Resonant Raman scattering in O₂

I. Simbotin, M. Marinescu,^{a)} H. R. Sadeghpour,^{b)} and A. Dalgarno Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138

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Raman scattering of molecular oxygen in the region of the Schumann–Runge absorption band system is calculated from first principles in the second order of perturbation theory in the interaction of photon–electron operator. Quantitative predictions are given for the cross sections for scattering of photons and a detailed comparison is made with available measurements. The behavior of Raman spectra near the predissociating rovibronic level (v' = 5, N') in the $B \ ^3\Sigma_u^-$ electronic state of O_2 is investigated and shown to have significant dependence on the detuning of the incident laser frequency. By casting the Raman transition matrix in a form similar to the Fano formalism, we are able to investigate the nature of the resonant and nonresonant scattering in the language of configuration interaction. By varying the predissociating width of the (v' = 5, N') resonance, we make a comparison with an earlier time-dependent wave-packet analysis. We also calculate the depolarization ratio of the scattered photons parallel and perpendicular to the polarization of the incident laser beam for the different Raman branches for lines terminating in the v'' = 1 and v''= 6 levels and comment on the relationship between resonant Raman scattering and fluorescence emission. © 1997 American Institute of Physics. [S0021-9606(97)02742-6]

I. INTRODUCTION

Raman scattering of molecular oxygen in the region of the Schumann–Runge (SR) absorption band system modifies the transmission of solar radiation through the atmosphere. The SR system is the dipole-allowed electronic transition connecting the ground $X^{3}\Sigma_{g}^{-}$ state of O₂ to the excited $B^{3}\Sigma_{u}^{-}$ state. Most of the absorption oscillator strength from the lowest vibrational level, v''=0, in the $X^{3}\Sigma_{g}^{-}$ potential lies in the vibrational continuum of the $B^{3}\Sigma_{u}^{-}$ state which separates to O(${}^{3}P$)+O(${}^{1}D$). The discrete levels of the $B^{3}\Sigma_{u}^{-}$ state predissociate into one of several states of O₂, producing two ground-state oxygen atoms, O(${}^{3}P$). A considerable body of experimental data exists on the predissociation widths of the rovibronic levels in the *B* electronic state.¹⁻⁴

A photon with frequency ω incident on a diatomic molecule in a state with vibrational and rotational quantum numbers $(v''N_0'')$, can Raman scatter via an intermediate rovibronic molecular state (v',N'), producing a photon of frequency ω' and leaving the molecule in a final rovibrational level (v'',N'') with an energy equal to E(v'',N'') $=E(v'',N_0'')+\hbar(\omega-\omega')$, see Fig. 1.

Raman scattering of ultraviolet radiation by O_2 in the region of the SR absorption system has been studied in the laboratory^{5–7} and the major features of the spectral distribution of the scattered radiation have been successfully explained.^{8,9} However, a fully quantitative agreement between theory and experiment has been lacking and only relative scattering cross sections have been obtained.

In the experiment of Zhang and Ziegler,⁸ the relative intensities of the scattered photons in which the O₂ molecule

was left in specific rotational states of the (v''=1,N'') to (v''=7,N'') rovibronic levels were measured as a function of detuning of the laser frequency from the predissociating rovibronic level (v'=5,N') in the $B^{3}\Sigma_{u}^{-}$ electronic state. The molecular oxygen was initially prepared in rovibronic states $(v''=0,N''_{0})$. It has been argued⁸⁻¹¹ that near a resonance the Raman scattering line profile is similar to that expected from fluorescence emission, but is altered markedly with increased detuning such that transitions terminating in low vibrational levels become relatively stronger and the rotational structure changes. This difference has been interpreted in a time-dependent analysis by Williams and Imre,^{9,11} who attributed the nonresonant scattering to short-time events with the resonant behavior evolving on a longer time scale.

We report here a detailed quantitative prediction of cross sections for Rayleigh (elastic) and Raman (inelastic) scattering within a time-independent framework and compare with the experimental data of Zhang and Ziegler.⁸ The resonant and nonresonant contributions to the infinite sums occurring in the second-order perturbation theory are treated exactly by casting the sums in the form of inhomogeneous differential equations, driven by the transition dipole term. The mixing of the resonant and nonresonant interactions is investigated in the language of Fano configuration interaction. We address the relationship between resonant Raman scattering and fluorescence by calculating the depolarization ratio of the scattered photons parallel and perpendicular to the polarization of the incident beam of photons.⁸ By varying the predissociating width of the (v'=5) level as a function of energy, we provide a mock "time-dependent" picture of the physical process, without resorting to a time-dependent Hamiltonian.^{9,11} The method we use, like the time-dependent procedure of Heller¹⁰ adopted by Williams and Imre,^{9,11} avoids the explicit summation over eigenstates of the Hamiltonian, present in the conventional Kramers-Heisenberg for-

^{a)}Present address: School of Physics, Georgia Institute of Technology, Atlanta, GA 30332.

^{b)}Also at ITAMP; Electronic mail: hsadeghpour@cfa.harvard.edu



FIG. 1. Schematic representation of the Raman process in molecular oxygen.

malism, and provides a characterization of the virtual Raman response function.¹⁰

II. THEORY

According to the Kramers–Heisenberg formula, the differential Raman scattering cross section is given in atomic units in the dipole approximation by

$$\frac{d\sigma}{d\Omega} = \frac{\omega \omega'^3}{(137)^4} |\mathcal{M}_{fi}(\omega)|^2, \tag{1}$$

where $\mathcal{M}_{fi}(\omega)$ is a second-order matrix element connecting the initial and final states, $|i\rangle$ and $|f\rangle$, at a photon energy ω . The matrix element $\mathcal{M}_{fi}(\omega)$ contains a summation over the complete set of intermediate states, allowed according to the electric dipole selection rule. For incident frequencies in the region of the SR absorption system, only the electronic $B^{3}\Sigma_{u}^{-}$ state is retained, which collapses the summation over the entire Born–Oppenheimer states to one over the rovibronic eigenstates ($|k\rangle \equiv |v',N'\rangle$) of the $B^{3}\Sigma_{u}^{-}$ state. Then the transition matrix element connecting the initial state $|i\rangle$ $\equiv |v''=0,N_{0}''\rangle$ to a final discrete state $|f\rangle \equiv |v'',N''\rangle$, can be written as

$$\mathcal{M}_{fi}(\boldsymbol{\omega}) = \sum_{\boldsymbol{v}_k, N_k} \left[\frac{\langle \boldsymbol{v}_f, N_f | \boldsymbol{\epsilon} \cdot \mathbf{D} | \boldsymbol{v}_k, N_k \rangle \langle \boldsymbol{v}_k, N_k | \boldsymbol{\epsilon}' \cdot \mathbf{D} | \boldsymbol{v}_i, N_i \rangle}{E_{\boldsymbol{v}_f N_f} - \boldsymbol{\omega} - E_{\boldsymbol{v}_k N_k}} \right] + \frac{\langle \boldsymbol{v}_f, N_f | \boldsymbol{\epsilon} \cdot \mathbf{D} | \boldsymbol{v}_k, N_k \rangle \langle \boldsymbol{v}_k, N_k | \boldsymbol{\epsilon} \cdot \mathbf{D} | \boldsymbol{v}_i, N_i \rangle}{E_{\boldsymbol{v}_f N_f} - \boldsymbol{\omega} - E_{\boldsymbol{v}_k N_k} + i \Gamma \boldsymbol{v}_k / 2}.$$
(2)

In Eq. (2), the two terms in the expansion referring to the two Feynman diagrams¹² are denoted, respectively, as the T1 and T2 terms, (ϵ, ϵ') , (ω, ω') , and **D** stand, respectively, for the polarization unit vectors and frequencies for the incident and scattered photons, and the transition dipole moment at an internuclear distance *R* connecting the $X^{3}\Sigma_{g}^{-}$ and $B^{3}\Sigma_{u}^{-}$ states. $|v_{k}, N_{k}\rangle \equiv |v', N'\rangle$ are the discrete and continuum nuclear wave functions in the ${}^{3}\Sigma_{u}^{-}$ electronic potential energy. In the discrete region of the spectrum, the predissociation is included via the imaginary term $\Gamma_{v_{k}}/2$ in the denominator of Eq. (2), where $\Gamma_{v_{k}}$ is the decay width of the predissociating resonance.



FIG. 2. The potential energy curves and the dipole transition matrix element D(R) connecting the ground electronic $(X \, {}^{3}\Sigma_{g}^{-})$ and the excited electronic $(B \, {}^{3}\Sigma_{u}^{-})$ states, from Ref. 15.

Expression (2) can be expressed formally in terms of the outgoing Green's function $G^{(+)}(E)$ corresponding to the Born–Oppenheimer Hamiltonian H_{BO} for the nuclear motion in the $B^{3}\Sigma_{u}^{-}$ potential, see Fig. 2. The reduction of the full Hilbert space to only one term in the BO expansion is justified because the absorption in the discrete bands in the SR system is controlled by the transition between the ground and the excited *B* electronic state of O₂.¹ Thus

$$\mathcal{M}_{fi}(\boldsymbol{\omega}) = \langle \boldsymbol{v}_f, N_f | \boldsymbol{\epsilon}' \cdot \mathbf{D} G^{(+)} (\boldsymbol{E}_{\boldsymbol{v}_i N_i} + \boldsymbol{\omega}) \boldsymbol{\epsilon} \cdot \mathbf{D} | \boldsymbol{v}_i, N_i \rangle + \langle \boldsymbol{v}_f, N_f | \boldsymbol{\epsilon} \cdot \mathbf{D} G^{(+)} (\boldsymbol{E}_{\boldsymbol{v}_i N_i} - \boldsymbol{\omega}) \boldsymbol{\epsilon}' \cdot \mathbf{D} | \boldsymbol{v}_i, N_i \rangle.$$
(3)

Using standard angular momentum algebra,^{13,14} we may extract the dependence on the rotational quantum numbers to obtain,

$$\mathcal{M}_{fi}(\omega) = \sum_{pq} \left[\langle v_f, N_f | F_q^{(p)} G^{(+)}(E_{v_i N_i} + \omega) G_{-q}^{(p)} | v_i, N_i \rangle \right. \\ \left. + (-1)^p \langle v_f, N_f | F_q^{(p)} G^{(+)} \right. \\ \left. \times (E_{v_i N_i} + \omega) G_{-q}^{(p)} | v_i, N_i \rangle \right],$$
(4)

where $F_q^{(p)}$ and $G_{-q}^{(p)}$ are given in terms of the spherical components of the polarization tensors, $\epsilon'_{\nu}^{(1)}$ and $\epsilon^{(1)}_{\nu}$, and the dipole moment tensor $D_{\mu}^{(1)}$,

$$F_{q}^{(p)} \equiv \sum_{\nu} (-1)^{q} (2p+1)^{1/2} \begin{pmatrix} 1 & 1 & p \\ \nu & q-\nu & -q \end{pmatrix} \epsilon_{\nu}^{\prime(1)} \epsilon_{q-\nu}^{(1)}$$
(5)

and

$$G_{-q}^{(p)} \equiv \sum_{\mu} (-1)^{q} (2p+1)^{1/2} \\ \times \begin{pmatrix} 1 & 1 & p \\ \mu & -q-\mu & -q \end{pmatrix} D_{\mu}^{(1)} D_{-q-\mu}^{(1)}.$$
(6)

Then the differential cross section is¹³

$$\frac{d\sigma}{d\Omega} = \frac{\omega \omega'^3}{(137)^4} \left| \sum_{p=0}^2 \sum_{q=-p}^p F_q^{(p)} \mathbf{M}_p(\omega) \right|^2, \tag{7}$$

where

$$\mathbf{M}_{p}(\boldsymbol{\omega}) = \sum_{N'} \mathscr{K}_{p}(N_{0}'', N', N'') [\langle \chi_{v_{f}, N_{f}} | D(R) \\ \times g_{N'}^{(+)}(E_{v_{i}N_{i}} + \boldsymbol{\omega}) D(R) | \chi_{v_{i}N_{i}} \rangle + (-1)^{p} \\ \times \langle \chi_{v_{f}, N_{f}} | D(R) g_{N'}^{(+)}(E_{v_{f}N_{f}} - \boldsymbol{\omega}) D(R) | \chi_{v_{i}N_{i}} \rangle], \quad (8)$$

and

$$\mathscr{X}_{p}(N_{0}'',N',N'') = (2N''+1)^{1/2}(2N'+1) \begin{pmatrix} N'' & 1 & N' \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} N' & 1 & N_{0}'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} p & N'' & N_{0}'' \\ N' & 1 & 1 \end{pmatrix}.$$
 (9)

If the scattered light is detected parallel $(\epsilon' \| \epsilon)$ or perpendicular $(\epsilon' \bot \epsilon)$ to the incident photon polarization vector, the scattering cross sections are given, respectively, by

$$\frac{d\sigma_{\parallel}^{(v''N'')}}{d\Omega} = (\frac{1}{137})^4 \omega \omega'^3 \sum_{p=0,2} (2p+1) \begin{pmatrix} 1 & 1 & p \\ 0 & 0 & 0 \end{pmatrix}^2 \\ \times \left| \sum_{N'} \mathscr{K}_p(N_0'', N', N'')^2 \mathscr{M}_p(\omega) \right|^2, \quad (10)$$

and

$$\frac{d\sigma_{\perp}^{(v''N'')}}{d\Omega} = (\frac{1}{137})^4 \omega \omega'^3 \sum_{p=1,2} (2p+1) \begin{pmatrix} 1 & 1 & p \\ 0 & -1 & 1 \end{pmatrix}^2 \\ \times \left| \sum_{N'} \mathscr{X}_p(N_0'', N', N'')^2 \mathscr{M}_p(\omega) \right|^2, \quad (11)$$

with $\mathcal{M}_p(\omega)$ to be defined in Eq. (14). In arriving at Eqs. (10) and (11), the full wave function in each BO potential is taken as a simple product of vibrational and rotational wave functions. In Eq. (8), $g_{N'}(E)$ is the radial Green's function for the nuclear motion of two oxygen atoms along the *B* electronic surface. The expressions in the large parentheses and curly brackets are, respectively, the 3-j and 6-j coefficients. Equation (9) is a mathematical confirmation of the diagrammatic representation in Fig. 1, that for the Raman excitation of O(N) and S(N) branches, for which, respectively, $N''=N''_0-2$ and $N''=N''_0+2$, only one value of N' contributes for each branch, whereas for the Q(N) Raman branch, for which $N''=N''_0$, both allowed values of N' contribute.

$$\left(H_{\rm BO}^{N'} - E_{v_i N_i} - \omega - i \frac{\Gamma_{v'}}{2}\right) |\Xi_a\rangle = -D|\chi_{v_i, N_i}\rangle$$

$$(H_{\rm BO}^{N'} - E_{v_f N_f} + \omega) |\Xi_b\rangle = -D|\chi_{v_f, N_f}\rangle.$$
(12)

dipole response functions $\Xi_a(\omega, R)$ and $\Xi_b(\omega, R)$ defined as the regular solutions of the inhomogeneous set of equations¹⁵

The scattering matrix element in Eq. (4) is now written in terms of the response functions,

$$\mathscr{M}_{fi}(\boldsymbol{\omega}) = \sum_{pqN'} F_q^{(p)} \mathscr{X}_p(N_0'', N', N'') \mathscr{M}_p(\boldsymbol{\omega})^2, \qquad (13)$$

with

$$\mathscr{M}_{p}(\omega) = \langle \chi_{v_{f},N_{f}} | D | \Xi_{a} \rangle + (-1)^{p} \langle \Xi_{b} | D | \chi_{v_{i},N_{i}} \rangle.$$
(14)

The Born–Oppenheimer Hamiltonian in the center-of-mass coordinates with reduced mass μ , $H_{BO}^{N'} = (1/2\mu)(d^2/dR^2) + V_{BO}(R) + (N'(N'+1)/2\mu R^2)$, describes the motion on the $B^{3}\Sigma_{u}^{-}$ electronic surface. A numerical algorithm for solving the coupled inhomogeneous differential equations in (12) has been developed.¹⁵ The resonance structure which occurs as ω approaches $(E_{v''N_{0}''} - E_{v'N'})$ emerges naturally in the numerical solution, but can be made explicit by redefining the solution $\Xi_{a}(\omega, R)$ as

$$|\Xi_{a}\rangle = |\Xi_{a}\rangle + \frac{|\chi_{v_{0}',N_{0}'}\rangle\langle\chi_{v_{0}',N_{0}'}|D|\chi_{v_{i},N_{i}}\rangle}{E_{v_{i}N_{i}} + \omega - E_{v_{0}} + i(\Gamma_{v_{0}}/2)},$$
(15)

where the quantum numbers (v'_0, N'_0) denote the resonance term and $|\chi_{v'_0, N'_0}\rangle$ is the nuclear wave function at the energy of the resonance E'_{v_0} .

III. DISCUSSION OF RESULTS

The potential energy curves of the $X^{3}\Sigma_{g}^{-}$ and $B^{3}\Sigma_{u}^{-}$ states of O₂ (Ref. 16) are shown in Fig. 2, together with the transition dipole moment.¹⁶ In the experiment of Zhang and Ziegler⁸ the incident photons had frequencies in the range $52\,435-52\,468\,\mathrm{cm}^{-1}$ which includes the SR P(11) and R(13) absorption lines of the (5,0) band. The P(11) and R(13) lines have predissociating widths of about 2 cm⁻¹ and the Q branch Raman lines, Q(11) and Q(13), are not resolved in the experiment which has a spectral resolution of about 6 cm^{-1} . Since the electric dipole selection rules restrict the Raman excitation to the range of N values ΔN =0, \pm 2, and since the ΔN =0 transitions are forbidden in $\Sigma - \Sigma$ transitions, the allowed final Raman branches are the O, Q, and S branches, Fig. 1. Due to symmetry considerations, only odd-numbered rotational levels (odd N''_0) are populated in the ground electronic state $X^{3}\Sigma_{a}^{-}$ of ${}^{16}O_{2}$.

A. Rotationally resolved Raman scattering spectra

Rotationally resolved resonant Raman spectra of ${}^{16}O_2$ at incident laser frequencies, $\omega = 52\,435$ and $52\,442 \text{ cm}^{-1}$ were obtained by Zhang and Zeigler.⁸ For both spectra, the inten-



FIG. 3. Franck–Condon factors for transition to v' = 5 from different vibrational levels (v'') in the ground electronic state.

sities of the lines terminating in levels v''>2 follow closely the ratio of Franck–Condon factors $|\langle v'=5|v''\rangle|^2$, shown in Fig. 3, that would be expected from the spontaneous decay of the v'=5 state. The relative intensities of the lines terminating in v''=1 and v''=2 are much different than those given by the Franck–Condon distribution and vary markedly with the frequency of the incident photon. With increasing detuning from the resonant P(11) and R(13) absorption lines, the intensities of the v''=1 and v''=2 lines grow relative to the v''>2 lines.

The intensity variations are characteristic of the change from resonant to nonresonant Raman scattering.^{8–11} Figures 4(a) and 4(b) illustrate the theoretical calculations for the laser tuned off and near resonance at $\omega = 52447$ and 52 451 cm⁻¹. The calculations were carried out for an initial thermal population of rotational levels and an excitation laser profile modeled with a Gaussian distribution of bandwidth $\gamma = 1.2$ cm⁻¹.⁸ The Raman scattering lines in Fig. 4 were convoluted with the experimental spectral resolution of 6 cm⁻¹.

A close match is found between the experimental spectra, Figs. 2 and 3 in Ref. 8, and the theoretical predictions in Figs. 4(a) and 4(b). The diffuse sidebands on each side of the dominant resonance arise from the finite resolution of the experiment. The high-resolution spectra at the laser frequency of $\omega = 52 \ 452 \ \text{cm}^{-1}$ are shown in Figs. 5(a) and 5(b). Figure 5(a) shows the spectrum for transitions terminating in the v''=1 level. The spectrum has peak contributions from resonant scattering of the O(11), Q(11), Q(13), and S(13)



FIG. 4. Resonant Raman spectrum of O₂ for comparison with the measurements in Ref. 8 at two different incident photon frequencies, (a) 52 447 cm⁻¹, and (b) 52 451 cm⁻¹. Notice the drastic change of the relative intensities of the $v'' \le 2$ as the laser frequency is tuned further from the v' = 5 resonance line.



FIG. 5. Calculated Raman spectra at infinite resolution for transitions terminating in the v''=1 (a) and v''=6 (b) lines, respectively. In (b), only four lines corresponding to O(11), Q(11), Q(13), and S(13) are visible. The photon frequency is $\omega = 52 452 \text{ cm}^{-1}$.



FIG. 6. Calculated Raman spectrum near the v''=1 fundamental band at 190.654 nm is convoluted with the experimental resolution.

lines, but also shows significant nonresonant scattering from the thermal population of rotational levels. The rotationally unresolved Q(N) branch lines pile up in intensity and produce the anomalous peak in Fig. 5(a). An expanded view is presented in Fig. 6 of the Raman spectrum for an incident frequency $\omega = 52 451 \text{ cm}^{-1}$ and scattered frequencies corresponding to the fundamental v''=1 band. It illustrates the

TABLE I. The rotationally resolved Raman scattering cross sections, resonant with the P(11) and R(13) absorption lines, in units of cm².

| | $\omega = 52 \ 452.37 \ \mathrm{cm}^{-1}$ | | |
|--------------|--|------------------------|------------------------|
| υ″ | O branch | Q branch | S branch |
| $N_0'' = 11$ | | | |
| 1 | 3.71×10^{-27} | 5.52×10^{-27} | 1.51×10^{-27} |
| 6 | 5.04×10^{-25} | 5.54×10^{-25} | 5.26×10^{-28} |
| $N_0'' = 13$ | | | |
| 1 | 1.20×10^{-27} | 4.67×10^{-27} | 3.60×10^{-27} |
| 6 | 3.19×10^{-28} | 1.19×10^{-25} | 1.26×10^{-25} |
| | $\omega = 52 \ 454.17 \ \mathrm{cm}^{-1} \ N_0'' = 11$ | | |
| υ″ | O branch | Q branch | S branch |
| $N_0'' = 11$ | | | |
| 1 | 3.43×10^{-28} | 1.80×10^{-27} | 1.52×10^{-27} |
| 6 | 1.18×10^{-25} | 1.30×10^{-25} | 5.85×10^{-28} |
| $N_0'' = 13$ | | | |
| 1 | 1.21×10^{-27} | 5.00×10^{-27} | 3.99×10^{-27} |
| 6 | 2.89×10^{-28} | 4.77×10^{-25} | 5.08×10^{-25} |



FIG. 7. Calculations of the Raman excitation profiles of the S(13), O(11), and Q(11,13) rovibronic transitions terminating in the v''=6 level. A small kink in the fundamental line near 190.65 nm is the same as that in Fig. 6.

prominent role of the unresolved Q branch lines, found also in the experiments of Zhang and Zeigler.⁸ In contrast, Fig. 5(b) shows the infinite resolution spectrum for transitions terminating in the v''=6 level. Its appearance is significantly different from that of Fig. 5(a). The spectrum consists of only four lines corresponding to the resonant O(11), Q(11), Q(13), and S(13) transitions. The nonresonant contribution is absent.

In Table I, we give the absolute resonant cross sections for the different Raman branches for transitions terminating in the v''=6 and v''=1 rovibrational levels at laser frequencies $\omega = 52 \ 452.37$ and 52 $454.17 \ \text{cm}^{-1}$. The rotationally resolved resonant cross sections (in cm²) are peak values of the cross sections for the resolved absorption resonances, P(11)and R(13). The values in Table I confirm that the absorption resonance P(11) contributes significantly to the Q(11) and O(11) branches and the absorption resonance R(13) contributes to the Q(13) and S(13) branches.⁸

The distinctions between resonant and nonresonant Raman scattering are also demonstrated in the experimental data, see Fig. 5 in Ref. 8, for the transitions terminating in v''=6 and v''=1 as a function of the laser frequency. The v''=1 transitions are flat as a function of the incident photon frequency, whereas the v''=6 lines show a resonant profile of the Q(11,13), O(11), and S(13) branches. The theoretical predictions, illustrated in Fig. 7, show that the v''=1intensity is not quite independent of the laser frequency. There is a small varying contribution from the resonant excitation of the Q(11,13) branch lines.



FIG. 8. Raman profiles for molecular oxygen at several photon frequencies near the v'=5 resonance level. The frequency is swept through many linewidths of the resonance. Notice the nearly constant behavior of the v''=1 and v''=2 lines in comparison with the higher vibrational levels.

We can now make explicit predictions of Raman scattering profiles for any applied frequency in the region of the SR absorption band. In Fig. 8, we present a three-dimensional view of the Raman profile as the excitation laser is swept in frequency through many predissociating linewidths of the P(11)R(13) overlapping resonances. The fundamental v''=1 band intensity remains constant over many laser frequencies while the rotational structures in the $v'' \ge 3$ bands change dramatically. The scattered photons in the range of 1450–1650 cm⁻¹ near the fundamental Raman band v''=1give rise to a rotational profile, illustrated in Fig. 9. The unresolved rotational lines of Q(11,13) produce the "midwall" structure near 1550 cm⁻¹ with a noticeable "kink" due to a small resonant scattering contribution to the Q(11,13) profile. The regular modulations are due to the excitation of different rotational levels. The two noticeable bumps on the rotational "rolling hills" are the O(11) and S(13) resonance Raman profiles.

To carry out a more detailed investigation of the resonant Raman lines and the nature of the resonant and background interactions, we cast the problem in the form of the Fano configuration interaction picture.¹⁷ We begin by writing down the resonant term in the matrix element in Eq. (8) as



FIG. 9. Raman profile for the fundamental v''=1 band as a function of the laser frequency and the scattered photon frequency. The dominant feature in the middle of the figure is the result of incoherent addition of many Q(N) lines. Also, notice the two bumps on the O(11) and S(13) rotational levels, giving the resonant population of these levels at specific laser frequencies.

$$\mathbf{M}_{p}(\omega) = \sum_{N'} \mathscr{K}_{p}(N_{0}'', N', N'') \\ \times \left[A_{p} + \frac{B_{p}}{E_{v''=0N_{0}''} + \omega - E_{5N'} + i\Gamma_{v'}/2} \right], \quad (16)$$

where

$$A_{p} = \sum_{v' \neq 5} \frac{\langle \chi_{v''N''} | D(R) | \chi_{v'N'} \rangle \langle \chi_{v'N'} | D(R) | \chi_{0} N_{0}'' \rangle}{E_{v''=0,N_{0}''} + \omega - E_{v'N'}} + (-1)^{p} \langle \chi_{v_{f},N_{f}} | D(R) g_{N'} (E_{v_{f}N_{f}} - \omega) D(R) | \chi_{v_{i},N_{i}} \rangle$$
(17)

and

$$B_{p} = \langle \chi_{v'',N''} | D(R) | \chi_{5,N'} \rangle \langle \chi_{5,N'} | D(R) | \chi_{0} N_{0}'' \rangle.$$
(18)

We next define the Fano parameter,

$$q_{p} = \frac{[B_{p}/(\Gamma_{v'}/2)]}{A_{p}}.$$
(19)

This parameter can, to a good approximation, be treated as a constant, because A_p which describes the background excitation, is a slowly varying function of the laser frequency. Equation (16) can then be rewritten as

$$\left|\mathbf{M}_{p}(\boldsymbol{\omega})\right|^{2} = A_{p}^{2} \left|1 + \frac{q_{p}}{\delta + i}\right|^{2}, \qquad (20)$$

where

$$\delta = \frac{E_{v_i N_i} + \omega - E_{5N'}}{\Gamma_{v'}/2},\tag{21}$$

is a dimensionless energy parameter, describing the detuning of the laser frequency. Upon expanding Eq. (20), we get

$$|\mathbf{M}_{p}(\omega)|^{2} = |A_{p}|^{2} \left[\frac{(\delta + q_{p})^{2}}{(\delta^{2} + 1)} + \frac{1}{(\delta^{2} + 1)} \right].$$
(22)

The first term in this expression produces the Fano profile whose asymmetry is defined by the parameter q_p , while the second term gives a Lorentzian modification. It is the mixing of these two terms as a function of the excitation laser frequency that is of interest.

We extract the limiting forms

$$|\mathbf{M}_{p}(\omega)|^{2} = |A_{p}|^{2}, \quad q_{p} = 0,$$

= $|A_{p}|^{2} \left[\frac{q_{p}^{2}}{\delta^{2} + 1} \right], \quad q_{p} \ge 1.$ (23)

Thus for low values of the asymmetry parameter q_p the Raman profile will show weak dependence with energy and the intensity of different excitation branches will be given by $|A_p|^2$. In the high q_p limit, the Raman profile will appear Lorentzian and the intensity of the branches will be determined by the variation in $|B_p|^2$.

The parameter $q_{p=2}$ is plotted in Fig. 10 as a function of δ for the S(13) Raman branch for different final-state vibrational levels v''. The parameter q_p depends on v'', but for a given v'' is constant over a range of energies. From the lim-



FIG. 10. The Fano parameter for the p=2 term and for the S(13) branch as a function of the dimensionless detuning parameter δ . For the low vibrational levels, q_p is small and nearly constant. For large asymmetry parameters, for large vibrational levels, we predict near Lorentzian Raman profiles.

iting forms in Eq. (25), we can infer the v''=0 Rayleigh profile $(q_p \leq 0.1)$ to have a weak dependence on energy, the v''=1 Raman line to show a typical asymmetric Fano profile $(q_p \approx 1)$, while $v'' \geq 2$ Raman lines (with $q_p \geq 1$) to have Lorentzian energy profiles. The resulting Rayleigh and Raman profiles for the S(13) branch are shown in Fig. 11 as a function of δ . We observe that indeed the v''=0 Rayleigh profile is nearly constant and the v''=1 fundamental Raman line has negative asymmetry $(q_p < 0)$. The $v'' \geq 2$ Raman profiles are all Lorentzian in shape.

B. Dependence of the Raman spectrum on lifetime

The calculations of Williams and Imre^{9,10} indicate that the Raman scattering spectra provide a signature of the time dependence of the Raman response function. By evolving initial wave packets in time on the *B* excited state, they showed that the "emission" spectrum exhibited time dependence and that the "anomalous" peaks at $v'' \le 2$ are indeed caused by short-time phenomena. In order to "model" the time dependence of the Raman spectrum, we varied the predissociating lifetime. Figure 12 displays our calculation of the Raman rovibronic spectrum at several $\Gamma_{v'}$. A noticeable variation in the v''=6 spectrum (*Q*, *S* branches) as a function of $\Gamma_{v'}$ is observed relative to the v''=0 and v''=1 spectra. As the decay lifetime of the excited v'=5 state increases, corresponding to an increasing number of



FIG. 11. The Raman profiles terminating in different vibrational levels, giving support to the predictions from Fig. 10. The profiles at higher vibrational levels show near Lorentzian behavior corresponding to large asymmetry parameter q_p .

vibrational periods, the relative intensity of the v''=6 lines grows. This amounts to the collapse of the Raman wave function onto a single eigenstate. Therefore we can identify the v''=6 Raman lines as due to long-time events corresponding to a resonant excitation in accord with the conclusions of William and Imre.

If results are required for only a limited number of frequencies, the method we describe is more economical computationally than obtaining the solution to the timedependent problem and, though time independent, can be manipulated to yield information on time dependence.

C. Depolarization ratio

We investigate the effect of resonant molecular excitation on the depolarization of the scattered radiation $\rho(\omega)$.^{8,18} The depolarization ratio is defined as the ratio of the intensities of the scattered light detected with the polarization perpendicular and parallel to the incident light polarization vector,

$$\rho(\omega) = \frac{I_{\perp}}{I_{\parallel}} = \frac{3\mathscr{K}_{1}^{2}|\mathscr{M}_{1}(\omega)|^{2} + 3\mathscr{K}_{2}^{2}|\mathscr{M}_{2}(\omega)|^{2}}{2\mathscr{K}_{0}^{2}|\mathscr{M}_{0}(\omega)|^{2} + 4\mathscr{K}_{2}^{2}|\mathscr{M}_{2}(\omega)|^{2}}, \quad (24)$$

where $\mathcal{M}_p(\omega)$ and \mathcal{X}_p are defined, respectively, in Eqs. (14) and (9). Figure 13 gives the calculated depolarization ratios of the Raman branches in the v''=6 vibrational band as the laser is tuned through the P(11)R(13) rovibronic absorption band. Excitation of the O(11) and S(13) Raman branches



FIG. 12. Variation of the Raman cross section with predissociating width and laser wavelength. The solid lines, dotted lines, long-dashed lines, and dot-dashed lines represent, respectively, the Q branch and the S branch in the v''=6 level, the Q branch in the v''=0 level and the Q branch in the v''=1 level. As the lifetime of the excited v'=5 level increases (Γ decreases), the intensity of the v''=6 lines grows in comparison with the v''=1 line.

proceeds via a single pathway, the P(11) and R(13) absorption branches, respectively. Consequently, $\rho(\omega)$ for these Raman branches reduces to ratios of geometric terms whose energy-independent value is $\rho(\omega) = 0.75$. The unresolved Q(11,13) Raman branch is excited via two interfering pathways, the P(11) and R(13) absorption branches, see Fig. 1. This is evident from Eq. (8) where a coherent sum over the intermediate angular momentum states leads to a dramatic variation of the depolarization ratio with wavelength. Our full-scale calculation is only in qualitative agreement with the experiment in Ref. 8. The behavior with wavelength is similar in shape near the unresolved P(11)R(13) resonance and has the same asymmetry, but is different for photon wavelengths detuned from the resonance. In particular, due to the interference of the two intermediate angular momentum states, we predict that the depolarization ratio peaks in value in between the P(11)R(13) absorption lines and the R(11) and P(13) absorption features and decreases in value as the photon energy nears the P(13) or R(11) lines from either direction.

We find qualitative agreement with the experiment.⁸ The theoretical results of Ref. 8 appear to produce a perfect match with experiment, see Fig. 8 in Ref. 8. The calculations in Ref. 8 retain only one term in Eq. (2), T1, and only the



FIG. 13. Depolarization ratios for scattering transitions ending in the v'' = 1 and v''=6 vibrational levels. When the Q(11) and Q(13) branches are resolved, markedly different ratios are predicted. The S(13) and O(11) lines have no dependence on the laser wavelength, $\rho=0.75$, whereas the v''=1 fundamental band ratio is small and shows a small variation with the wavelength.

resonant state in the infinite sum in the term *T*1. We attempted to repeat the calculations with one state in the sum in *T*1, with an *R*-independent transition dipole and spin–rotation resolved experimental energy levels from Ref. 19. The results are similar to our full-scale calculations, especially in the resonance region and they increase in value far from the resonance on either side of the resonance region and in particular $\rho(\omega)$ falls below 0.75, as in our more comprehensive calculation. They do not agree well with the reported calculated results in Ref. 8 and the measured values. We are unable to identify the origin of the discrepancy.

This energy-dependent aspect of the depolarization ratio can be seen if the overlapping resonances, Q(11) and Q(13), are resolved. The crossing depolarization curves in Fig. 13 result. We have also ignored the incoherent sum over N' in Eq. (8) and found that the depolarization ratio shows an asymmetric resonance behavior for energies near the P(11)R(13) absorption features and tends to the constant value of 0.75 on either side of the resonance.

In contrast, the fundamental v''=1 depolarization ratio shows little change with photon frequency, as expected from previous analysis. This depolarization ratio which contains significant contributions from background nonresonant excitation, as discussed in Sec. III A, has a mean value of ρ =0.14 in Fig. 13, in excellent agreement with the quoted observed value of ρ =0.14±0.02.⁸



FIG. 14. Absolute value of the matrix elements for the Q(11) and Q(13) Raman lines as a function of the laser detuning for the lines terminating in the v''=1, (b) and (d), and v''=6, (a) and (c), levels. The top two curves in each figure correspond to the T1 lines and are in all cases orders of magnitude larger than the T2 lines at the bottom of each figure. Notice that at resonance, each T1 line, P(11) or R(13), dominates over the T2 line.

Near a resonance, the Raman process is dominated by the T1 term in Eq. (8), and the T2 term is relatively small. To demonstrate this, we show in Fig. 14 the absolute value of the matrix elements in Eq. (14) as a function of the laser frequency. Figures 14(a) and 14(b) give the matrix elements for the Q(11) lines terminating in the v''=6 and v''=1 levels, respectively, and the matrix elements for the Q(13) lines are shown in Figs. 14(c) and (d). The top two curves in each figure correspond to the T1 matrix elements for the R(11)and P(13) branches. The two T2 matrix elements which are shown at the bottom in each figure are not distinguishable on the scale shown. The T1 terms are orders of magnitude larger than the T2 terms. At resonance, the two T1 terms in Figs. 14(a) and 14(c), for lines terminating in the v''=6 levels, are appreciably different-the resonant term is much larger, whereas in Figs. 14(b) and 14(d), for lines terminating in the v''=1 levels, the two T1 matrix elements are similar in magnitude, because the resonant contribution is small.

Zhang and Ziegler showed that if the cross terms originating from the summation over $N' = N''_0 \pm 1$ in Eq. (9) are neglected, and only one term is retained in the sum at any one time, the expression for the depolarization ratio for the Q(N) branch reduces to

$$\rho = \frac{3 \begin{cases} 2 & N_0'' & N_0'' \\ N_0'' \pm 1 & 1 & 1 \end{cases}^2 + 3 \begin{cases} 1 & N_0'' & N_0'' \\ N_0'' \pm 1 & 1 & 1 \end{cases}^2}{4 \begin{cases} 2 & N_0'' & N_0'' \\ N_0'' \pm 1 & 1 & 1 \end{cases}^2 + 2 \begin{cases} 0 & N_0'' & N_0'' \\ N_0'' \pm 1 & 1 & 1 \end{cases}^2},$$
(25)

where \pm signs refer to the *R* and *P* absorption branches. Equation (25) has explicit values of

$$\rho = \frac{6N_0''^2 + 7N_0''}{8N_0''^2 + 16N_0'' + 10} \tag{26}$$

for the R branch and

$$\rho = \frac{6N_0''^2 + 5N_0'' - 1}{8N_0''^2 + 2} \tag{27}$$

for the *P* branch.¹⁴ These expressions are given in Refs. 8, 14, and 20. They are approximations to Eq. (9) for resonance fluorescence.

IV. CONCLUSION

We have calculated absolute values of the resonant and nonresonant Raman scattering cross sections of molecular oxygen in the region of the SR absorption band system at ultraviolet wavelengths. We have investigated the behavior of the Raman response function for transitions terminating in different rovibronic levels of the ground electronic state of the molecule at energies within several linewidths of the v'= 5 predissociating level of the excited electronic state of O₂. Excellent agreement between the calculated relative scattering photon intensities in strength and in profile and the measurements is found. We show that the variation of different line intensities in the experimental spectra is a result of the resonant and nonresonant behavior of the Raman response functions.

We find as the laser frequency is tuned on the v'=5 resonance, the relative intensities of the transitions terminating in the higher rovibronic levels grow in strength, similar to an emission profile, and when the laser frequency is tuned off the resonance, the transitions terminating in low vibrational ($v'' \leq 2$) levels become relatively stronger. We varied the predissociating width of the excited rovibronic state in order to study these effects. We find that as the lifetime of the excited state increases, the relative intensities of the transitions ending in the high vibrational levels grow. This is in agreement with the measurements⁸ and wave-packet analysis.¹⁰

The depolarization ratio of the scattered photons perpendicular and parallel to the incident photon polarization vector has markedly different behavior with frequency for the different O, Q, and S Raman branches. Whereas the S(13) and O(11) ratios are constant with photon frequency, the resolved Q(11) and Q(13) ratios vary rapidly. We find qualitative agreement with the measurement of the Q(11,13) depolarization ratio for lines terminating in the v''=6 level and excellent agreement with the Q(11,13) depolarization ratio data for lines terminating in the v'=1 level. By making two successive approximations, we recover the depolarization ratio usually assigned to resonance fluorescence.

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