Anomalous Intensities in Zero-Kinetic-Energy Spectra

William A. Chupka*

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520-8107

Edward R. Grant*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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A number of reasons for the appearance of anomalous intensities in zero-kinetic-energy (ZEKE) spectroscopy are briefly reviewed and extended. Particular attention is paid to a recent paper of Matsui, Behm, and Grant in which the authors detect, in the ZEKE spectrum of NO_2, a number of Franck−Condon forbidden transitions of significant intensity which they attribute in large part to channel interaction between allowed continua and Franck−Condon forbidden discrete Rydberg series. A quantitative approximate analysis of their data is given here which supports this claim. Implications of these results for final state interactions in photoelectron spectroscopy are discussed.

I. Introduction

The technique of zero-kinetic-energy (ZEKE) spectroscopy[1−3] can yield spectra of diatomic and polyatomic ions with resolutions of the order of 0.1 cm^{-1} or less. However, relative intensities in both rotational and vibrational structure have often not conformed to predictions based on simple theoretical considerations and also on comparison with standard single-photon (e.g., HeI) photoelectron spectra. Some of these discrepancies have been explained earlier. It is the purpose of this paper to expand on these earlier explanations and to suggest other possible effects, especially as they relate to some recent experiments. The reasons for these anomalies can be divided into two types, namely, (1) variations in the lifetimes of the ZEKE states due to differences in the type of excitation of the ion core and (2) factors affecting the excitation probabilities of the ZEKE states. This paper is concerned primarily with the second type of reason and will deal very cursorily with the first.

II. Core-Dependent Lifetimes of ZEKE States

Crucial to the success of ZEKE spectroscopy is the long lifetime[1−5] of ZEKE states which allows delays of up to about 20 μs between excitation of the ZEKE state of an atom or molecule and its ionization by a pulsed electric field. Significant core-dependent decay of ZEKE states during this delay obviously can lead to time-dependent relative intensities of ZEKE spectra. A simple example is the well-known dependence of the autoionization rate of Rydberg states on the detailed rotational, vibrational, and electronic state of the ion core, although for many, if not most, molecules, the dominant decay mechanism is some nonionizing radiationless transition (e.g., predissociation, internal conversion) with negligible electron emission on the ZEKE time scale and with varying dependence on the state of the ion core.

The extent to which such a core-dependent lifetime can affect the relative intensities of a ZEKE spectrum depends on the molecule, the states being excited, the experimental conditions, and the characteristics of the exciting laser. The effects of core-dependent lifetimes have been used to explain anomalous ZEKE intensities by a number of workers[6,7] whose publications should be consulted for details.

III. Excitation of ZEKE States

In many ZEKE experiments, the final excitation of the ZEKE states takes place from an excited state of the molecule, usually a lower lying Rydberg state. Photoionization of such Rydberg states is simplistically expected to be governed by diagonal Franck−Condon factors, and this is often the case. However, anomalous relative intensities in vibrational band structure of the resulting photoelectron spectra have sometimes been observed even for such simple and well-known systems as molecular hydrogen.[8,9] At least three reasons have been suggested[10] for such behavior and all three can apply not only to excitation of ionization continua but also to ZEKE states converging to such continua. Two of these three reasons are not expected to be as common as the third. These two are shape resonances (as observed experimentally for diatomic oxygen)[11,12] and Cooper minima, both of which can lead to unusually large variation of transition moment with internuclear distance. The third and more common reason is absorption by the ion core of the Rydberg state to form a doubly electronically excited state which can decay by autoionization as well as by other mechanisms. Since ionization or Rydberg excitation of a closed-shell species produces an open-shell ion or ion core, which usually absorbs, often very strongly, at visible or near-ultraviolet wavelengths, such core absorption is expected to be quite common.

Another factor responsible for anomalous intensities has long been recognized in ZEKE spectroscopy[13,14] and still much longer in more general photoionization studies. This factor results from the well-studied complex interactions among the various Rydberg series (and with their adjoining and underlying continua) converging to every state of the ion. Thus, every slice of ZEKE states will be straddled by Rydberg series converging to higher limits. The members of these series are usually broadened to some degree by interaction with various continua (or ZEKE quasicontinua) in which the Rydberg states are embedded. The coincidence of one or more of such series members (or of

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continua) with the slice of ZEKE states can lead to an interaction which can either increase or decrease the ZEKE intensity as compared with that expected in the absence of such interaction. There exists an enormous amount of literature on this general subject of channel interactions[15] and their effects on ZEKE spectra.[14,16−18] However, this paper is concerned mainly with one special aspect of this phenomenon which is highlighted by the recent work of Matsui et al.[19] These workers present plausible evidence for significant excitation of ZEKE states of NO_2 molecules, which have essentially zero (or at least very low) direct excitation probability, by means of their interaction with an optically allowed ionization continuum. It is a major purpose of this paper to examine their data quantitatively and attempt to estimate the fraction of the "forbidden" ZEKE intensity which is due to this interaction. The ideal approach to this problem would involve the use of multichannel quantum defect theory (MQDT) with parameters extracted from all available experimental data as was done elegantly by Softley and Hudson[20] to explain similar anomalies[14] in the more tractable case of H_2. However, the complexity of the system and the data available do not appear to justify such effort in this case. A simplified approximate approach, which may be found useful in similar circumstances, will be used here.

For clarity, we present the following condensed results of Fano's 1961 paper[21] in which he treated the case of interaction of a single discrete state with a single continuum and derived the well-known line shape function given by (Fano's eq 21)

$$\sigma(\epsilon) = (q + \epsilon)^2/(1 + \epsilon^2) \tag{1}$$

where ϵ is a reduced energy variable and q is given by Fano's eq 20,

$$\mathrm{q} = (\Phi|T|i)/\pi V(\psi_E|T|i) \tag{2}$$

where the numerator is the transition moment to the discrete state Φ (the "modification" to the discrete state given by Fano's eq 17 may be neglected here), V is the interaction matrix element, and the denominator contains the transition moment to the continuum. Then, Fano's eq 22,

$$\pi q^2/2 = |(\Phi|T|i)|^2/|(\psi_E|T|i)|^2\ \Gamma \tag{3}$$

gives the ratio of transition probabilities to the discrete state Φ and to a bandwidth Γ (fwhm) $= 2\pi V^2$ of unperturbed continuum states, where Γ is the resonance full width at half-maximum (fwhm).

Matsui et al.[19] have observed significant ZEKE intensity in Franck−Condon off-diagonal transitions from the (000) vibrational ground state of a Rydberg state whose potential energy surface they determine to be essentially parallel to that of the ion. Thus, their transitions could be expected to have $q = 0$ in the above formalism, i.e., resulting in so-called "window resonances" in the absorption (ionization) spectrum. From Fano's results above, one can deduce the ratio of indirect (via the discrete state) to direct (continuum) excitation as the expression given in eq 3 above, multiplied by the ratio of the resonance width to the width of continuum between adjacent resonances, i.e., n^{-3} au:

$$\text{indirect/direct} = (\pi q^2/2)(\Gamma/n^{-3}) = \pi q^2 \Gamma n^3/2 \tag{4}$$

where Γ is in au.

This equation implies that the indirect excitation is zero for $q = 0$, as is indeed already given by eq 3, and cannot explain the result of Matsui et al. of indirect excitation considerably different from zero. However, eq 3, and therefore eq 4, is suspect mainly for the following reason. As already noted by Fano and discussed in more detail by Comes and Sälzer,[22] this formalism does not properly conserve transition probability as can be seen from Fano's eq 23, which gives the excess transition probability due to the discrete state as proportional to $(q^2 - 1)$, which is clearly incorrect for $q = 0$ for which zero is expected. Also, it is clear that eq 3 is not correct for $q = 0$ since the discrete state must be mixed by configuration interaction into the actual stationary states in a range proportional to Γ centered on the (unperturbed) energy of the discrete state as given by Fano's eq 13. It is precisely this mixture which is responsible for the interference which results in the window resonance. As discussed by Fano and Cooper,[23] the simple Fano profile, eq 1 above, leads incorrectly to complete removal of oscillator strength in the $q = 0$ case, whereas it must be conserved by being simply "pushed away" from that region. They comment on the internally more consistent, but still not completely correct, treatment of Comes and Sälzer,[22] which attempts to conserve oscillator strength, as can be seen from the case of $q = 0$ in their Figure 1. For the present purposes, this deficiency can be repaired heuristically by simply replacing the quantity q^2 by $(q^2 + 1)$ in both eqs 3 and 4 above, as well as in Fano's eq 23, which then gives the correct result for $q = 0$.

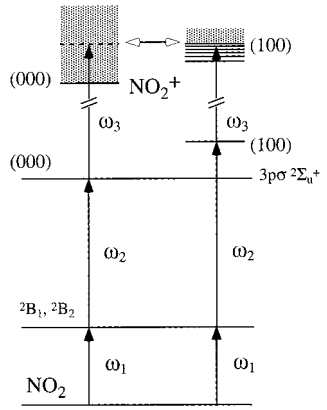

Figure 1. Schematic energy level diagram showing on the right the three-photon excitation path for the photoionization spectrum of Campos et al. (Figure 2 of this paper) and on the left that for the ZEKE spectrum of Matsui et al. described in the text.

Recently, F. Robicheaux[24] has carried out a careful treatment of what is essentially the same problem. Specifically, he has calculated the time dependence of electron emission in the case of excitation of several members of an autoionizing Rydberg series by a very short photon pulse. He obtained a prompt burst of electrons (direct) followed by a decaying emission (indirect) with the integrated ratio given by

$$\text{indirect/direct} = \pi(q^2 + 1)\Gamma n^3/2 \tag{5}$$

which is just eq 4 above, with q^2 replaced by (q^2+1) as argued above. (His rigorous derivation preceded and stimulated the above heuristic treatment, which some may find more transparent.) Thus, the claim of Matsui et al.[19] is supported by theory which also provides a method for quantitative determination from available experimental data.

The paper of Matsui et al.[19] shows only the experimental ZEKE spectra of the (000), (100), (02°0), and (010) cation state with relative intensities 15:3:2:1, as excited from the 3pσ (000) $N' = 3$ Rydberg state of NO_2. The most intense (100) threshold is the best one for comparison with theory. To apply eq 5 to this problem, we must know the value of Γ. Unfortunately,

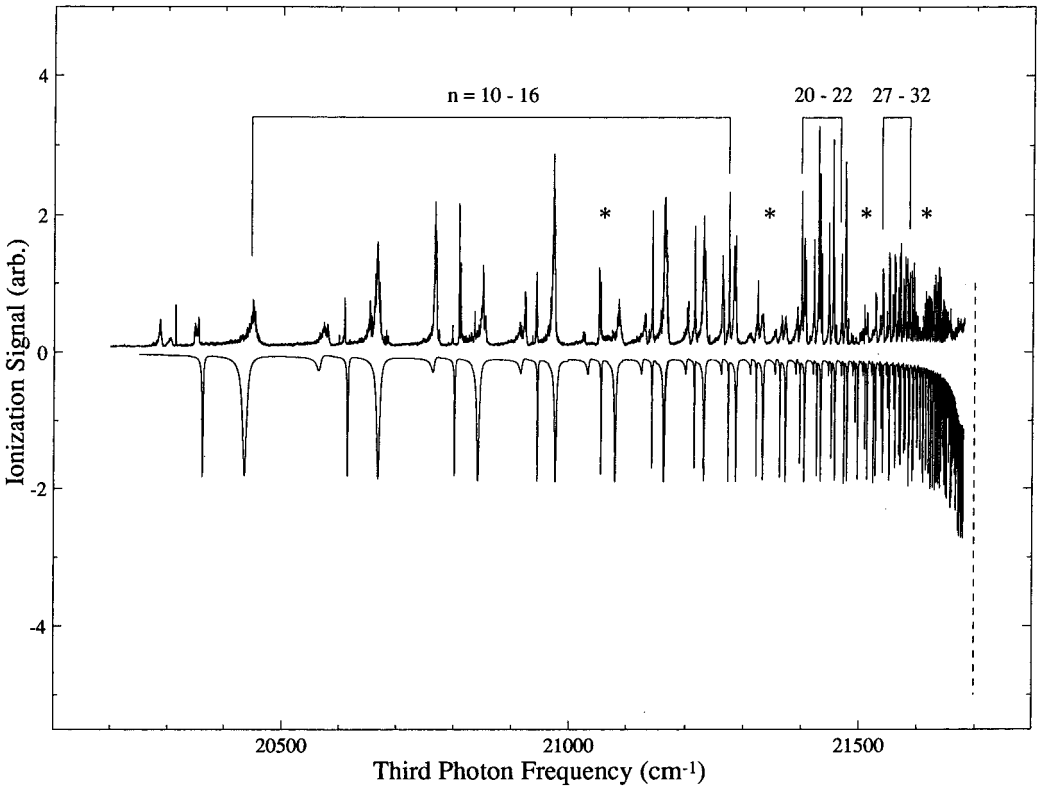

Figure 2. Vibrationally autoionizing states of NO_2 excited by one photon from the $N' = 1$ level of the 3pσ $^2\Sigma_u^+$(0,0,0) state (top). Also shown (bottom) is a simulated spectrum calculated with the assumption of no interloper states. Asterisks above the experimental spectrum indicate the location of window resonances due to interaction with a (110) series. Although the experimental intensities are uncorrected for dye laser output, this output is locally constant over the region of each window resonance and hence the relative shapes are unaffected. Also indicated in the experimental spectrum are the ranges of $n = 20-22$ and $n = 27-32$ which are estimated to be least affected by the interaction. Simulated series with quantum defects of 0.68 ($ns\sigma$), 0.94 ($nd\pi$), and 0.16 ($nd\sigma$) converge to the (100) $N^+ = 2$ threshold at 21 699 cm^{-1}. Fano parameters (Γn^3, q) used are (8000, 20), (2000, 20), and (8000, 3), respectively, where Γn^3 is in units of cm^{-1}.

Matsui et al.[19] do not show the photoionization spectrum from the (000) ionization threshold to the (100) limit, from which values of q and Γ could be obtained, at least in principle, for use in eq 5. However, values of Γ are properties of states rather than of transitions and can be obtained from the data of Campos, Jiang, and Grant,[25] who recorded ionization spectra of the (100) vibrationally autoionizing states of NO_2 excited from the 3pσ (100) Rydberg state with the spectra extending from the (000) threshold to very near the (100) limit (see Figure 1). The values of q for these peaks which autoionize by interaction with the (000) continuum, are, of course, very much larger than zero, whereas they should be very small for excitation from the (000) state. In the ideal case of exactly diagonal Franck−Condon factors, q should be infinite (producing Lorentzian peaks) in the former case and zero (pure window resonances) for the latter. As was recognized by Campos et al.,[25] there is a significant amount of (000) continuum produced by direct excitation from (100), resulting in (100) peaks with pronounced asymmetric Fano line shapes rather than pure Lorentzian shapes. A very crude estimate of the ratio of oscillator strength densities of Franck−Condon "forbidden" to allowed transitions in the data of Campos et al.[25] is of the order of 0.05 or so. A schematic energy level diagram which shows the relation between the experiments of Mastsui et al. and of Campos et al. is given in Figure 1.

The immediately preceding comments indicate that one should not expect values of q to be exactly zero for the (100) series embedded in the (000) continuum excited from the 3pσ (000) intermediate state. However, the value of q will be taken to be zero in order to determine to what extent the continuum interaction invoked by Matsui et al. could be responsible for their observed Franck−Condon forbidden (100) intensity. Values of q greater than zero imply nonzero Franck−Condon factors due to effects such as those mentioned in the first paragraph of this section as well as others. The values of Γ are taken from expanded sections of Figure 2 (see also Figures 3−6 of Campos et al.[25]). However, even the most cursory glance at these figures and at Figure 7 of Campos et al., which is a plot of phenomenological quantum defects as a function of principal quantum number, shows the enormous complexity of this system as compared with the ideal two-channel case of a single Rydberg series interacting with a single continuum. There are three series of significant intensity and line width, namely, $ns\sigma$, $nd\sigma$, and $nd\pi$ as expected in excitation from the 3pσ state. However, in addition to autoionization, there is evidence that predissociation contributes to line width in at least some cases, and various other perturbations cause the three series to behave in an irregular manner. Thus, if there were only a number of series converging to exactly the same limit and embedded in a single continuum, quantum defects and perfectly resolved peak heights would be constant within each series and line widths (hence integrated areas) of all members of each series would scale as n^{*-3}. This is very far from the case.

The most obvious perturbation involves at least four members of an interloper series (or more likely several unresolved series) assigned tentatively by Campos et al. as converging to the (110) state of the ion. These interlopers, indicated by asterisks in Figure 2, appear to have the shapes of Fano near-window resonances, i.e., with $q < 1$, in the average oscillator strength of the dense manifold of states converging to (100), although the pervasive irregularity of intensities in that series makes determination of q and Γ for this interloper series very

inaccurate. Nevertheless, it appears that the overall shape is mainly determined by Fano-type interference, although there is also evidence for intensity loss by predissociation enhanced by the admixture of (110) character since lines about the center of the windows appear to be broadened somewhat as compared to lines of the same series on either side, as discussed by Campos et al.

It is of interest to use, for the moment, the parameters of this interloper series to make some very crude estimates of consequences at higher energies. The energies (dip centers) of the four members [above the 3pσ (100) intermediate state] are given by Campos et al.[25] as 21 076, 21 345, 21 493, and 21 605 cm^{-1} with widths of about 100, 100, 70, and 20 cm^{-1}, respectively. If the lowest and highest energy values are used to determine the parameters of the Rydberg series, the series limit is calculated to be at about 22 318 cm^{-1}. This is in satisfactory agreement with the value 22 338 cm^{-1} obtained by adding ν_2 = 639 cm^{-1} [26] to the limit 21 699 cm^{-1} of the (100) series. The quantum defect is calculated to be about 0.6, i.e., the four series members have effective principal quantum numbers of approximately 9.4, 10.4, 11.4, and 12.4, respectively. The next member is then calculated to lie at about 21 707 cm^{-1}, i.e., very close to the (100) series limit at 21 699 cm^{-1}. If this resonance does fall on or near (within Γ or so) this limit, the corresponding ZEKE signal would be diminished accordingly, providing an example of the effect of series interaction mentioned earlier. Because of the nonideal behavior of this series, both in line positions and widths, this prediction cannot be considered very accurate. (A particularly striking example of such an effect of a window resonance is shown by the work of Merkt and Softley.[14])

The nonideal behavior of these window resonances is readily understood by considering the effects of other series which are expected to interact significantly with the intense (100) series observed by Campos et al. Foremost among these are the (200) series which will interact strongly according to the $\Delta v = \pm 1$ propensity rule and in accord with the finding that the ν_1 symmetric stretch vibration is the most vibronically active. The ionization limit of these series lies at about 23 095 cm^{-1}. If we continue to use a quantum defect of 0.6, the $n^* = 8.4$ member of this series lies at about 21 540 cm^{-1}, very near the $n^* = 11.4$ member of the (110) series at 21 493 cm^{-1} and is probably responsible for much of the reported width of 100 cm^{-1}. These series can be further perturbed significantly by other series which interact directly only weakly (e.g., with $\Delta v = \pm 2$) with the (100) series of Campos et al.

Of the four window resonances identified by Campos et al., calculations indicate that the highest member at 21 605 cm^{-1}, with $n^* = 12.4$ and Γ given as 20 cm^{-1}, is the least likely to be perturbed by other series. We make a more careful estimate of Γ (fwhm) as 12 cm^{-1} which, when used in the Robicheaux equation, gives the ratio (indirect/direct) as 0.16. While this value is certainly not very accurate, especially since unresolved rotational and fine (λ) structure as well as predissociation probably contribute to overestimated widths, it suggests that the ratio of the Franck−Condon forbidden (110) ZEKE peak intensity to that of the allowed (100) ZEKE peak excited from the 3pσ (100) state will be comparable to the analogous ratio observed by Matsui et al.[19] In any experimental determination of this ratio, it should be kept in mind that the allowed (100) ZEKE intensity may be significantly depressed as mentioned earlier. Despite the crudeness of the determinations of Γ for the near-window resonances just discussed, the appearance of these features lends support to the hypothesis that the (100) series measured by Campos et al. would form near-window resonance series in the (000) continuum excited from the 3pσ (000) state.

It should be emphasized again that the Robicheaux eq 5 has been derived for, and is strictly applicable only to, the simple two-channel case. Its validity in the present case of three (neglecting rotation) series interacting with three continua rests on a number of assumptions which are reasonable based on the properties of Rydberg states, of their adjoining continua, and of Rydberg−Rydberg transitions in the absence of interlopers, ion-core absorption and other effects, many of which have been mentioned earlier. It is also fortunate that the members of the three series are well-separated by many times their respective widths, which simplifies determinations of widths. In the case of ideal behavior, the only data required are the autoionization widths and effective principal quantum numbers of a single set of all lines corresponding to a single principal quantum number. Since there is at least one interloper series, sets of lines which are estimated to be least affected by interlopers were chosen. Two such sets, shown in Figures 3 and 4, correspond to n = 20−22 and n = 27−32. The large set, n = 10−16, was also used even though much of this energy region is obviously perturbed by low-n members of several interloper series in such a way that relatively unperturbed regions could not be identified easily. The necessary widths, Γ (fwhm), were measured from expanded versions of Figures 2−4 and corrected for the 0.2 cm^{-1} laser bandwidth to give corrected widths, Γ_c.

The experiments of Campos et al. were carried out in the presence of a constant electric field of 1 V cm^{-1}. While such a field would produce significant Stark broadening for high-n Rydberg states with quantum defects, δ, of zero, it does not do so for the states considered here for the following reasons. Some of the states in the range n = 10−16 do have quantum defects very near zero, but the width of the Stark manifold, given by $(12.8 \times 10^{-5})n^2F$ (V/cm) cm^{-1}, has the negligible value 0.03 cm^{-1} for n = 16 and δ = 0. For $n \geq 20$ the smallest values of $|\delta|$ range between about 0.15 and 0.20. The state of Table 1 most sensitive to the Stark effect is 32dπ for which $n^* = 32.16$. Even this state is about 1.0 cm^{-1} above the nearest member of the n = 32, δ = 0 manifold of total width 0.13 cm^{-1} with negligible effect. Quadratic shifts due to the varied electric fields of randomly positioned ions would produce broadening which is estimated to be negligible. All such external sources of line broadening are estimated to be negligible except possibly for the largest values of n. Since fully resolved or deconvoluted widths should be used, unresolved rotational structure can be a source of some error. However this is mitigated to some extent by the fact that lines of such very large values of q are nearly Lorentzians for which widths are simply additive. All sources of error are estimated to be such that they do not invalidate the main conclusions of this paper.

The lines considered here have such high values of q that it is not necessary to fit the data to Fano profiles. A measurement of full-width at half-height measured from the adjacent minimum is sufficiently accurate for present purposes. (Note that the assumption of q = 0 implies that all the intensity of forbidden transitions results from interaction with the allowed continuum, and the width, $\Gamma = 2\pi V^2$, gives the strength of this interaction. Thus, no account need be taken of relative intensities as would be necessary for $q > 0$). The effective principal quantum numbers were taken from Table 1 of Campos et al. Corrected widths (cm^{-1}) were converted to "reduced" widths ($\Gamma_r = \Gamma_c n^{*3}$) in atomic units, and they are then introduced in eq 5 to calculate the ratio R = indirect/direct expected to be observed in the

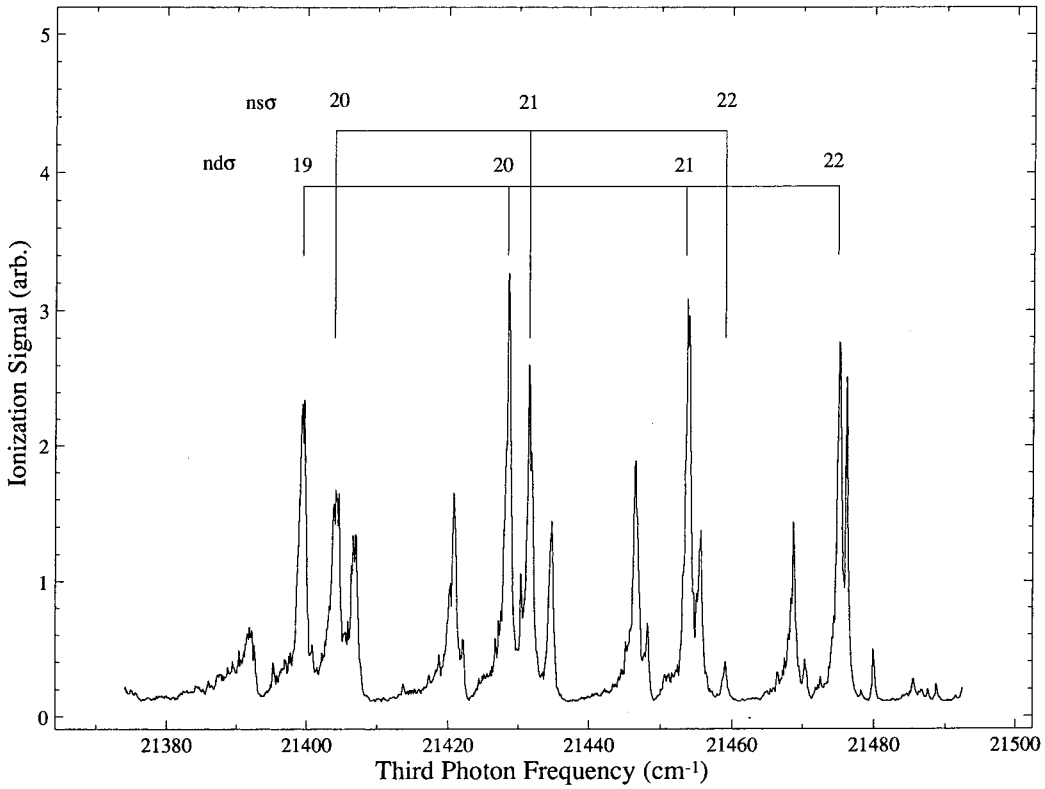

Figure 3. Expanded section of the experimental range of $n = 20-22$ of Figure 2.

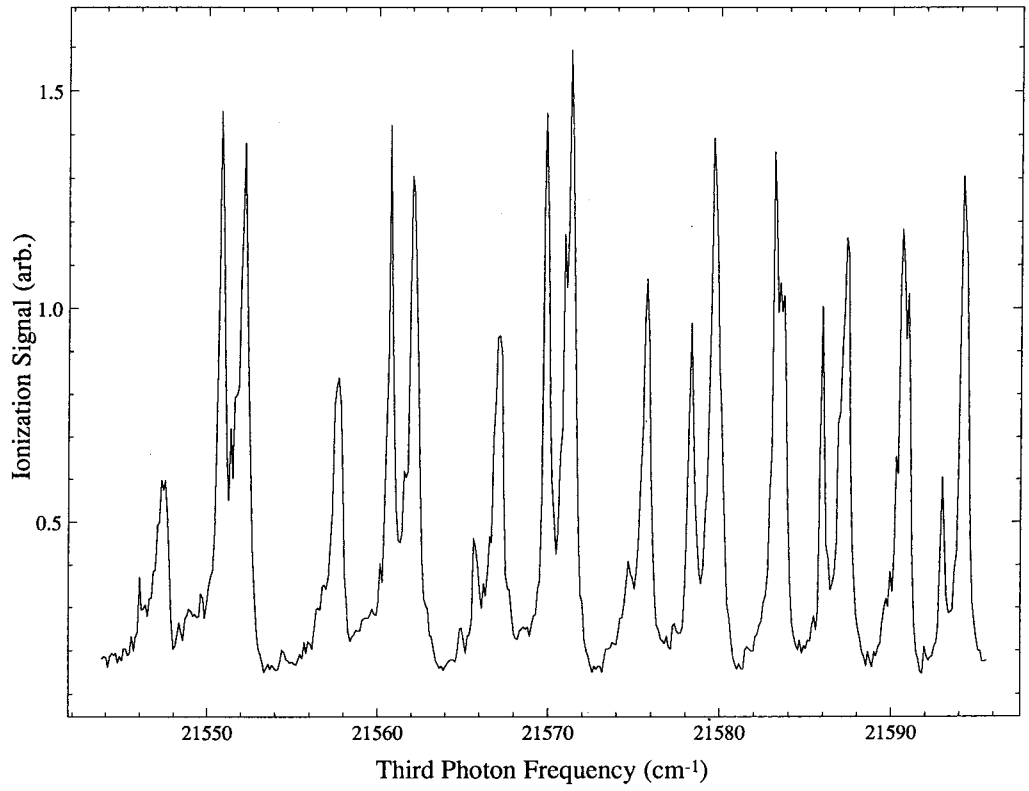

Figure 4. Expanded section of the experimental range of $n = 27-32$ of Figure 2.

ZEKE spectra. The results are given in Table 1. If the series were well-behaved, the values of Γ_r and R within each column would be constant. The average value of R (total) is 0.221. The widths of the broader peaks of lower n ($n = 11-16$) could be measured with greater accuracy and are less affected by finite laser bandwidth, unresolved structure, and external perturbations but are more affected by the intrinsic internal perturbations mentioned earlier since they are not selected. The data from selected peaks of highest n ($n = 27-32$) are most affected by bandwidth corrections, power broadening, and other external perturbations. The data of intermediate values of n ($n = 20-22$) are judged to be most reliable overall and yield an average value of R (total) = 0.205, which agrees well with the overall average value of 0.221. If we consider the value of R (total) =

TABLE 1: Widths (Γ), corrected widths (Γ_c), reduced widths (Γ_r), and ratios (R) of indirect to direct processes[a]

	$ns\sigma$				$nd\sigma$				$nd\pi$				
n	Γ (cm^{-1})	Γ_c (cm^{-1})	Γ_r (au)	R	Γ (cm^{-1})	Γ_c (cm^{-1})	Γ_r (au)	R	Γ (cm^{-1})	Γ_c (cm^{-1})	Γ_r (au)	R	R (total)
10	13.0	13.0	.049	.076	13.50	13.50	0.059	0.093	0.750	0.700	0.003	0.005	0.174
11	13.52*	13.51*	0.067*	0.105*	4.46	4.45	0.026	0.041	1.56*	1.46*	0.009*	0.014*	0.160
12	6.96	6.96*	0.046*	0.072*	10.69*	10.47*	0.079*	0.124*	1.83	1.81	0.014	0.023	0.219
13	4.57	4.56	0.039	0.061	3.61*	3.56*	0.034*	0.053*	1.62*	1.38*	0.014*	0.022*	0.136
14	5.78	5.77	0.063	0.099	4.91	4.90	0.060	0.094	1.13	1.09	0.014	0.022	0.215
15	5.00	4.99	0.067	0.105	2.12*	2.04*	0.031*	0.049*	0.910	0.866	0.014	0.021	0.175
16	5.45	5.44	0.089	0.139	2.73	2.72	0.050	0.078	1.09	1.05	0.020	0.031	0.248
20	2.28*	2.21*	0.073*	0.114*	1.08*	0.88*	0.032*	0.050*	0.75	0.70	0.026	0.041	0.205
21	1.58*	1.49*	0.057*	0.089*	1.23*	1.09*	0.045*	0.071*	0.79	0.74	0.032	0.050	0.210
22	1.43*	1.32*	0.058*	0.091*	1.05*	0.89*	0.042*	0.066*	0.63	0.57	0.028	0.044	0.201
27	1.13	1.10	0.092	0.144	0.83	0.79	0.069	0.109	0.33	0.22	0.020	0.032	0.285
28	0.67	0.60	0.056	0.088	0.67	0.60	0.059	0.093	0.23	0.09	0.009	0.014	0.195
29	0.62	0.55	0.057	0.089	0.66	0.59	0.065	0.101	0.37	0.27	0.031	0.048	0.238
30	0.79	0.74	0.085	0.133	0.53	0.45	0.054	0.085	0.39	0.29	0.036	0.057	0.257
31	0.67	0.60	0.076	0.120	0.81	0.76	0.101	0.158	0.25	0.12	0.016	0.025	0.303
32	0.67	0.60	0.084	0.132	0.71	0.65	0.096	0.150	0.27	0.14	0.021	0.033	0.315
												average:	0.221

[a] Asterisks mark those entries for which more than one peak has been identified by Campos et al. and given in their Table 1. In those cases, each peak, deconvoluted when necessary, was separately corrected for laser bandwidth and the resulting widths were added together to produce the values given in this table.

0.205 to be the most reliable, we find the standard deviation for all the data to be 0.05. The fact that all values of R (total) lie between 0.136 and 0.315, for a range of n over which all possible sources of error (except for error in the estimate of 0.05 for the direct process in the data of Campos et al.) must vary greatly in kind and importance, provides assurance that no great systematic error nullifies the main conclusion of this paper, namely that the intensity of Condon off-diagonal transitions observed by Matsui et al. is indeed due primarily to the channel interactions they invoke. Misidentification of peaks could affect the values of R within a column, but less so the values of R (total) since the latter results from addition of the reduced widths of all peaks between values of n^* and $n^* + 1$. Furthermore, perturbations which displace peaks into adjacent intervals of n^* would also mostly be averaged out by our procedure which essentially averages the sum of widths of all lines for three considerable ranges of n.

There is a correction which should be taken into account when the intensities of two ZEKE spectra are compared as in the present case. This correction is made necessary by the fact that the (direct) continuum cross section in the energy region of the (indirect) ZEKE states will not be equal in general to that at the threshold of the direct continuum, and the two ZEKE intensities are in each case proportional to these cross sections. In the absence of more accurate information, this correction can be estimated for a Rydberg state by using a hydrogenic approximation given by Bokor et al.[27] (see also p 308 of Bethe and Salpeter[28] and eq 1 of ref 10 as well as the review of Pratt[29]) according to which the photoionization cross section is proportional to $(h\nu/U)^{-3}$ where $h\nu$ is the photon energy and U the ionization potential of the Rydberg state. For the $3p\sigma(000)$ state of NO_2, U is 21 711 cm^{-1} and the photon energy at the (100) threshold (from the $3p\sigma$ state) is 23 107 cm^{-1} so that the cross section ratio is 0.83. While this correction should not be considered very accurate, it serves to illustrate the magnitude expected. (Note that, for the same vibrational spacing, this correction becomes very rapidly larger for higher intermediate Rydberg states with lower ionization potentials, while it is very small for excitation from the ground state, for which the approximation is of doubtful validity.) When this correction is applied to the value of R (total) = 0.205, the corrected value is 0.170. Since Campos et al. show that there is also a significant direct component which we estimate to be on the order of 0.05, the resulting sum is 0.22, which compares well with the experimental value of 3/15 = 0.2 of Matsui et al. While the close agreement must be considered fortuitous in light of possible effects of interlopers as well as the crude estimate of the direct component, we consider that agreement within a factor of 2 or so would suffice to support the contention of Matsui at al. that their observations of Franck−Condon forbidden thresholds in the ZEKE spectrum of NO_2 are due in large part to interaction of forbidden ZEKE states with an allowed continuum.

IV. Relevance to Photoelectron Spectroscopy

By the well-known continuity relation between the oscillator strength density of a Rydberg series and that of its adjoining continuum, the above results must also apply to the two continua above the ZEKE ionization limit. That is, the one-photon photoelectron spectrum of the $3p\sigma(000)$ state should exhibit a (100) peak of intensity about 3/15 of that of the (000) peak, at least for some undetermined energy range immediately above the (100) threshold. This phenomenon can be considered to result from continuum−continuum (a special case of final state) interaction, a phenomenon well-known in photoionization studies of atoms (as well as of a simple molecule such as H_2[14,20]). It has recently been shown[30] that, at least for atoms, such electronic continua channel interactions persist even to kiloelectronvolt energies and it is predicted that this effect should apply to electronic continua of molecules as well. In the present case, there is no obvious reason the vibronic channel interaction should decrease rapidly with increasing energy. Rotational, electronic, and other interactions should have similar effects. All these phenomena serve to emphasize the dangers of using overly simplistic descriptions of ionization continua and a blind reliance on Franck−Condon factors in ionization processes.

The Robicheaux equation and its consequences in photoelectron spectroscopy would be most convincingly tested using an appropriate simple (ideally two-channel) atomic system with a small value of q. One such nearly ideal system has been studied by Madden et al.[31] and more recently by Berrah et al.[32] These workers made very accurate measurements of the necessary quantities for the Ar $3s \rightarrow np$ series embedded in the $Ar^+ 3s^2 3p^5 + e^-(ks, kd)$ continuum. The measured average values are $\Gamma_r = 0.0373$ au and $q = 0.130$ which give $R = 0.060$. Berrah

et al. measured angle-resolved photoelectron spectra for $n = 4-16$. Unfortunately, they do not report photoelectron spectra above the $3s^{-1}$ ionization limit, although it would have been very simple to do that experiment in order to verify the above predicted ratio. Note that the correction discussed above for relative intensities of ZEKE spectra is not necessary for photoelectron spectra, at least not for spectra taken just above the second threshold.

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