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Non-Lorentzian line shapes for interfering rotational resonances in the predissociation of O$_2$

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Rotationally resolved measurements are presented of interacting predissociating resonances in the Schumann-Runge bands of O$_2$ that exhibit destructive quantum interference for energies between the line centers. The interacting resonances are described using a coupled line shape derived by treating simultaneously the perturbation and predissociation processes using the method of Fano [Phys. Rev. **124**, 1866 (1961)]. [S1050-2947(97)02206-3]

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The concept of resonance is ubiquitous in physics. In particular, reactions involving particles with internal structure may lead to the formation of short-lived intermediate states (resonances) that profoundly affect the energy dependence of the reaction cross section. Resonant effects occur in nuclear reactions, electron scattering from atoms and molecules (negative-ion resonances) [1], atomic and molecular photo-ionization, and molecular photodissociation. When the widths of resonances are comparable with the spacing between resonances, interference effects may occur. Interacting resonances have received particular attention in the fields of nuclear reactions [2,3] and atomic and molecular autoionization [4,5], but there have been only two observations reported for molecular predissociation below the first ionization limit, using photoemission [6] and photofragmentation [7] spectroscopies.

In this work we present high-resolution photoabsorption measurements that show a particularly instructive example of closely interacting resonances in molecular predissociation. In the language of spectroscopy, a rotational level of a state that is predissociated is perturbed by a nearby rotational level of a different electronic state. This situation, apart from the narrow width of the perturber, is somewhat analogous to the ''complex resonance'' [8] of atomic and molecular autoionization, with the perturbing level playing the role of the ''interloper'' [8], and is amenable to theoretical treatment using either the configuration-interaction method of Fano [9] or the multichannel quantum-defect analysis (MCQDA) of Mies [10]. For the example reported here, the line-shape formula for the interacting resonances is particularly simple, containing only five adjustable parameters: the energies and widths of each resonance and an overall intensity factor.

The Schumann-Runge (SR) band system of O$_2$, $B\,^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ (1750–2050 Å), plays an important role in the photochemistry of the terrestrial atmosphere by controlling the depth of penetration of the solar vacuum ultraviolet (vuv) radiation necessary for the dissociation of many atmospheric species. The normal line-by-line techniques used by atmospheric modellers to describe SR band absorption assume that the predissociation component of the line shape is Lorentzian and that the actual line shape may be represented by a Voigt profile (the convolution of the predissociation and Doppler line shapes). These techniques have proven successful in reproducing the observed line shapes for energies not too far from the line centers. Here we show that, under certain conditions, interferences result in departures from the Lorentzian (Voigt) profile.

The mechanisms for the predissociation of O$_2(B\,^3\Sigma_u^-)$ were described fully by Julienne and Krauss [11] and Julienne [12]. They showed that a consideration of the coupling between the bound B state and four repulsive states whose potential-energy curves crossed the B-state potential allowed the experimental predissociation linewidths to be explained. The relevant potential-energy curves are shown in Fig. 1. The principal predissociative mechanism is spin-orbit coupling with the $1\,^5\Pi_u$ state, but spin-orbit coupling with the $1\,^1\Pi_u$ and $2\,^3\Sigma_u^+$ states and spin-orbit and orbit-rotation coupling with the $1\,^3\Pi_u$ state play significant roles. All vibrational levels of the B state are subject to predissociation, with
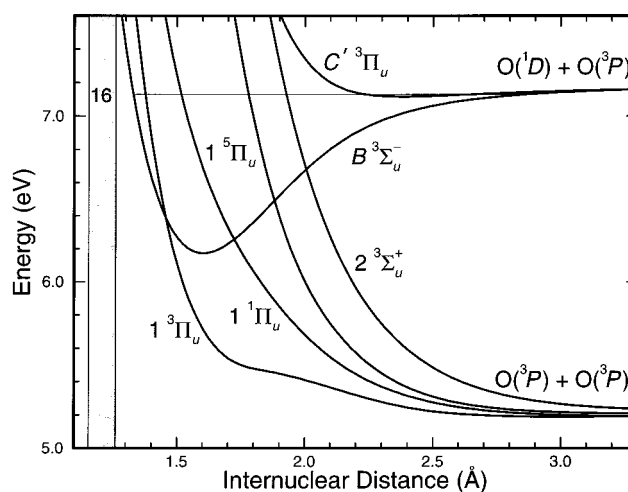

FIG. 1. Potential-energy curves for electronic states of O$_2$ relevant to the predissociation and perturbation of the $B\,^3\Sigma_u^-$ state. The Franck-Condon region for absorption from $X\,^3\Sigma_g^-(v=0)$ is shown shaded. Energies are given relative to the minimum of the X-state potential-energy curve.
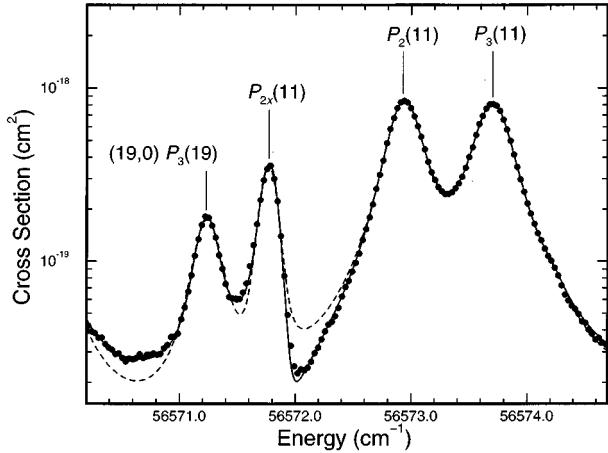
FIG. 2. Photoabsorption cross section for $^{16}O_2$ in the region of the $P_2(11)$ line from the (16,0) band of the $B\ ^3\Sigma_u^- \leftarrow X\ ^3\Sigma_g^-$ system, measured at $T = 293$ K with an instrumental resolution of ~ 0.06 cm^{-1} FWHM (points). Also shown are fitted cross sections based on the Voigt line shape (dashed line) and the coupled line shape Eq. (20) for the interacting resonances $P_2(11)$ and $P_{2x}(11)$ (solid line).

FIG. 3. Schematic diabatic picture of the transitions and interactions involving the $B\ ^3\Sigma_u^-$ state of O_2.

linewidths in the range 0.03–4 cm^{-1} full width at half maximum (FWHM) [13].

Bound-bound perturbations occur for B-state levels with $v \geq 16$. In an associated work [14], we show that the perturber is the second valence state of $^3\Pi_u$ symmetry, $C'\ ^3\Pi_u$. An *ab initio* potential-energy curve for the C' state [14] is shown in Fig. 1. In Fig. 2 we present a high-resolution measurement of the room-temperature photoabsorption cross section for $^{16}O_2$ in the region of the perturbed rotational line $P_2(11)$ from the (16,0) SR band. The measurements were taken using tunable, narrow-bandwidth vuv radiation generated by the two-photon-resonant difference-frequency four-wave mixing of excimer-pumped dye-laser radiation in Xe [15,16]. A full description of the experimental apparatus is given elsewhere [14]. The resolution achieved (~ 0.06 cm^{-1} FWHM) is the highest reported in this spectral region. The perturbed extra line $P_{2x}(11)$, shown in Fig. 2, can be assigned on the basis of observed perturbations in the rotational term values of $B(v = 16, F_2)$ and known combination differences. The measured cross section in Fig. 2 is notable for the unusually deep minimum between the main and extra lines $P_2(11)$ and $P_{2x}(11)$. An attempt to reproduce the measured cross section using a model in which each rotational line was described by a Voigt profile (Fig. 2, dashed line) failed completely for the minimum near 56 572 cm^{-1}. Apparently, destructive interference is occurring for energies between the centers of the main and extra lines that have interacting upper states sharing the common rotation $J' = 10$. Since the symmetric Lorentzian predissociation line shape is unable to describe the measured cross section, we must develop a more appropriate theoretical treatment of the interacting predissociating resonances shown in Fig. 2.

To obtain an expression for the energy dependence of the cross section for photoabsorption into these coupled states, we employ the method of Fano [9] for treatment of the decay of bound states to continua, as formulated and extended by Mies [17]. It is convenient to start with a diabatic picture of
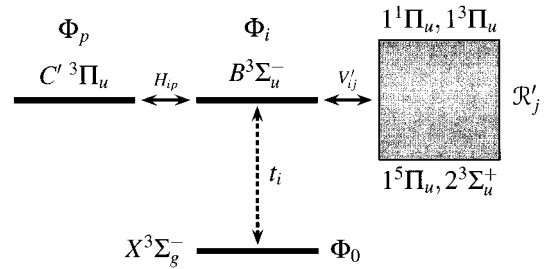
the relevant electronic states and interactions, summarized schematically in Fig. 3. In this picture, there is an electric-dipole-allowed transition between the $X\ ^3\Sigma_g^-$ ground state (Φ_0) and the B state (Φ_i), which is both perturbed by the C' state (Φ_p) and predissociated by four noninteracting dissociative continuum states ($\mathcal{R}_j$). In principle, transitions from the X state into the states of $^3\Pi_u$ symmetry are electric-dipole allowed. However, due to the location of the bound part of the $C'\ ^3\Pi_u$ potential at large internuclear distances R (Fig. 1), the corresponding Franck-Condon overlap with the X state is negligible. In addition, there are no repulsive states correlating with the lowest dissociation limit of O_2 that cross the C' potential. This allows two simplifying assumptions: there are no direct transitions into the C' state and there is no direct predissociation of the C' state. These assumptions have been verified experimentally [14]. Transitions from the X state into the predissociating continua are electric-dipole forbidden, except for those into the $1\ ^3\Pi_u$ state. However, the small Franck-Condon factors for the $1\ ^3\Pi_u \leftarrow X\ ^3\Sigma_g^-$ transition result in a negligible transition probability for energies in the region of the SR bands [18]. Thus it may be assumed that there are no transitions from the X state into the predissociating continua. This assumption leads to the conclusion that *unperturbed* lines of the SR system may be described accurately by Lorentzian predissociation line shapes [13]. Finally, the repulsive states that predissociate the B state are well separated in R and have only weak electronic interactions. Thus it may be assumed that the predissociating continua are noninteracting [19].

In the diabatic basis, the bound-state energies are

$$E_n = H_{nn} = \langle \Phi_n | \mathcal{H} | \Phi_n \rangle, \quad n = i, p, \tag{1}$$

where $\mathcal{H}$ is the total Hamiltonian and the Φ_n are real, normalized wave functions. Since there is a perturbation between the bound states in this basis, the interaction matrix element

$$H_{ip} = \langle \Phi_i | \mathcal{H} | \Phi_p \rangle \neq 0. \tag{2}$$

However, the bound basis states used in the development of the Fano-Mies theory [9,17], which we label 1 and 2, do not interact, i.e., $H_{12} = 0$. Such states may be related to the diabatic states using standard bound-state perturbation formulas [20], which we write in the form

$$\Phi_1 = \Phi_i \cos\alpha + \Phi_p \sin\alpha,$$

$$\Phi_2 = -\Phi_i \sin\alpha + \Phi_p \cos\alpha, \tag{3}$$

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where $\tan 2\alpha = 2H_{ip}/(E_i - E_p)$. The bound-state energies are related by

$$E_1 + E_2 = E_i + E_p \qquad (4)$$

and

$$|E_1 - E_2| = \sqrt{|E_i - E_p|^2 + |2H_{ip}|^2}, \qquad (5)$$

where $E_1 = H_{11}$ and $E_2 = H_{22}$.

The diabatic continua obey the relation

$$\langle \mathcal{R}_k'' | \mathcal{H} | \mathcal{R}_j' \rangle = E' \delta_{kj} \delta(E'' - E'), \qquad (6)$$

where $\mathcal{R}_j'$ represents the real, energy-normalized wave function of energy E' for the continuum j. The amplitude for dissociation of state n to the energy E' continuum j is given by

$$V_{nj}' = \langle \mathcal{R}_j' | \mathcal{H} | \Phi_n \rangle, \quad n = 1,2, \qquad (7)$$

and the total dissociation amplitude V_n' by $(V_n')^2 = \Sigma_j (V_{nj}')^2$. Since the perturber is not predissociated, $V_{pj}' = 0$ and it follows from Eq. (3) that

$$V_{1j}' = V_{ij}' \cos\alpha \quad \text{and} \quad V_{2j}' = -V_{ij}' \sin\alpha. \qquad (8)$$

The V_{nj}' are of the form $V_{nj}' = f_j' V_n'$, where $V_1' = V_i' \cos\alpha$, $V_2' = -V_i' \sin\alpha$, and the branching ratios $f_j' = V_{ij}'/V_i'$, where $\Sigma_j (f_j')^2 = 1$. These expressions emphasize that states 1 and 2 dissociate in the same way. Consequently, each state interacts only with that part of the energy E' continuum having the wave function

$$\mathcal{R}' = \sum_j f_j' \mathcal{R}_j'. \qquad (9)$$

The dissociation amplitude of state n to $\mathcal{R}'$ is the total dissociation amplitude for that state

$$V_n' = \langle \mathcal{R}' | \mathcal{H} | \Phi_n \rangle. \qquad (10)$$

Having found suitable basis states for the application of the Fano-Mies [9,17] theory, we note that there will be an energy E wave function Ψ that is a linear combination of Φ_1, Φ_2 and the $\mathcal{R}'$ of various energies E'. Although there are no direct interactions between basis states 1 and 2, they interact indirectly through $\mathcal{R}'$. Following Fano [9], we treat the predissociation by introducing modified orthonormal bound states $\hat{\Phi}_1$ and $\hat{\Phi}_2$, related to the diabatic and perturbed basis states by

$$\hat{\Phi}_1 = \Phi_1 \cos\beta + \Phi_2 \sin\beta = \Phi_i \cos\gamma + \Phi_p \sin\gamma,$$

$$\hat{\Phi}_2 = -\Phi_1 \sin\beta + \Phi_2 \cos\beta = -\Phi_i \sin\gamma + \Phi_p \cos\gamma, \quad (11)$$

where $\gamma = \alpha + \beta$, $\tan 2\beta = 2F_{12}/(F_{11} - F_{22})$ and

$$F_{nm} = E_n \delta_{nm} + \text{P} \int dE' \frac{1}{E - E'} V_n' V_m', \qquad (12)$$

where P indicates a principal-part integral. The F matrix for the modified bound states is diagonal, i.e.,

$$\hat{F}_{mn} = \langle \hat{\Phi}_m | \mathcal{H} | \hat{\Phi}_n \rangle + \text{P} \int dE' \frac{1}{E - E'} \sum_j \hat{V}_{mj}' \hat{V}_{nj}'$$

$$= \hat{\varepsilon}_n \delta_{mn}, \qquad (13)$$

where $\hat{\varepsilon}_n$ is the resonance energy of state $\hat{\Phi}_n$ and $\hat{V}_{nj}' = \langle \mathcal{R}_j' | \mathcal{H} | \hat{\Phi}_n \rangle$. $\hat{F}_{12}$, the amplitude for direct and indirect interactions between $\hat{\Phi}_1$ and $\hat{\Phi}_2$, is zero. The total dissociation amplitude $\hat{V}_n$ for state $\hat{\Phi}_n$ is given by $\hat{V}_n^2 = \Sigma_j \hat{V}_{nj}^2$.

Applying the method of Fano [9] to the modified orthonormal basis and energy normalizing the large-R form of the continuum wave function according to the usual scattering-theory techniques [2], it can be shown that the energy E wavefunction becomes

$$\Psi = \frac{1}{\sqrt{1 + \left(\sum_n 1/\hat{\epsilon}_n \right)^2}} \left(\sum_n \frac{\hat{Y}_n}{\pi \hat{V}_n \hat{\epsilon}_n} + \mathcal{R} \right), \qquad (14)$$

where $\hat{\epsilon}_n = (E - \hat{\varepsilon}_n)/\pi \hat{V}_n^2$ and

$$\hat{Y}_n = \hat{\Phi}_n + \text{P} \int dE' \frac{1}{E - E'} \hat{V}_n' \mathcal{R}'. \qquad (15)$$

As there is no photoabsorption into the continua, the photoabsorption amplitude from the initial state into the state Ψ may be written

$$t = \langle \Psi | \mathcal{T} | \Phi_0 \rangle = \frac{\sum_n \hat{t}_n /(\pi \hat{V}_n \hat{\epsilon}_n)}{\sqrt{1 + \left(\sum_n 1/\hat{\epsilon}_n \right)^2}}, \qquad (16)$$

where $\hat{t}_n$ is the photoabsorption amplitude to state $\hat{\Phi}_n$ and $\mathcal{T}$ is the transition operator. From Eq. (11), since there is no absorption into the perturbing state p,

$$\hat{t}_1 = t_i \cos\gamma, \quad \hat{t}_2 = -t_i \sin\gamma, \qquad (17)$$

and since state p does not dissociate,

$$\hat{V}_1 = V_i \cos\gamma \quad \text{and} \quad \hat{V}_2 = -V_i \sin\gamma. \qquad (18)$$

It follows from Eqs. (17) and (18) that

$$\hat{t}_1 / \hat{V}_1 = \hat{t}_2 / \hat{V}_2 = t_i / V_i. \qquad (19)$$

The total photoabsorption cross section is the sum of the resonant cross section into Ψ and the nonresonant absorption into that part of the continuum space orthogonal to $\mathcal{R}$. As all photoabsorption into the continuua is negligible, the cross section is given by

$$\sigma(E) \propto \nu t^2 = \nu \left(\frac{t_i^2}{\pi V_i^2} \right) \frac{(1/\hat{\epsilon}_1 + 1/\hat{\epsilon}_2)^2}{1 + (1/\hat{\epsilon}_1 + 1/\hat{\epsilon}_2)^2}, \qquad (20)$$

where ν is the transition energy. The dimensionless energy factors $\hat{\epsilon}_n$ may be expressed as

$$\hat{\epsilon}_n = 2(E - \hat{\varepsilon}_n)/\hat{\Gamma}_n, \qquad (21)$$

where $\hat{\Gamma}_n = 2\pi \hat{V}_n^2$ is the resonance width of state $\hat{\Phi}_n$.

The line shape of Eq. (20) may be regarded as a special case of the two-bound-state, single-continuum expressions given elsewhere [4,9,17] and also follows from MCQDA [10]. Over the small range of energy applicable to the study of interacting predissociating resonances, the energy dependences of ν, t_i, V_i, and $\hat{\Gamma}_n$ can be neglected. In the case of a single bound state, Eq. (20) reduces to a Lorentzian line shape, appropriate for the case of an isolated predissociating resonance where there is no absorption into the continuum. For interacting resonances, we have an ''interfering Lorentzian'' profile. From Eq. (21), for energies between the resonance centers, $1/\hat{\epsilon}_1$ and $1/\hat{\epsilon}_2$ have opposite signs and the numerator of Eq. (20) must reach zero at some energy in this range. This prediction of destructive interference between the resonance centers is in agreement with our observations, but the measured cross section does not reach zero due to instrumental effects and contributions from other line wings. We have fitted the measured cross section of Fig. 2 using the coupled predissociation line shape of Eq. (20) to describe the interacting resonances $P_2(11)$ and $P_{2x}(11)$, allowing for the effects of the Doppler component of the line shape and the instrumental resolution. An excellent fit was obtained (Fig. 2, solid line) with resonance widths $\hat{\Gamma}_1 = 0.266$ cm^{-1} $[P_2(11)]$ and $\hat{\Gamma}_2 = 0.046$ cm^{-1} $[P_{2x}(11)]$ and a resonance separation $\hat{\varepsilon}_1 - \hat{\varepsilon}_2 = 1.155$ cm^{-1}.

Simple relationships between the physical observables associated with the resonances $\hat{\Phi}_n$ and the analogous (unobservable) quantities in the diabatic basis enable Eq. (20) to be used successfully to deperturb predissociated molecular spectra [14]. For example, from Eqs. (17) and (18) it follows that $\hat{\Gamma}_2/\hat{\Gamma}_1 = (\hat{t}_2/\hat{t}_1)^2 = \tan^2\gamma$, $\hat{\Gamma}_1 + \hat{\Gamma}_2 = 2\pi V_i^2 = \Gamma_i$, and $\hat{t}_1^2 + \hat{t}_2^2 = t_i^2$. In other words, the interloper ''borrows'' width and strength from the original predissociating resonance in an identical fashion such that the total width and strength is conserved. In addition, it can be shown that the effects of perturbation and dissociation act separately in a simple way on the resonance energies: the dissociation shifts the dissociating state as if it were isolated and the perturbation acts on the shifted energy as if it were a bound-state energy. This allows standard bound-state perturbation formulas [20] to be used in the deperturbation of rotational series of predissociating resonances and the determination of the interaction matrix elements H_{ip} [14].

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