PHYSICAL REVIEW A VOLUME 12, NUMBER 6 DECEMBER 1975

Interference effects in the excitation of resonances with fine structure—an application to the predissociation in the $B \longrightarrow A$ system of the deutroxyl radical

Cosmo Carlone
Département de Physique, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1 Canada
(Received 12 May 1975)

The predissociation in the $B \longrightarrow A$ system of the deutroxyl radical has been reinvestigated. The experimental line shapes $P17$, $P18$, $R18$, $P20$, and $P21$ of the (0,9) band of the system are analyzed in the framework of the Mahaux-Lejeune theory. The $P18$ and $R18$ transitions contain a Q component. This lends support to existing calculations that a $^4\Pi$ repulsive state is responsible for the predissociation. The transition probability to the continuum is not contant, but varies as the predissociated half-width.

INTRODUCTION

The phenomenon of resonance occurs in practically all branches of physics. The basic model is the driven damped simple harmonic oscillator, which is capable of absorbing a large amount of energy at frequencies close to the "resonant" frequency. The frequency (ω) dependence of the power P absorbed is the well-known function

$$P(\omega)=\frac{1}{1+4(\omega-\omega_0)^2/\Gamma^2}\,, \tag{1}$$

where ω_0 is the resonance frequency and Γ is the full width at half-maximum. Γ is related to the damping of the oscillator.[1]

The concept of resonance is extended to an atomic system which has associated with it "resonance radiation" when the driving force is electromagnetic in nature.[2] The emission of radiation viewed as a resonance process has been described in detail by Shore.[3] Whereas atoms absorb photons with the proper resonance frequency, nuclei absorb neutrons in the vicinity of resonances. This experimental fact led Breit and Wigner[4] to justify Eq. (1) quantum mechanically. Although the language is different—in electrical circuits it is the response of the system or the transfer function, in optical transitions it is the line shape, in nuclear resonances it is the excitation function, and in scattering theory it is the cross section—these processes represent the same physical phenomenon since they are all expressed mathematically by Eq. (1).

When closely spaced resonances are observed, that is, when the difference between the frequencies of two resonances is of the same order of magnitude as the resonance width, interference effects take place which change the basic resonance profile given by Eq. (1). Experimental data from nuclear physics and a theory suitable for their interpretation have been given by Mahaux.[5] The cross section L as a function of the frequency for two closely spaced resonances is

$$L(\omega)=\left|\frac{I_1e^{i\phi_1}}{1+2i(\omega-\omega_1)/\Gamma_1}+\frac{I_2e^{i\phi_2}}{1+2i(\omega-\omega_2)/\Gamma_2}\right|^2\,, \tag{2}$$

where I is the intensity and ϕ is the phase of each resonance. The lengthy quantum-mechanical expressions for these parameters have been given by Mahaux.[5] The cross section thus consists of two Lorentzians centered about ω_1 and ω_2, respectively, plus a cross term which represents an interference term between the two Lorentzians.

The excitation function (2) is quite general and applies even when $\Gamma_2 \gg \Gamma_1$. This case corresponds to excitation of a discrete state and a continuum, and Mahaux[5] shows that Eq. (2) then becomes (we replace the frequency by the energy E)

$$L(E)=\frac{AE^2+BE+C}{1+4(E-E_0)^2/\Gamma^2}\,, \tag{3}$$

where A, B, and C are energy-independent constants. Lejeune[6] has extended the theory of Mahaux[5] to include two discrete states and one continuum. He showed essentially that excitation of the continuum is no different from excitation of a discrete state, except that the half-width of the continuum is much larger, sometimes infinitely large. While the phase of an isolated resonance is not directly observable, the relative phase can be determined, and the data analyzed by Lejeune indicate that this relative phase can assume any value. Similarly, the relative intensity of the resonances does not have to be unity.

Interference effects have also been treated by Blatt and Biedenharn.[7] These authors were primarily interested in deducing the various angular momenta associated with a resonance, and the theory is particularly useful in the analysis of an isolated resonance split by spin interactions. The theory has been applied by Von Brentano *et al.*[8]

The same interference effect has been observed in other branches of physics. The Fano[9] profile

$$F(E)=\frac{[q+2(E-E_0)/\Gamma]^2}{1+4(E-E_0)^2/\Gamma^2} \tag{4}$$

results from an interference between excitation of a discrete state and an autoionizing continuum. Although the Fano effect is usually associated with autoionization, it too has been observed in nuclear physics,[10] where it is understood as an interference between the Breit-Wigner term and the continuum. The Fano effect is the special case of Eqs. (2) for which $\Gamma_2 \gg \Gamma_1$, $I_2=I_1$, and $\phi_2-\phi_1=\pi$. When these conditions are satisfied, the interference is very strong and leads to a very asymmetric profile. The parameter q introduced by Fano determines the asymmetry and has the following physical meaning: It is the ratio of the transition probability amplitude to the final state, which is a linear combination of the discrete state and the continuum state, to the transition probability amplitude to the continuum state. Since q is the ratio of two transition probability amplitudes, it can be real or complex. In autoionization q is always real, whether positive or negative. In the Mahaux theory, it is a complex quantity. When $q\to\infty$, that is, when the continuum is not excited, only one resonance can be observed and Eq. (4) reduces to Eq. (1).

A comprehensive theory of autoionization has been given by Fano,[9] who treated the case of one discrete state perturbed by two continua and also the case of several discrete states perturbed by one continuum. Mies[11] extended the theory to include overlapping resonances. These cases are encountered experimentally in autoionized Rydberg series, for example.[12]

The Fano profile is observed when the resonance is excited not only by photons but also by other particles such as electrons.[13] A review of electron-molecule resonance scattering has been given[14] and progress in this field is continuing.[15-17]

Autodissociation or predissociation is similar to autoionization, and one expects to find interference effects. Herzberg[18] has found asymmetric line shapes in the $D\to X$ and $B''\to X$ systems of H_2, and he has successfully explained the asymmetries by the Fano theory.

The predissociation of the $B\to A$ system of OD has been investigated experimentally and theoretically by Czarny *et al.*[19] The half-widths associated with the diffuse transitions have a peculiar dependence on the electronic, vibrational, and rotational energies. A general treatment of this variation of the half-width has been given.[20] Similar phenomena have been found in O_2.[21] According to Eq. (2), the line shape is characterized also by its phase. Asymmetric line shapes in the $B\to A$ system of OD have been reported,[22] but the Fano theory has not successfully explained these profiles.

We have reexamined and extended the experimental data on the $B\to A$ system of OD in order to reconcile experiment with theory. In those transitions for which the predissociation is strongest, we find a Q component whose intensity depends on the half-width. This supports the calculation of Czarny *et al.*[19] that a $^4\Pi$ repulsive state is responsible for the predissociation. We find that the transition probability to the continuum is not constant and that the Mahaux-Lejeune equations describe the results much more satisfactorily than Fano's equation.

The theory of molecular resonances has been given by Nitzan and Jortner.[23] These authors show that there is an interference effect upon excitation of the discrete state and the continuum no matter which order approximation of the molecular wave functions is the starting point. Although we have used the Mahaux-Lejeune theory in predissociation, the justification of Eq. (2) using molecular physics approximations is as yet nonexistent.

THEORY

Mahaux has derived Eq. (2), which is a very convenient form of the line shape when two resonances are excited.[24] We plot in Fig. 1 this line shape for $\phi_2-\phi_1=0$. This case is known in the literature as the two coherent Breit-Wigner terms.[25] In Fig. 1, the two transitions have equal intensities and equal half-widths. We vary $\omega_2-\omega_1$ in order to study the effect of the interference. Obviously, the effect is biggest when $\omega_2-\omega_1$ is smallest. For two coherent resonances, the interference is destructive between the resonances, but the opposite can happen for incoherent resonances. In Fig. 2 we study the effect of the phase on the line shape and see that the relative intensity depends very much on this phase. The question arises[26]: Can the interference term give rise to a third peak in the line shape? We plot in Fig. 3 a case where a third peak is generated, but we note that it is extremely weak. No such "fictitious" peaks have been observed yet.

The Mahaux function given by Eq. (3) can be derived from Eq. (2) by setting

$$4(E-E_2)^2/\Gamma_2^2=q^2\ ,$$

where q is a constant. This corresponds to one resonance being much larger than the other. If, in addition, $\phi_2-\phi_1=\pi$ and $I_2=I_1$, then Eq. (2) becomes

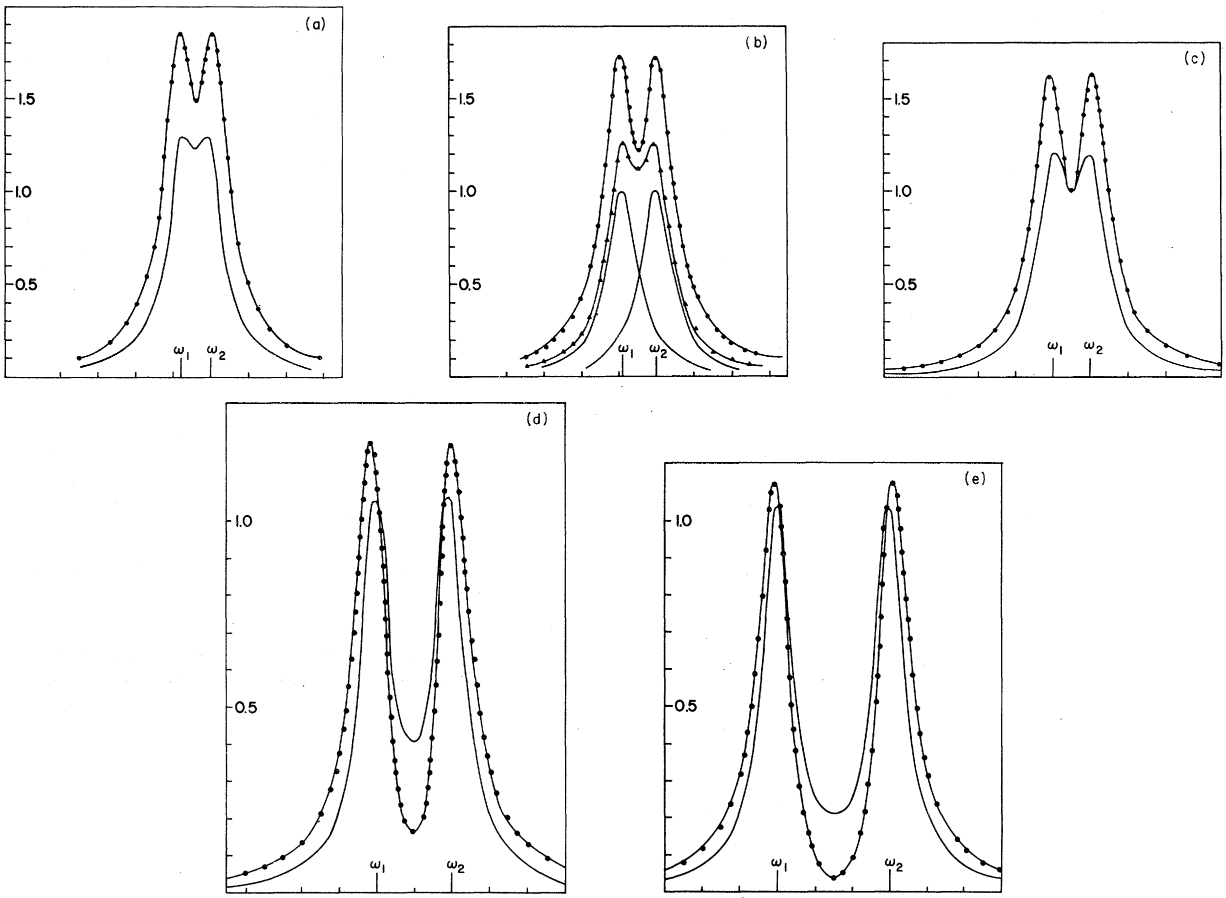

FIG. 1. Interference of two coherent Breit–Wigner terms i.e., $\phi_1 - \phi_2 = 0$. In each case we give the sum of the two Lorentzians (smooth curves) and the total cross section which includes the interference term (dotted curves). Only in part (b) do we plot each isolated resonance. In these figures the two resonances are equally intense, and Γ and $\omega_2 - \omega_1$ have the same arbitrary units. $\Gamma_1 = \Gamma_2 = 0.1$ in all five parts; $\omega_2 - \omega_1 = 0.08$, 0.09, 0.1, 0.2, and 0.3 in parts (a)–(e), respectively.

$$L(E) = \frac{[q - 2(E - E_1)/\Gamma_1]^2}{(1+q^2)[1 + 4(E - E_1)^2/\Gamma_1^2]} ,$$

which is recognized as a Fano function normalized to unity.

When two discrete states are perturbed by a continuum, Lejeune has shown that the line shape is

$$L(E) = \left| \frac{I_1 e^{i\phi_1}}{1 + 2i(E - E_1)/\Gamma_1} + \frac{I_2 e^{i\phi_2}}{1 + 2i(E - E_2)/\Gamma_2} + I_3 e^{i\phi_3} \right|^2 . \qquad (5)$$

It is assumed that $\Gamma_1 \sim \Gamma_2$ and $\Gamma_3 \gg \Gamma_1$. It is evident how one can include a finite continuum or more resonances or both.

EXPERIMENTAL

The experimental conditions used to excite and detect the $B \to A$ system of OD have been given previously.[22] The monochromator used had an instrument profile which was approximately Lorentzian, with its width $\Gamma_I = 0.4$ cm^{-1}. The observed profile is then the convolution of Eq. (2) with a Lorentzian. The explicit expression for the cross term in Eq. (2) is

$$2I_1I_2\left(\frac{[1 + 4(\omega - \omega_1)(\omega - \omega_2)/\Gamma_1\Gamma_2]\cos(\phi_1 - \phi_2)}{[1 + 4(\omega - \omega_1)^2/\Gamma_1][1 + 4(\omega - \omega_2)^2/\Gamma_2^2]} + \frac{[2(\omega - \omega_1)/\Gamma_1 - 2(\omega - \omega_2)/\Gamma_2]\sin(\phi_2 - \phi_1)}{[1 + 4(\omega - \omega_1)^2/\Gamma_1^2][1 + 4(\omega - \omega_2)^2/\Gamma_2^2]}\right)$$
$$= \frac{L + M[2(\omega - \omega_1)/\Gamma_1}{1 + 4(\omega - \omega_1)^2/\Gamma_1^2} + \frac{P + Q[2(\omega - \omega_2)/\Gamma_2]}{1 + 4(\omega - \omega_2)^2/\Gamma_2^2} ,$$

where L, M, P, and Q are constants determined by direct substitution. It may be shown that

$$\int_{-\infty}^{\infty} \frac{1}{1+4(\omega-\omega'-\overline{\omega}_0)/\Gamma_I^2} \frac{2(\omega'-\omega_0)/\Gamma}{1+4(\omega'-\omega_0)^2/\Gamma^2} d\omega' = \frac{\pi}{2} \frac{\Gamma\Gamma_I}{\Gamma_I+\Gamma} \frac{2(\omega-\omega_0-\overline{\omega}_0)/(\Gamma+\Gamma_I)}{1+4(\omega-\omega_0-\overline{\omega}_0)^2/(\Gamma+\Gamma_I)^2} . \tag{6}$$

It is also known that the convolution of two Lorentzians gives a third Lorentzian whose width is the sum of the first two,[27] that is,

$$\int_{-\infty}^{\infty} \frac{1}{1+4(\omega-\omega'-\overline{\omega}_0)^2/\Gamma_I^2} \frac{1}{1+4(\omega'-\omega_0)^2/\Gamma^2} d\omega' = \frac{\pi}{2} \frac{\Gamma\Gamma_I}{\Gamma+\Gamma_I} \frac{1}{1+4(\omega-\omega_0-\overline{\omega}_0)^2/(\Gamma+\Gamma_I)^2} . \tag{7}$$

Thus the convolution of Eq. (2) with a Lorentzian having width Γ_I gives Eq. (2) but Γ_1 is replaced by $\Gamma_1+\Gamma_I$ and Γ_2 is replaced by $\Gamma_2+\Gamma_I$. The relative intensity of each transition is affected in a predictable way.

RESULTS

The effect of the predissociation in the $A\,^2\Sigma^+$ state[19] is largest in the $v = 9$ state of OD (v is the vibrational level). The (0, 9) band of the $B \rightarrow A$ system is characterized by the following facts:

(a) The half-width increases significantly with N when N is low (N is the rotational quantum number).

(b) The spin splitting increases linearly with N.

(c) The spin components become barely resolved at $N=11$.

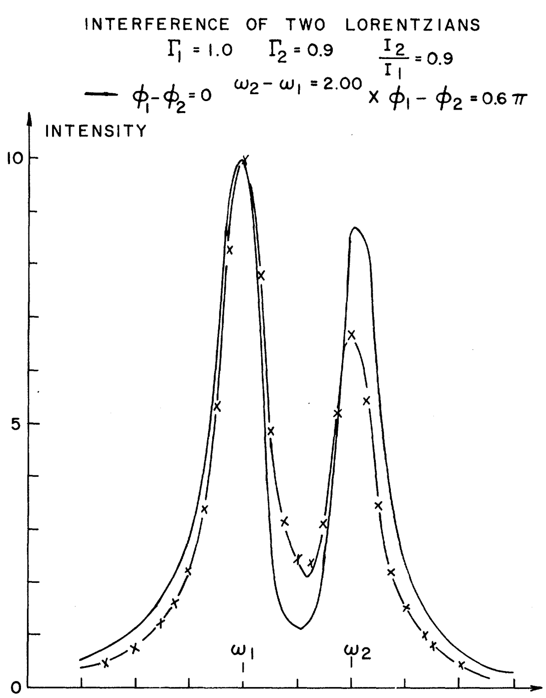

FIG. 2. Interference of two Lorentzians for which $\phi_1 - \phi_2 = 0$ and $\phi_1 - \phi_2 = 0.6\pi$. We wish to point out the effect of the interference on the relative intensities.

(d) The half-width increases more dramatically at $N=16$ and decreases just as dramatically at $N=21$.

(e) The transitions beyond $N=21$ are hardly detectable.

The numerical details and a satisfactory explanation of the N dependence of the half-widths has been given.[19] The line shapes of the $P17$, $R18$, $P18$, $P20$, and $P21$ transitions are given in Fig. 4. These transitions are recorded photoelectrically and are considerably more accurate than previous measurements. The $P19$ transition was masked by impurity transitions and is not given. The $R18$ and $P18$ transitions, which really contain three transitions, show the effect of the interference. The theoretical reproduction of these line shapes is based on Eq. (2) extended for three or four resonances as the case may be. The parameters associated with these transitions are given in Table I.

The intensity of a transition can give useful information, and we plot in Fig. 5 the logarithm of

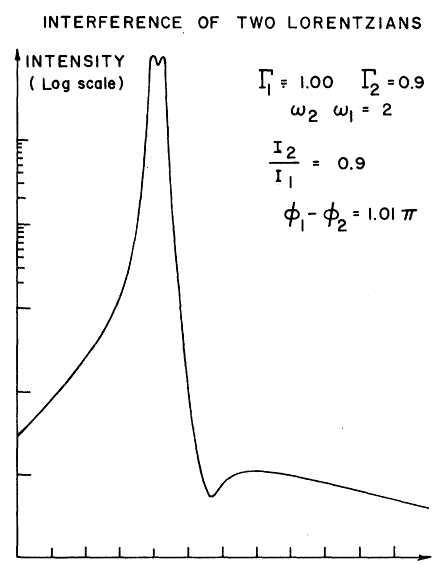

FIG. 3. Interference of two Lorentzians can give three peaks as shown. The "false" peak is five orders of magnitude weaker and several orders of magnitude broader.

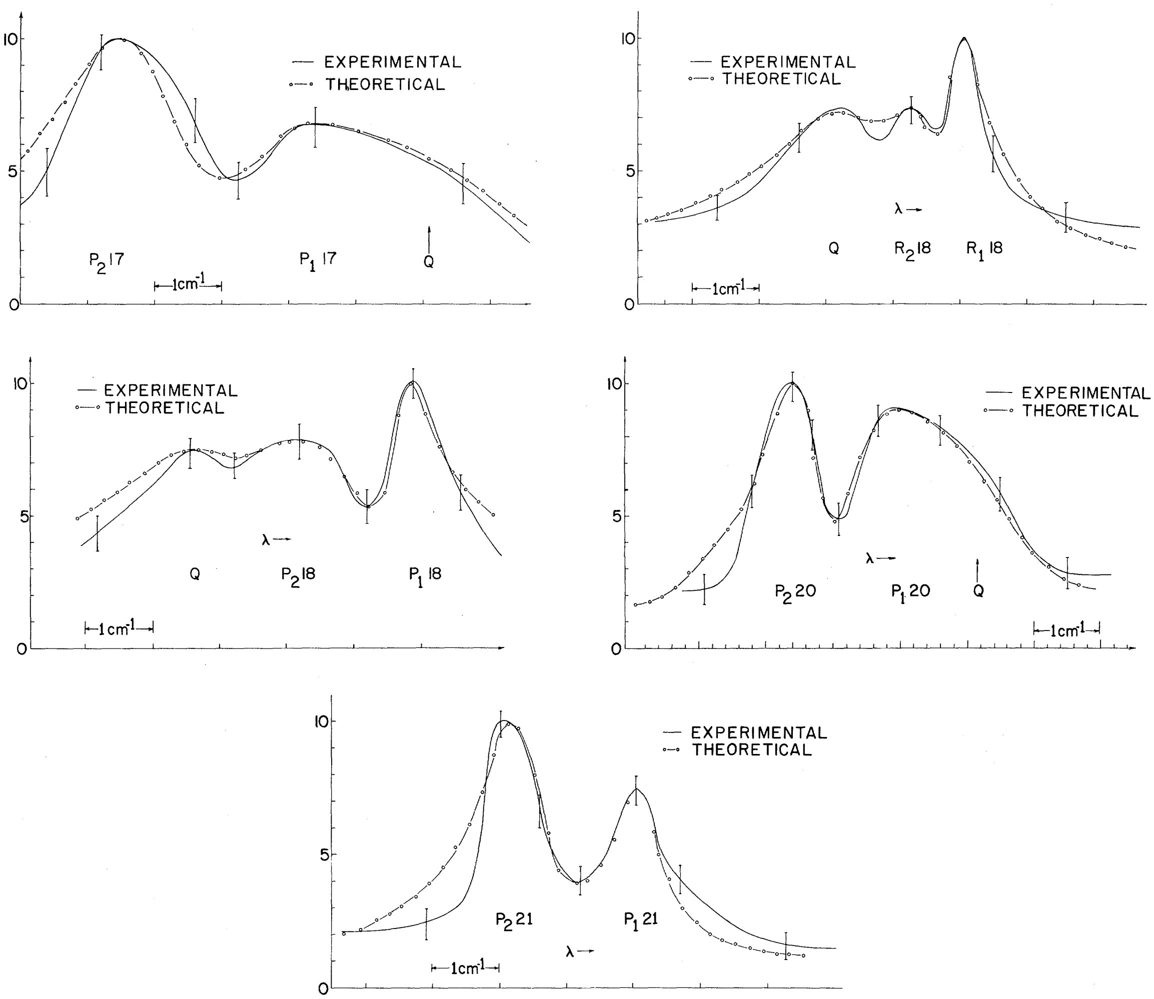

FIG. 4. Experimental line shapes of some predissociated transitions in the (0, 9) band of the $B \rightarrow A$ system of OD. The theoretical line shapes are based on the Mahaux-Lejeune theory. The intensity is given in arbitrary units.

the intensity vs $N(N+1)$ for the unresolved doublets of the (0, 9) transition (the prime refers to the upper state, the double prime to the lower state).

The perturbation in $v=10$ is quite different from that in $v=9$. The transitions are slightly diffuse at very low N, but become sharper as N increases. The spin doublets are resolved for $N=3$. At about $N=11$, the transitions become diffuse again. The half-widths in $v=10$ are always less than 0.5 cm^{-1}. In contrast the half-widths are about 3 cm^{-1} at $N=18$ in $v=9$. Since configuration interaction introduces a shift in the energy, we plot in Fig. 6 the spin splitting as a function of N for the $v=10$ level of the $A\,^2\Sigma^+$ state of OD.

DISCUSSION

Our experimental evidence indicates that the half-width associated with the continuum is large but finite. For example, the signal in the wings of the $P21$ transition is considerably larger than the photomultiplier dark noise, but about 10 cm^{-1} away from the transitions it is buried in the noise. A model of the $P21$ transition using only the interference of two Lorentzians gave very poor agreement. This experimental fact led us to use Eq. (2) extended to include a continuum.

While the reproduction of the $P21$ profile is adequate using two discrete transitions and one very broad transition, the same cannot be said for the other transitions of Fig. 4. It has been shown that the curvature of $P_1 20$ is opposite in sign on the long-wavelength side to that predicted by the Fano theory.[22] $P17$ has a profile remarkably like $P20$. By studying Figs. 1 and 2 we can see that the Mahaux equations will not change the curvature of $P_1 20$ and $P_1 17$. We suppose that the broad bump in

TABLE I. Parameters associated with the predissociated transitions shown in Fig. 4. We have arbitrarily chosen $E=0.0$ and $\phi=0.0$ for the P_1 or R_1 transitions as the case may be. The absolute energy of the P_1 and R_1 transitions can be found in Ref. 31. We estimate the errors in these parameters to be about 40%.

Transition	E (cm^{-1})	Γ (cm^{-1})	ϕ (rad)	I (arbitrary units)
$P_2 17$	0.0	3.1	0.0	1.0
$P_2 17$	2.1	1.9	0.4	1.8
$Q17$	−2.0	2.6	0.2	0.6
$^2\Sigma \to {}^4\Pi$	1.0	15	0.1	1.2
$R_1 18$	0.0	0.2	0.0	1.0
$R_1 18$	0.7	1.2	0.1	0.7
$Q18$	1.1	2.4	0.7	0.9
$^2\Sigma \to {}^4\Pi$	0.6	45	0.3	0.3
$P_1 18$	0.0	0.2	0.0	1.0
$R_1 18$	1.8	2.8	0.1	1.1
$Q18$	2.5	2.5	0.8	0.7
$^2\Sigma \to {}^4\Pi$	1.2	45	0.3	0.3
$P_1 20$	0.0	3.1	0.0	1.0
$P_2 20$	1.3	0.3	0.5	2.6
$Q20$	−1.2	1.8	0.2	0.7
$^2\Sigma \to {}^4\Pi$	0.7	15.0	−0.1	1.2
$P_1 21$	0.0	0.5	0.0	1.0
$P_2 21$	1.8	0.8	0.1	1.0
$Q21$	···	···	···	negligible
$^2\Sigma \to {}^4\Pi$	1.1	30	−0.2	0.6

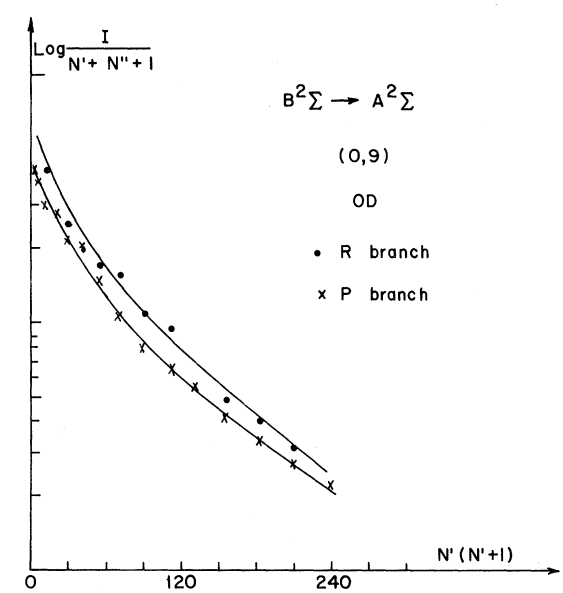

FIG. 5. Intensity of the spin-unresolved transitions in the (0,9) band of the $B \to A$ system of OD. The relationship should be linear, but the predissociation splits it into two nonlinear components.

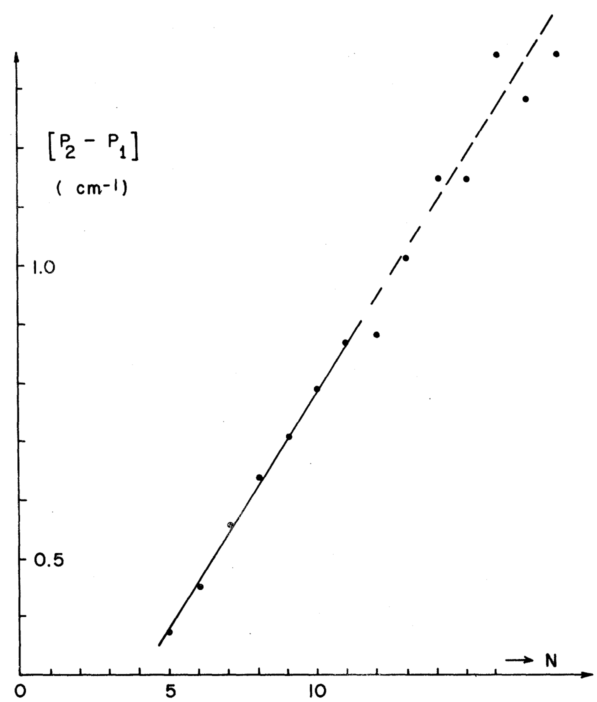

FIG. 6. Spin splitting in the $v=10$ level of the A state of OD. The deviation from linearity above $N=11$, just as the predissociation becomes stronger, indicates the shift in the energy position produced by the perturbation.

$P_1 17$ and $P_1 20$ is due to another transition. The third transition is clearly evident in $P18$ and $R18$, but it is not present in $P21$. The third line is most likely the Q component of a ${}^2\Sigma \rightarrow {}^2\Sigma$ transition,[28] which is normally much weaker than the P or R branch, but it is enhanced in this case because of interaction with the continuum.[29] Numerical calculations have shown that a ${}^4\Pi$ state is responsible for the predissociation of the $A\,{}^2\Sigma^+$ state.[19] Owing to the perturbation, the A state assumes the characteristics of the ${}^4\Pi$ state, and since $\Delta J = 0, \pm 1$ for $\Sigma \rightarrow \Pi$ transitions (J is the total angular momentum), the Q branch is enhanced. The appearance of the Q transitions coincides with the transitions which have the largest half-widths, and this effect is qualitatively understandable on the basis of Fano's theory. Fano shows that the product $\Gamma^2 q$ is constant. Since q is inversely proportional to the transition probability to the continuum, the transition probability to the continuum is proportional to Γ^2. Since it is known that Γ varies significantly in these transitions (from less than 0.2 cm^{-1} to 3 cm^{-1}), it is plausible that the transition probability to the continuum also varies significantly. This idea is supported by the fact that the N dependence of the Q branch coincides in every detail with the N dependence of the predissociated half-widths.

We note, however, that the position of the Q transition relative to the positions of the P and R transitions is not constant. In general, the structure of such a triplet depends on the relative spin splitting of the upper and lower states. The lower state in this case is further perturbed by the continuum. The experimental evidence indicates that the continuum can make the spin levels either approach or repel one another. This is particularly evident in Fig. 6, where the spin splitting in $v = 10$ is studied. For $3 < N < 10$, the perturbation is small ($\Gamma < 0.2$ cm^{-1}) and the relationship is linear,[28] as it should be. As the widths become larger, the linear relationship is roughly valid by considering the average effect, but one sees that the spin levels do approach and repel each other depending on N. The half-widths for the transitions in Fig. 4 are about ten times larger than those for $N > 10$ in $v = 10$, and the shifts involved are considerably larger.

The $P18$ and $R18$ profiles are quite similar. This is because both transitions end on the same rotational levels of the A state. The parameters associated with these transitions are not quite the same, because each transition has a different initial state. This fact is also understandable on the basis of Fano's theory, because the q parameter depends on the initial state. This kind of effect is responsible for the intensity anomalies in Fig. 5. The relationship shown in Fig. 5 is normally linear,[28] but in the $B \rightarrow A$ transitions studied it splits into two nonlinear components. This effect has already been reported.[30]

SUMMARY AND CONCLUSIONS

We find that the predissociated transitions shown in Fig. 4 can be satisfactorily explained by assuming a transition probability to a ${}^4\Pi$ continuum. The half-width associated with the continuum transition is large but not infinite. While the phase of an isolated resonance cannot be measured, the relative phase between resonances causes an interference effect which alters the form of the resonance. The interference effects caused by excitation of the discrete states and the continuum are adequately described by the Mahaux-Lejeune equations. The transition probability to the continuum, as demonstrated by the presence of the Q branch, is not constant, but varies as the predissociated half-width.

ACKNOWLEDGMENT

I wish to thank A. D. Bandrauk for many helpful discussions.

[1]A discussion can be found in any book on classical mechanics, such as K. R. Symon, *Mechanics* (Addison-Wesley, Reading, Mass., 1960).

[2]The function given by Eq. (1) is also known as a Lorentz function. H. A. Lorentz first applied simple classical mechanics to atomic systems.

[3]B. W. Shore, Rev. Mod. Phys. 19, 439 (1967).

[4]G. Breit and E. Wigner, Phys. Rev. 49, 519 (1936).

[5]C. Mahaux, Nucl. Phys. 71, 241 (1965).

[6]A. Lejeune, Nucl. Phys. A 116, 72 (1968).

[7]J. M. Blatt and L. C. Biedenharn, Rev. Mod. Phys. 24, 258 (1952).

[8]P. Von Brentano, N. Marquardt, J. P. Wurm, and S. A. A. Zaidi, Phys. Lett. 17, 124 (1965).

[9]U. Fano, Phys. Rev. 124, 1866 (1961).

[10]L. M. Bollinger, D. A. Dahlberg, R. R. Palmer, and G. E. Thomas, Phys. Rev. 100, 126 (1955).

[11]F. H. Mies, Phys. Rev. 175, 164 (1968).

[12]G. V. Marr, *Photoionization Processes in Gases* (Academic, New York, 1967).

[13]U. Fano and J. W. Cooper, Phys. Rev. 137, A1364 (1965).

[14]P. G. Burke, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Eastermann

(Academic, New York, 1968), Vol. 4, p. 173.
[15]H. S. W. Massey, E. H. S. Burhap, and H. B. Gilbody, *Electronic and Ionic Import Phenomena*, 2nd ed. (Clarendon, Oxford, England, 1969).
[16]J. J. Quenerer, C. Paquet, and P. Marmet, Phys. Rev. A 4, 494 (1971).
[17]L. Sanche and G. J. Schultz, J. Chem. Phys. 58, 479 (1973).
[18]G. Herzberg, in *Topics in Modern Physics—A Tribute to Edward U. Concon* (Colorado Associated University, Boulder, 1971), p. 191.
[19]J. Czarny, P. Felenbok, and J. Lefevre-Brion, J. Phys. B 4, 124 (1971).
[20]A. D. Bandrauk and M. S. Child, Mol. Phys. 19, 95 (1970).
[21]J. N. Murrell and J. M. Taylor, Mol. Phys. 16, 609 (1969).
[22]C. Carlone, Phys. Rev. A 9, 606 (1974).
[23]A. Nitzan and J. Jortner, Mol. Phys. 24, 109 (1972).
[24]The formulas derived by Mahaux contain an energy shift due to the interaction. Since these shifts are not directly observable, we include them in the resonance position.
[25]W. D. Callender and C. P. Browne, Phys. Rev. C 2, 1 (1970).
[26]The question is also posed in Ref. 5.
[27]H. C. Van de Hulst and J. J. M. Reesnick, Astrophys. J. 106, 121 (1947).
[28]For details see G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, Toronto, 1950).
[29]Efforts to reproduce the third peak in $R18$ and $P18$ by assuming that it is a false peak were unsuccessful.
[30]J. Czarny and P. Felenbok, Ann. Astrophys. 31, 141 (1968).
[31]C. Carlone and F. W. Dalby, Can. J. Phys. 47, 1945 (1969).