

Shape-resonance-induced non-Franck-Condon effects in (2+1) resonance enhanced multiphoton ionization of the $C^3\Pi_g$ state of O_2

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Resonance enhanced multiphoton ionization (REMPI) coupled with high resolution, angle-resolved photoelectron spectroscopy is becoming an important probe of the photoionization dynamics of excited molecular states.¹ Recent measurements of (2+1) REMPI spectra of the $C^3\Pi_g$ ($3s\sigma_g$) Rydberg state of O_2 by Miller *et al.*² (preceding paper) and Katsumata *et al.*³ show pronounced non-Franck-Condon effects, as evident by the observation of intense off-diagonal ($\Delta v = v^+ - v' \neq 0$) peaks for alternative vibrational states of the ground state ion. Miller *et al.* have also suggested that the non-Franck-Condon behavior arises from autoionization of the $(1\pi_g 3\sigma_u)^3\Pi_u$ valence state which would be equivalent, in the present context, to the formation of a shape resonance in the σ_u ionization continuum.⁴ The dependence of the energy and width of shape resonances on internuclear distance induces strong variations in the electronic transition dipole moment to specific vibrational states of the ion. This mechanism for inducing non-Franck-Condon vibrational distributions in the photoionization of ground state molecules was first predicted and observed in N_2 and CO .⁵

The purpose of this Letter is to present *ab initio* calculations of the O_2 $C^3\Pi_g$ state photoelectron spectra which have been measured by Miller *et al.* These calculations establish that in photoionization of this resonantly prepared Rydberg state, a shape resonance at threshold significantly alters vibrational distributions from those based on the Franck-Condon principle. Such resonantly induced distributions will strongly influence the preparation of state-selected ions by REMPI, and perhaps more importantly, complicate the extraction of state populations from REMPI signals. Although these calculations account for a significant part of the observed non-Franck-Condon intensity, some discrepancies between theory and experiment remain for certain portions of the spectrum. These discrepancies are tentatively interpreted by invoking mechanisms involving initial-state correlation and final-state channel interaction with excited valence states.

To account for non-Franck-Condon effects due to the shape resonance, we have included^{6,7} full kinetic energy and R dependence in the bound-free transition dipole moment $r_{fv^+iv'} = \int dR \chi_v^*(R) r_{fi}(k;R) \chi_{v'}(R)$. Here $r_{fi}(k;R)$ is the transition moment calculated at fixed internuclear distance R and electron momentum k , for a bound (Rydberg) initial state $|i\rangle$ and continuum (photoelectron + ionic core) final states $|f\rangle$. For the $C^3\Pi_g$ initial state we used a Hartree-Fock SCF wave function,^{8,9} and for the final state we used continuum Hartree-Fock orbitals for the dipole-allowed $^3\Pi_u$, $^3\Delta_u$, $^3\Sigma_u^+$, and $^3\Sigma_u^-$ channels. The continuum orbitals were obtained using the iterative Schwinger variational tech-

nique.¹⁰ For the $C^3\Pi_g$ state vibrational wave functions we constructed and numerically integrated an RKR potential curve, employing vibrational constants measured by York and Comer¹¹ and the rotational constant measured by Sur *et al.*¹² The vibrational wave functions for the $X^2\Pi_g$ ion were obtained by numerically integrating the RKR potential curve given by Krupenie.¹³ The range of R included in calculating all transition matrix elements $r_{fv^+iv'}$ varied from 1.7 to 3.2 a_0 . Further details of the calculations will be reported in a separate paper.

The calculated photoionization cross sections for the $(1\pi_g 3s\sigma_g^{-1} k\sigma_u)^3\Pi_u$ channel (not shown) predict a σ_u (f -wave) shape resonance, whose position and width are extremely sensitive to changes in the internuclear distance. The R dependence of the transition moment, particularly near the equilibrium bond distance and ~ 0 –2 eV photoelectron kinetic energy, is responsible for the non-Franck-Condon effects in the vibrational distributions. The cross sections for final states associated with $k\pi_u$ ionization channels are relatively small and reveal almost negligible variation with R . The ground state, fixed-nuclei calculations of Gerwer *et al.*¹⁴ for $3\sigma_g$ and $1\pi_g$ photoionization predict this resonance near the ionic thresholds. Theoretical studies¹⁵ which include R dependence in ground state photoionization confirm the presence of the low-energy σ_u resonance, and further predict significant non-Franck-Condon effects.

In Fig. 1 we show our calculated branching ratios for the $v' = 1$ –3 levels of the $C^3\Pi_g$ state, compared with the peak intensities obtained from the measured photoelectron spectra. The calculations predict for all v' levels pronounced non-Franck-Condon distributions: the vibrational wave functions for the $C^3\Pi_g$ and $X^2\Pi_g$ potentials are nearly identical, and the ratios $\Delta v \neq 0$ of Franck-Condon factors are *negligible* when plotted on the scale in Fig. 1. For the $v' = 2$ and 3 levels, the $\Delta v < 0$ ratios are in satisfactory agreement with experiment, while those for $\Delta v > 0$ appear to show systematic deviation. Our results for the $v' = 1$ level account for some of the observed $\Delta v \neq 0$ intensity, although there is substantial disagreement. We mention two mechanisms which could underly these discrepancies. First, several experiments^{9,12,16} have suggested perturbations of the low vibrational levels of the $C^3\Pi_g$ state, particularly involving the $v' = 1$ level. It has been proposed^{9,12} that the perturbations arise from weak configuration interaction with the $(3\sigma_g 1\pi_g^2)^3\Pi_g$ valence state. Inclusion of this configuration in the present theory (as initial-state correlation) would introduce R -dependent expansion coefficients into the dipole amplitude $r_{fi}(R)$. Due to the R dependence induced by the resonance, these coefficients could alter the calculated distributions for the $v' = 1$ transition such that the off-diagonal v^+ components in-

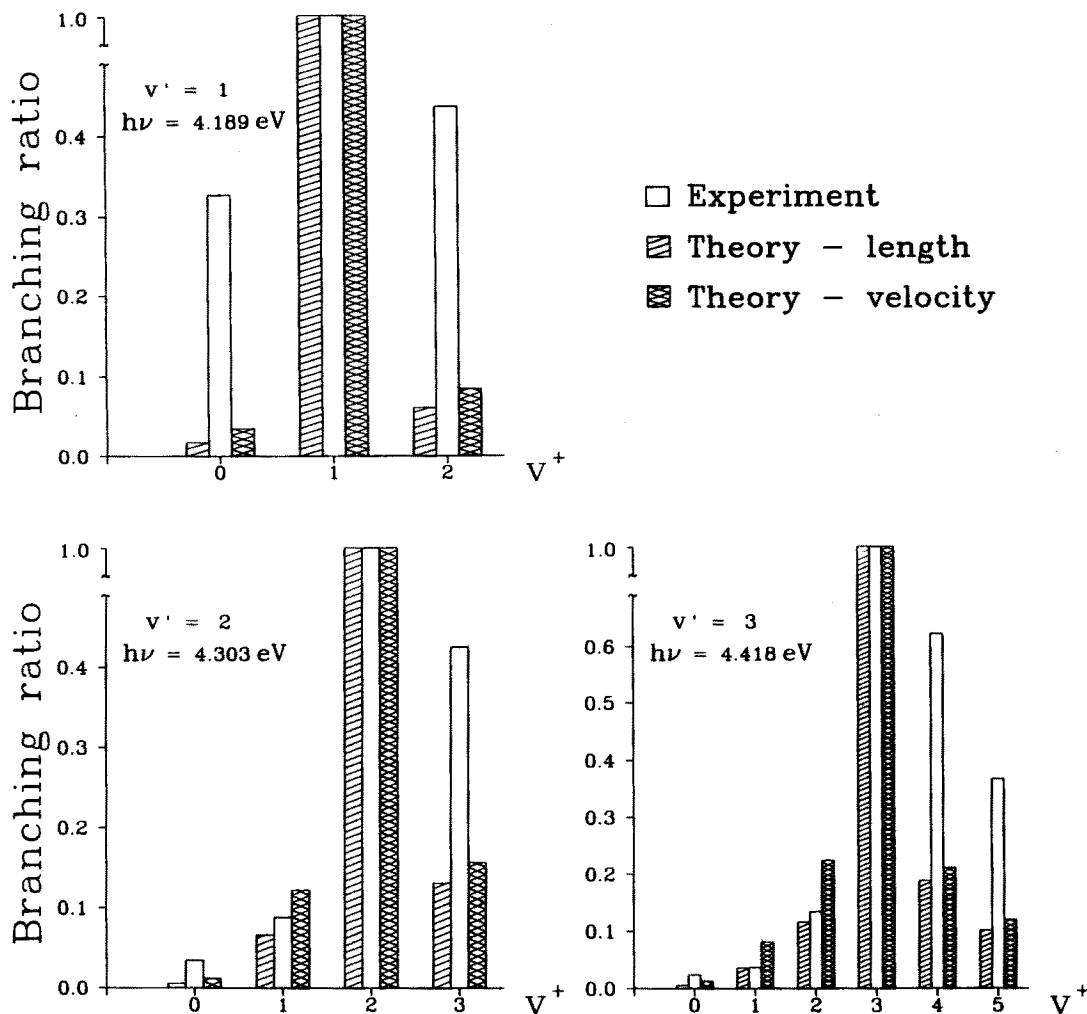


FIG. 1. Calculated vibrational branching ratios for $O_2 C^3\Pi_g$ ($v' = 1-3$) photoionization, compared with the measurements of Miller *et al.* (Ref. 2). The theoretical results were normalized to experiment by dividing by the $\Delta v = 0$ peak.

crease their relative magnitudes. Second, the deviations observed in the $\Delta v > 0$ components of the $v' = 2, 3$ levels could arise from electronic autoionization of $^3\Pi_u$, $^3\Delta_u$, $^3\Sigma_u^+$, and $^3\Sigma_u^-$ bound states into the four continuum final states of identical symmetry. Accurate bound-state calculations^{17,18} predict $^3\Delta_u$ and $^3\Sigma_u^+$ dissociative states arising from terms of the $1\pi_u^3 1\pi_g^3$ electronic configuration, which intersect the inner region of the ion curve near the $v^+ = 3-5$ levels. Autoionization of the $B^3\Sigma_u^-$ state could perturb the vibrational intensity for the $v^+ = 1$ level as well. These valence-shell excitations are not dipole accessible from the $C^3\Pi_g$ state, however, residual Coulomb interactions exist between continuum and bound configurations which differ by two molecular orbitals. The energy and R dependence of the bound-continuum mixing coefficients could substantially modify the present one-electron results for the higher v^+ levels.

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Quantum oscillations in rotationally inelastic molecule-surface scattering: Energy dependence of transition probabilities

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Scattering of H₂, HD, and D₂ from surfaces shows strong quantum effects which are intuitively expected because of the light masses of these molecules.¹⁻⁵ For instance, experiments on rotationally mediated selective adsorption resonances in these systems can only be interpreted in a quantum mechanical framework. For heavier molecules, a much more classical behavior is expected to prevail. Indeed, many of the treatments of the scattering of molecules such as NO or N₂ by surfaces have utilized classical trajectories (CT) and the authors generally find that they are able to quantitatively account for the experimental findings.⁶⁻⁹ In particular, Tully *et al.*⁶ found that they could account for the detailed rotational distribution in the scattering of NO by Ag(111).

It is, therefore, of considerable interest to ask whether significant, qualitative quantum effects exist in rotationally inelastic scattering from surfaces of molecules much heavier than H₂. The purpose of this communication is to predict the occurrence of a new quantum effect in the rotationally inelastic scattering of molecules such as N₂ (and probably heavier) from surfaces manifested as oscillations in the energy dependence of individual rotational transition probabilities. The basis of this prediction is a numerically exact quantum wave packet calculation.¹⁰⁻¹³ These calculations¹⁰ are herein compared against detailed CT results. Finally, a qualitative interpretation of the oscillations is provided on the basis of the sudden approximation.¹⁴ Figure 1 shows the results of the quantum mechanical and the classical calculations for the particular transition $j = m_j = 0$, $m = 0$, $n = 0 \rightarrow j = 2$, $m_j = 0$, $m = 1$, $n = 0$ where m, n label the diffraction state; i.e., the figure pertains to a diffracted direction. The results are for a model system representing the scattering of N₂ from a corrugated surface having a rectangular lattice. The interaction potential employed and other parameters are given in Ref. 10. The quantum results show a pronounced oscillation of the transition probability as function energy while the CT behavior is essentially smooth. While not given here, the same effect of quantum oscillations vs smooth classical behavior was found in the calculations

for many of the transitions of the type $j = 0$, $m_j = 0$, $m = n = 0 \rightarrow j$, $m_j = 0, m, n$. The same effect was also found when the calculations were carried out for flat target surface. To interpret the result, we consider the sudden approximation for the scattering amplitude¹⁴

$$S_{j m_j \rightarrow j m_j} = \int_0^{2\pi} d\psi \int_0^\pi \sin \theta d\theta Y_{j m_j}^*(\theta, \psi) \times \exp[2i\eta(\theta, \psi)] Y_{j m_j}(\theta, \psi) \quad (1)$$

which for simplicity we have restricted to the flat surface framework. In this case, $\Delta m_j = 0$, and nonzero diffraction transition cannot occur so one is dealing only with Δj transitions (it is important to note that the m_j -quantization axis is normal to the surface for all calculations discussed here). We take a pairwise additive (dumbbell) model potential,¹⁴ which when expressed in terms of the diatom center of mass and orientation angles of the diatom axis, results in a potential $V(x, y, z, \theta, \psi)$. To simplify the calculation of the phase shift $\eta(\theta, \psi)$ appearing in Eq. (1), we then assume that for total energy E , the turning point for a given orientation of the rotor defines an equivalent hard wall interaction. Thus, the turning point of the molecular center of mass, z_t , is a function of the molecular orientation at impact and a function of energy. In this case, the phase shift for an impulsive collision at fixed θ is $-k_z z_t(\theta)$, where k_z is the wave vector for the normal incidence considered here. In the semiclassical sudden limit, and assuming initial $j = 0$, one has¹⁴

$$S_{0 \rightarrow j} \propto \int \exp[2i\eta(\theta)] P_j(\cos \theta) d(\cos \theta) \quad (2)$$

$$\cong \frac{1}{i\sqrt{2\pi j}} \int_0^\pi d\theta \sin^{1/2} \theta \left\{ \exp i \left[\left(j + \frac{1}{2} \right) \theta - 2k_z z_t(\theta) + \frac{\pi}{4} \right] - \exp - i \left[\left(j + \frac{1}{2} \right) \theta + 2k_z z_t(\theta) + \frac{\pi}{4} \right] \right\}. \quad (3)$$