Missing Bands in the Multiphoton Excitation of Coupled Molecular States

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Measurements are reported of (3 + 1) resonance-enhanced multiphoton ionization of O_2 via the $F\,^3\Pi_u$ state which show near-vanishing intensity for F-$X(1,0)$, the strongest band in one-photon spectra. Using a coupled-channel treatment of the $^3\Pi_u$ Rydberg-valence interactions, this dramatic result is attributed to destructive interference between the amplitudes for transitions into the Rydberg and valence components of the heavily mixed F state, indicating a significant dependence of the relative transition amplitudes on the mode of excitation. Thus, "missing bands" in the multiphoton spectra of coupled states provide important information on relative multiphoton transition probabilities. [S0031-9007(99)09195-4]

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Intensity anomalies in diatomic molecular excitation arise from interference effects occurring when there are nonzero probabilities for transitions into interacting electronic states. Such anomalies have been well documented [1], but there are few examples [1–3] involving the near-disappearance of a complete vibrational band. This dramatic phenomenon is most likely to occur in the excitation of strongly interacting Rydberg and valence states of the same symmetry [2,3], the configurations of which differ by one ("Rydbergization") or two orbitals [1]. Since one- and n-photon Rydberg:valence transition-moment ratios may well differ significantly, multiphoton excitation has the potential to produce specific missing bands which do not occur in one-photon spectra. However, the range of variation from the one-photon ratio would be expected to be smaller in the case of multiphoton excitation of a Rydbergized state, where there is a one-to-one correspondence between intermediate transition pathways to the final Rydberg and valence components. In this Letter, we report the first example of a missing band in multiphoton molecular excitation, a band which occurs strongly in one-photon spectra. This effect is observed in transitions to a Rydbergized state.

Strong Rydberg-valence (RV) interactions occurring in the $^3\Sigma_u^-$ and $^3\Pi_u$ states of O_2 [4] are responsible for a number of irregularities and unusual features [5–7] observed in one-photon-allowed transitions from the ground state $X\,^3\Sigma_g^-$. Although these transitions are also three-photon allowed, only the $E\,^3\Sigma_u^-(v = 0)$ state has been studied previously in three-photon experiments [8]. Below, we describe measurements of the (3 + 1) resonance-enhanced multiphoton-ionization (REMPI) spectrum of O_2, via the RV-mixed $F\,^3\Pi_u$ state, which contain a particularly dramatic example of a missing band. The three-photon and corresponding one-photon spectra are compared, and each is explained using a coupled-channel Schrödinger-equations (CSE) theoretical model of the $^3\Pi_u$ RV interactions.

The experimental apparatus was similar to that used in two-color pump-probe studies of collisional processes involving O_2 in the Herzberg states [9–11] and described in detail elsewhere [10], but only a single laser was employed for this work. Briefly, frequency-doubled, Nd:YAG-pumped dye-laser radiation [peak pulse energy ~5 mJ, bandwidth ~0.3 cm^{-1} full-width at half-maximum (FWHM)] was focused (lens focal length 20 cm) into a continuous-flow gas cell containing ~1 Torr of O_2 and the total positive-ion yield was recorded as a function of fundamental wavelength in the range 670–702 nm. An experimental room-temperature (3 + 1)-REMPI spectrum of O_2 in the region of the $F\,^3\Pi_u \longleftarrow\!\longleftarrow\!\longleftarrow X\,^3\Sigma_g^-(0,0)$–$(3,0)$ bands, corrected for variations in laser intensity and plotted as a function of the vacuum three-photon wavelength, is shown in Fig. 1(a). A corresponding one-photon spectrum, compiled from the laser-based absolute photoabsorption cross sections of Ref. [7] (resolution ~0.5 cm^{-1} FWHM), is shown in Fig. 1(b). The triplet structure of the F state is evident in both spectra [12], but there are vast differences in the relative intensities of the vibrational bands. In particular, while the (1, 0) band is the strongest in the one-photon spectrum, it almost disappears from the three-photon spectrum which is dominated by the (0, 0) band.

The F state of O_2 is a mixed state involving the bound $\ldots(3\sigma_g)^2(1\pi_u)^4(1\pi_g)\,np\sigma_u\,^3\Pi_u$ Rydberg states with $n = 3$ and 4, and the $\ldots(3\sigma_g)^2(1\pi_u)^4(1\pi_g)\,(3\sigma_u)1\,^3\Pi_u$ repulsive valence state [7]. Diabatic potential-energy curves for these interacting states are shown in Fig. 2 (dashed lines). Since the configurations of the Rydberg and valence states differ by a single orbital, in the diabatic basis there is a strong electrostatic RV interaction leading to adiabatic potential-energy curves (Fig. 2, solid

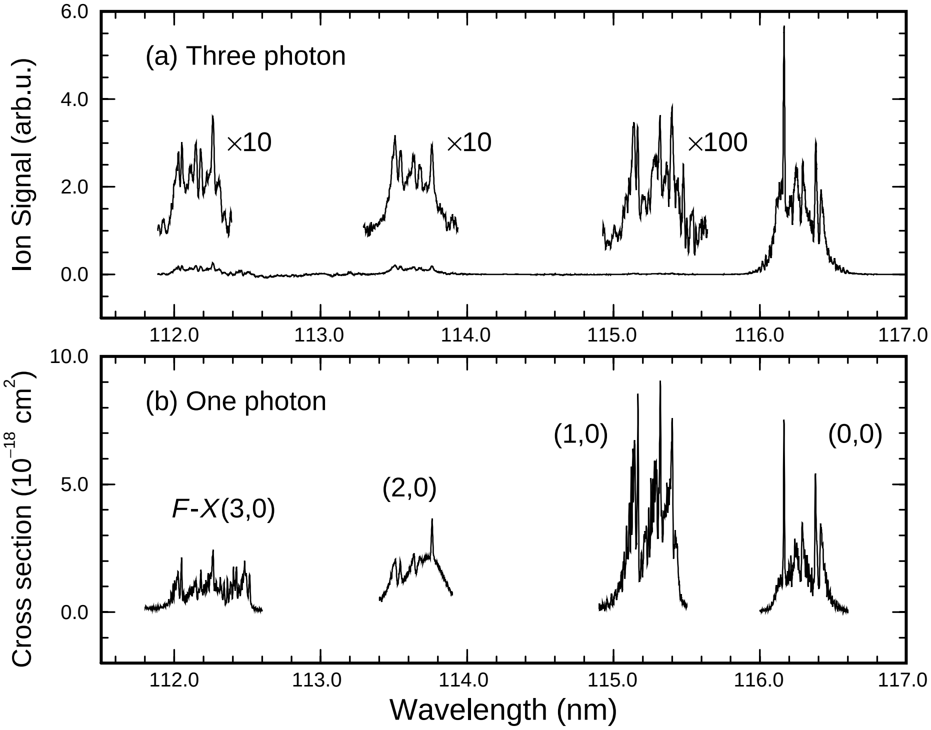

FIG. 1. Comparison of experimental spectra for one- and three-photon excitation of the $F\,^3\Pi_u$ state of O_2 at room temperature, plotted as a function of the vacuum transition wavelength. (a) (3 + 1)-REMPI spectrum for the $F \leftarrow\leftarrow\leftarrow X(0,0){-}(3,0)$ bands, corrected for variations in laser intensity. (b) Absolute one-photon absorption cross sections for the same bands, from Ref. [7]. Relative vibrational intensities vary markedly with the mode of excitation, the (1, 0) band almost disappearing in the three-photon case.

lines) which exhibit strongly avoided crossings. In the adiabatic picture, the lowest RV interaction is an example of Rydbergization, with the $3\sigma_u$ valence orbital becoming the $3p\sigma_u$ Rydberg orbital as the internuclear separation R decreases [1]. The double-minimum adiabatic potential in Fig. 2 may be associated with the F state. The adiabaticity parameter [13] for the $n = 3$ RV crossing, $\zeta = 2.9$ [7], is significantly greater than unity, suggesting near-adiabatic behavior for the F state. However, residual nonadiabatic coupling between the adiabatic states affects the F-state energy-level pattern and causes significant predissociation. Therefore, proper treatment of the $^3\Pi_u$ RV interaction requires coupled-state calculations in which the techniques of scattering theory [14] are applied to the calculation of molecular photodissociation cross sections [15], allowing the determination of vibrational intensities.

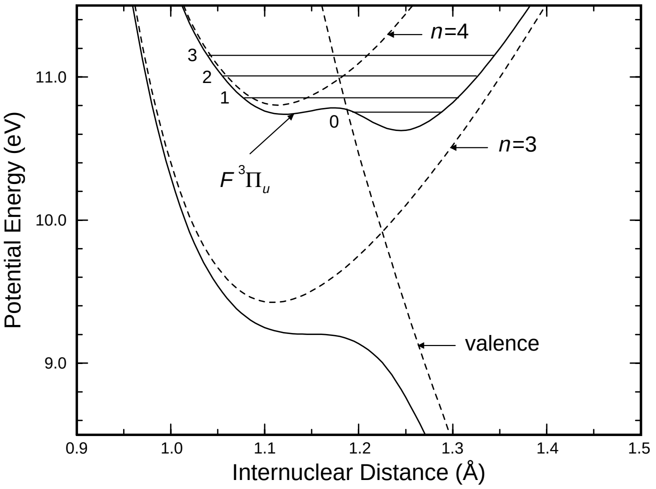

FIG. 2. Potential-energy curves for the $^3\Pi_u$ states of O_2, with energies referred to the minimum in the $X\,^3\Sigma_g^-$ potential. Diabatic curves (dashed lines) are shown for the repulsive valence state and the bound $np\sigma_u$ Rydberg states with $n = 3$ and 4, together with corresponding adiabatic curves (solid lines). Observed vibrational levels of $^{16}O_2$ are also indicated, associated with the second adiabatic potential $F\,^3\Pi_u$.

Here, we employ a simplified three-state diabatic CSE model, including the open valence channel and the closed $n = 3$ and $n = 4$ Rydberg channels, which is adapted from the six-state model of England *et al.* [7]. Briefly, ignoring rotation and the triplet structure of the $^3\Pi_u$ states, the cross section for photoabsorption from the $v'' = 0$ level of the ground state into the RV-coupled upper states at an energy E is given by

$$\begin{aligned}\sigma_{\mathrm{abs}}(\nu) \propto \nu |M^e_{\mathrm{val}} \langle \chi^E_{\mathrm{val}}(R) \mid \chi^0_X(R)\rangle \\ + M^e_{n=3}\langle \chi^E_{n=3}(R) \mid \chi^0_X(R)\rangle \\ + M^e_{n=4}\langle \chi^E_{n=4}(R) \mid \chi^0_X(R)\rangle|^2, \qquad (1)\end{aligned}$$

where ν is the transition energy, $\chi^0_X(R)$ is the ground-state vibrational wave function, the M^e are diabatic electronic transition moments, assumed to be independent of R, and the $\chi^E(R)$ are energy-normalized diabatic coupled-channel wave functions. These wave functions are elements of the vector $\boldsymbol{\chi}^E(R)$ which is the solution of the diabatic-basis coupled-channel Schrödinger equations, expressed in matrix form,

$$\left\{\mathbf{I}\,\frac{d^2}{dR^2} + \frac{2\mu}{\hbar^2}[E\mathbf{I} - \mathbf{V}(R)]\right\}\boldsymbol{\chi}^E(R) = 0\,, \qquad (2)$$

where μ is the molecular reduced mass, $\mathbf{I}$ is the identity matrix, and the potential matrix

$$\mathbf{V}(R) = \begin{pmatrix} V_{\mathrm{val}}(R) & 0.872 & 0.422 \\ 0.872 & V_{n=3}(R) & 0 \\ 0.422 & 0 & V_{n=4}(R) \end{pmatrix}. \tag{3}$$

The diagonal elements of $\mathbf{V}(R)$ are the diabatic potential-energy curves shown in Fig. 2, and the nonzero off-diagonal elements, in eV, are the $n = 3$ and $n = 4$ RV couplings, assumed to be R independent, and scaling approximately with $(n^*)^{-3/2}$, where $n^* = n - a$ and a is the quantum defect [1]. The elements of $\mathbf{V}(R)$ differ slightly from those of Ref. [7] because of reoptimization for the three-state model.

In Eq. (1), there is the possibility of interference between the amplitudes for transitions into the coupled states. Elements of $\boldsymbol{\chi}^E(R)$, calculated for energies near the $F(v = 0)$–$F(v = 3)$ levels by solving Eq. (2) using the renormalized Numerov method [16], are shown in Fig. 3, together with numbers proportional to the corresponding overlap factors with the ground-state wave function $\chi_X^0(R)$ [17], i.e., the constituent radial matrix elements of Eq. (1). To simplify the discussion, we assume that the Rydberg transition moments obey the $(n^*)^{-3/2}$ scaling rule [1] and take $M^e_{n=4}/M^e_{n=3} = 0.5$ [18]. Thus, the character of the interference effects is determined essentially by the ratio of the valence and Rydberg transition moments, $\mathcal{R} = M^e_{\mathrm{val}}/M^e_{n=3}$. Under certain conditions, the cross section defined by Eq. (1) vanishes. For example, the F-$X(0,0)$ band vanishes for $\mathcal{R} = -0.73$, while the $(1,0)$ band vanishes for $\mathcal{R} = -4.7$. Whether these conditions are achievable experimentally depends on the details of the excitation process.

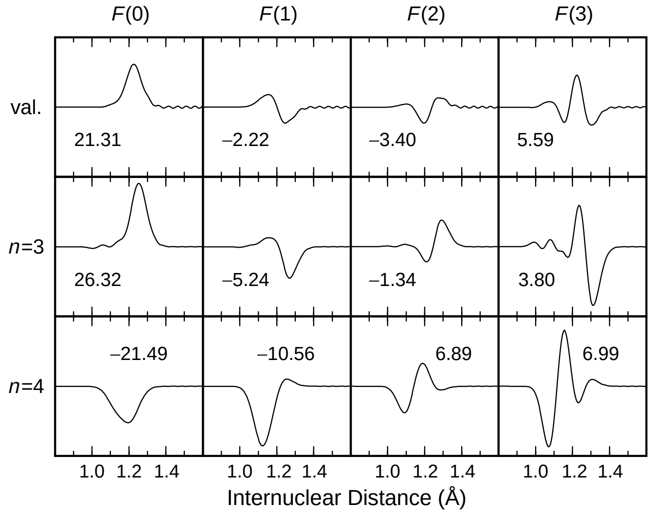

FIG. 3. Coupled-channel radial wave-function vectors $\boldsymbol{\chi}^E(R)$ (columns) calculated at energies E corresponding to the $F(v = 0)$–$F(v = 3)$ levels. The wave functions (lines) are labeled according to the character of the corresponding diabatic state, i.e., valence, $n = 3$ Ry, and $n = 4$ Ry, respectively. Also shown are numbers proportional to the corresponding overlap factors between these wave functions and the ground-state $v'' = 0$ vibrational wave function, i.e., the constituent radial matrix elements of Eq. (1).

Vibrational band intensities may be obtained by integrating Eq. (1):

$$I^{v'0}_{\mathrm{abs}} \propto \int_{\mathrm{line}} \sigma_{\mathrm{abs}}(\nu)\, d\nu\,. \tag{4}$$

In the case of one-photon absorption, England *et al.* [7] found that a value of $\mathcal{R} \approx -0.3$ was necessary to explain the observed intensities [19]. Relative experimental intensities for the $F \leftarrow X(0,0)$–$(3,0)$ bands, obtained from the absorption oscillator strengths of Ref. [7], are shown in Table I compared with values calculated using Eqs. (1)–(4) with $\mathcal{R} = -0.35$. Good agreement is found between the experimental intensities and those calculated using our CSE model. The unusually small value of the diabatic valence transition moment necessary for this agreement is supported by *ab initio* calculations [20].

(3 + 1) REMPI may be regarded as a two-step process involving three-photon absorption to the resonant intermediate state, followed by one-photon ionization out of it [21]. When the resonant intermediate state is of mixed character, the vibrational REMPI intensities may be subject to interference effects in both the absorption and ionization steps [22]. However, it is impossible for a missing band to originate from interference in the ionization step when the *total* ionization signal, i.e., the sum over all vibrational levels of the ion, is recorded. Further, under normally applicable experimental conditions of weak excitation and saturated ionization, it is expected that observed REMPI intensities will reflect those in the three-photon absorption process [22]. However, in our case it is also necessary to allow for competition between predissociation and ionization, the alternative mechanisms leading to depopulation of the resonant intermediate state. Assuming that predissociation dominates ionization, relative three-photon absorption intensities may be deduced from the observed REMPI intensities using the relation

$$I^{v'0}_{\mathrm{abs}} \propto I^{v'0}_{\mathrm{REMPI}} \Gamma^{v'}_{\mathrm{pred}}\,, \tag{5}$$

where $\Gamma^{v'}_{\mathrm{pred}}$ is the predissociation linewidth [7].

TABLE I. Comparison of experimental and calculated $(v',0)$ intensities for one- and three-photon excitation of the $F\,^3\Pi_u$ state of O_2, normalized to unity for $v' = 0$.

	One-photon		Three-photon		
v'	Expt.[a]	Calc.[b]	REMPI[c]	Abs.[d]	Calc.[e]
0	1.0	1.0	1.0	1.0	1.0
1	2.4	2.4	0.007	0.005	0.004
2	0.50	0.69	0.075	0.22	0.24
3	0.45	0.39	0.067	0.070	0.040

[a] From experimental absorption oscillator strengths of Ref. [7].

[b] From CSE calculations with $\mathcal{R} = -0.35$.

[c] From experimental (3 + 1)-REMPI spectrum of Fig. 1(a).

[d] Relative three-photon absorption intensities obtained by correcting the REMPI intensities for competition between predissociation and ionization using the experimental predissociation linewidths of Ref. [7] in Eq. (5).

[e] From CSE calculations with $\mathcal{R} = -3.5$.

Relative (3 + 1)-REMPI vibrational intensities obtained by integrating the spectrum of Fig. 1(a) are shown in Table I, together with corresponding absorption intensities for the $F \leftarrow\leftarrow\leftarrow X(0,0)-(3,0)$ bands estimated using Eq. (5) with the known predissociation linewidths [7]. These experimental intensities have uncertainties of $\sim$50%. Relative intensities calculated with $\mathcal{R} = -3.5$ and shown in Table I are in fairly good agreement with the experimental three-photon intensities.

These indicative calculations show that a CSE model of the ${}^3\Pi_u$ RV interaction in which only the single parameter $\mathcal{R}$ is varied is capable of explaining both the one- and three-photon relative intensities for four vibrational bands, including the near disappearance of the $(1,0)$ band in the three-photon spectrum. The dramatic behavior of the $(0,0)$ and $(1,0)$ intensities can be understood by substituting the radial matrix elements of Fig. 3 and the model transition moments into Eq. (1). In the one-photon case, there is partial destructive interference between the Rydberg and valence transition amplitudes for the $(0,0)$ band, while the $(1,0)$ intensity is dominated by a strong Rydberg contribution; in the three-photon case, the $(0,0)$ intensity is dominated by a stronger valence contribution, while there is near-complete destructive quantum interference between the valence and Rydberg amplitudes for the $(1,0)$ band.

Our principal conclusion is that the constituent Rydberg and valence transition amplitudes in Eq. (1) interfere in significantly different ways in one- and three-photon excitation. However, the explanation for the apparently increased importance of the valence transition moment in three-photon excitation is not clear. A near-resonance at the two-photon level with the lowest ${}^3\Pi_g$ valence state may lead to significant energy dependence of the transition moments. Interactions between the virtual intermediate states contributing to the three-photon transition moments [23] are likely to result in additional complexities. For example, strong RV interactions in the virtual intermediate states, e.g., the $E\,{}^3\Sigma_u^-$ state at the one-photon level, may play a significant role. We are unaware of any theoretical treatments of RV interactions in the virtual intermediate states of multiphoton transitions, but it is possible that such interactions in O_2 will lead to marked R dependence of the three-photon moments. Therefore, the empirical R-independent relative three-photon electronic transition moments described in this Letter should be regarded only as *effective* moments which implicitly include unmodeled effects such as residual energy dependence in the ionization step and the R and energy dependence of the actual three-photon transition moments. In addition, the role of autoionization requires clarification.

Nevertheless, observations that bands are missing in the multiphoton excitation of coupled states clearly have the potential to provide significant information on the relative multiphoton transition probabilities. In addition, the present study suggests that excitation processes in which the effective relative transition moments can be varied *continuously*, e.g., electron-impact excitation [24], would be of particular interest in tracing the development of missing bands in the excitation of coupled states.

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[19] Signs of individual matrix elements have no meaning, but the observed intensities imply that $M_{\mathrm{val}}^e H_{n=3}^e M_{n=3}^e < 0$, where $H_{n=3}^e$ is the $n = 3$ RV coupling.

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