(A6)

where

$$X = \left[ (J + 1/2)^2 + \lambda (\lambda - 4) \right]^{1/2},$$

(A7)

and $\lambda = A/B$. These energies correspond to the F1 and F2 components, respectively, and agree with Eq. (V28) of Ref. 26. The associated eigenvectors are

$$\psi_{\pm} = \sqrt{\frac{X \pm (\lambda - 2)}{2X}} |^3\Pi_{1/2};$$

$$1/2JM \mp \sqrt{\frac{X \pm (\lambda - 2)}{2X}} |^3\Pi_{3/2};$$

$$3/2JM \right).$$

(A8)

In the notation of Sec. II,

$$c_1 = \sqrt{\frac{X \pm (\lambda - 2)}{2X}},$$

(A9)

and

$$c_2 = \sqrt{\frac{X \pm (\lambda - 2)}{2X}}.$$

(A10)

Although these eigenvalues are widely available,26 expressions for the corresponding eigenfunctions necessary in evaluating transition amplitudes are not.

APPENDIX B

Here we list the composite wave functions for $1\pi_g$ photodetachment of $O_2 (^3\Sigma_u^-)$ used to evaluate expressions in Eq. (14). The initial state wave functions are

$$M_s = 1: |1\pi_g^+ 1\pi_g^- |,$$

(B1a)

$$M_s = 0: \frac{1}{\sqrt{2}} [ |1\pi_g^+ \bar{1}\pi_g^- | + |\bar{1}\pi_g^+ 1\pi_g^- | ],$$

(B1b)

$$M_s = -1: |\bar{1}\pi_g^+ \bar{1}\pi_g^- |. $$

(B1c)

The final state wave functions for $\lambda = 0$, overall $^3\Pi_u$ symmetry are

$$M_s = 1: |1\pi_g^+ k\sigma_u |,$$

(B2a)

$$M_s = 0: \frac{1}{\sqrt{2}} [ |1\pi_g^+ \bar{k}\sigma_u | + |\bar{1}\pi_g^+ k\sigma_u | ],$$

(B2b)

$$M_s = -1: |\bar{1}\pi_g^+ \bar{k}\sigma_u |. $$

(B2c)

The final state wave functions for $\lambda = \pm 1$, overall $^3\Sigma_u^-$ symmetry are

$$M_s = 1: \frac{1}{\sqrt{2}} [ |1\pi_g^+ k\pi_u^- | - |1\pi_g^- k\pi_u^+ | ],$$

(B3a)

$$M_s = 0: \frac{1}{2} [ |1\pi_g^+ \bar{k}\pi_u^- | - |\bar{1}\pi_g^- k\pi_u^+ | + |\bar{1}\pi_g^+ k\pi_u^- | - |1\pi_g^- \bar{k}\pi_u^+ | ],$$

(B3b)

$$M_s = -1: \frac{1}{\sqrt{2}} [ |\bar{1}\pi_g^+ \bar{k}\pi_u^- | - |\bar{1}\pi_g^- \bar{k}\pi_u^+ | ]. $$

(B3c)

The final state wave functions for $\lambda = -2$ of overall $^3\Pi_u$ symmetry are

$$M_s = 1: |1\pi_g^+ k\delta_u^- |,$$

(B4a)

$$M_s = 0: \frac{1}{\sqrt{2}} [ |1\pi_g^+ \bar{k}\delta_u^- | + |\bar{1}\pi_g^+ k\delta_u^- | ],$$

(B4b)

$$M_s = -1: |\bar{1}\pi_g^+ \bar{k}\delta_u^- |. $$

(B4c)

11 R. G. Tonkyn, J. W. Winniczek, and M. G. White, J. Chem. Phys. 91,
13 P. J. Miller and W. A. Chupka (private communication).