TWO CLASSES OF ZEKE SPECTROSCOPY

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Dedicated to Professor Rudolf Zahradnik of the occasion of his 70th birthday.

A classification of ZEKE spectra into two classes based on operational criteria is useful for discussion. The proposal is that some of the different and seemingly conflicting effects reported for different molecular (or the same molecule for different excitations), such as the role of an external field, are due to these two distinct classes of states which can be optically accessed. Class A is the direct, "front door" entry where the states excited are those which are detected by the delayed ionization. Class B is a very prevalent but indirect "backdoor" route where it is only the interaction of the Rydberg electron with the core, possibly aided by external perturbations, that allows a signal to be detected upon ionization. The operational criteria for distinguishing between or even exploiting the features of the two classes are discussed. Such attention might be useful as new techniques for class B spectra are developed.
Key words: Zero electron kinetic energy; ZEKE spectroscopy; Electric field; Rydberg; Core interaction; Frank–Condon; Nitric oxide cation.

Zero electron kinetic energy[1–10] (ZEKE) spectroscopy enables high resolution studies of ionized species. It analyzes by a delayed ionization, typically by a pulsed field, the presence of long lived states which lie just below the energy of the ionized species. One can produce not only the ground state of the ion, in which case the energy is the lowest ionization potential (IP) but also higher ionic states. With this technique narrow bands just below such ionic eigenstates which have abnormally long lifetimes even for these highly excited states are detected. Typically in ZEKE experiments, the precursor is neutral so that one is studying all the energy levels of the positively charged ion. The ZEKE spectrum will then appear just below the ionization threshold of any ionic state within the range of excitation. One can, however, study negative ions as precursors in

which case the ionized species is neutral[11]. This is particularly useful for extremely short lived species – transition states being just one such example[12].

The point of this paper is to emphasize that ZEKE spectroscopy has a unique, as yet unexploited feature involving "lateral" transitions, not typically found in ordinary spectroscopies – in addition to the conventional vertical transitions familiar in spectroscopy. This leads to conceptually two different mechanisms. The distinction between these two, although known, is often glossed over in discussions of practical ZEKE spectroscopy and this can lead to needless confusions. A clear conceptual distinction between these two mechanisms makes the interpretation of ZEKE results considerably more transparent.

It is thus useful to distinguish two main classes of ZEKE spectra with important theoretical and practical consequences. Several operational criteria can distinguish between the two classes. Stated in a different way, it need not be the case that a given variable (*e.g.*, the DC electrical field present during excitation) will have the same effect in all experiments. It need not even be the case that the same molecule (*e.g.*, the well studied NO (refs[13–24]), see Fig. 1) will be in the same class irrespective of the mode of excitation (*e.g.*, two *vs* one photon). Even for a resonance enhanced two photon excitation, it is possible to generate different cases by changes in the state of the resonant intermediate.

The further point of this paper is that the two classes are not only distinguishable by purely operational criteria. There is also a theoretical underpinning to this distinction. A theoretical approach provides a unified view of the origin of the different experimental signatures.

We shall distinguish between vertical processes which we term class A or "front door" processes and these less common class B processes which enter by the "backdoor". In Tables I and II is a listing of the experimental consequences of these two

TABLE I
Direct transitions

Direct transitions	(front door)	Class A
Theoretical calculations agree (McKoy *et al.*[25])		
Selection rules apply		
Franck–Condon principle holds		
Photoelectron spectroscopy correlates		
Field effect is monotonic – typically producing single peaks that disappear with field		

classes. Much as these class B processes are presumed understood, there is no example to date of their direct exploitation.

The ZEKE states usually encompass a narrow band to some energy below the IP or the other relevant ionic eigenstates, typically down to a principle quantum number of $n \approx 150$, producing $a \approx 5$ cm^{-1} wide band hugging each eigenstate of the ion from below.

These bound states are the states of class A and, if they have been optically pumped, can be detected by the delayed field ionization ZEKE spectroscopy. In other words, below any new threshold in the eigenspectrum of the ion there are states of class A, which are long lived and above which they will be manifested as a photoelectron signal.

In other words, states of class A are a continuation, to just below the threshold, of the states of the continuum which are just above that threshold.

States of class A are those that will give rise to a typical ZEKE spectrum because they lie just below the threshold for the production of ions. An electric field lowers the
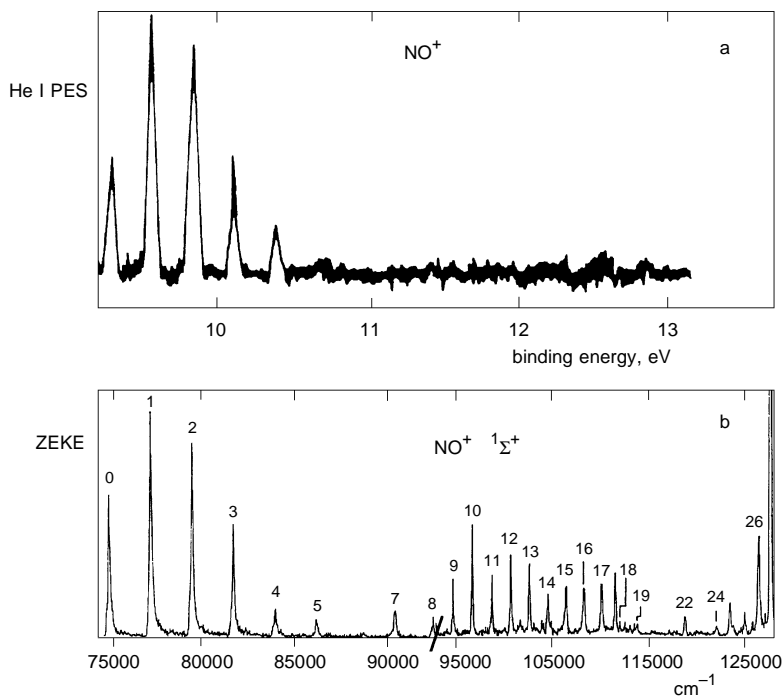

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Comparison of photoelectron and ZEKE spectra for nitric oxide. **a** Photoelectron spectrum taken from Turner *et al.*[13]. **b** Threshold ZEKE spectrum[24]. The lower vibrations in the ion are found in the photoelectron spectrum and in the ZEKE spectrum, whereas the higher vibrational levels are only seen in the ZEKE spectrum

threshold and hence states of class A can be detected by their ionization in a delayed field. Since a ZEKE peak is typically seen hugging every threshold, it is suggestive to equate states of class A alone with ZEKE spectroscopy. This picture is somewhat incomplete, but we certainly agree that states of class A provide the typical "front door" to ZEKE spectroscopy.

From their very definition as the continuation of the states of the photoionization continuum to below the threshold it follows that the theoretical techniques used to study photoelectron spectroscopy can be readily adapted for the description of states of class A. Even more, since the state of the ion is the same in states of class A and at an energy a shade higher when ionization is allowed, it follows that one can compute the states of the ion in a ZEKE spectrum by computing the states of the ion in a photoelectron spectrum at a slightly higher energy. In the hands of McKoy and collaborators this has become a very important tool[6,25].

The very description of states of class A raises the question about alternate descriptions. (In fact, more than one class – more on this later.) Let us begin with the experimental evidence, that is by comparing the photoelectron spectrum to a ZEKE spectrum. The results for NO are shown in Fig. 1. Clearly, many more vibrational states of the ionic core, NO^+, are seen in the ZEKE spectrum. How can we describe these extra states?

Clearly these are states that have all the characteristics of all ZEKE states except that they are inaccessible by normal vertical transitions (class A). Then how are they produced? In the present understanding they belong to a different class of excitation not

TABLE II
Indirect transitions

Indirect transitions	(back door)	Class B
Excitation into other Rydberg manifolds usually from ro-vibronic excited ground states		
Channel coupling proceeds from lower n, but hot cores into the highest values of n		
Transitions into Franck–Condon gap appear to violate the Franck–Condon principle, but rather follow selection rules for other transitions		
Almost all transitions are allowed, with no apparent selection rules		
Transitions proceed to regions dark in photoelectron spectroscopy		
Field effects are typically non monotonic – new resonances open up due to channel coupling – single peaks may appear now		
Theoretical calculations become more complex		

typically found in spectroscopy, what is generally termed lateral transitions. Hence, we term them class B. They are produced by excitation into the many other Rydberg ladders that exist. The higher n states are then produced by lateral channel coupling (see Fig. 2), which is a generalization of coupling processes known from autoionization – but now on a far broader scale.

The interesting situation at present is though such channel couplings have been invoked to explain forbidden regions in the Franck–Condon region, there appears to be no case to date where the experiment has been purposely modified to turn on such channel coupling when it is not present naturally. This would be a unique possibility here to turn on transitions not seen in conventional spectroscopy. So far, such transitions have not been turned on in ZEKE spectroscopy either, though they are present by serendipidity. This alone serves to demonstrate that these class B processes are a neglected species. We wish to discuss here this mechanism and methods to make use of it.

To summarize: An ionization treshold corresponds to the appearance of ions in a particular internal state. States of class A are states at energies below that treshold which are Rydberg states built on the particular internal state of the core. States of class B are also Rydberg states but built on higher energy internal states of the core, but have Rydberg states at the energy of lower thresholds. The classification A *vs* B is thus with reference to a threshold. If several thresholds are near in energy (as will be the case for different rotational states of a heavy ion) it may be convenient to have the designation
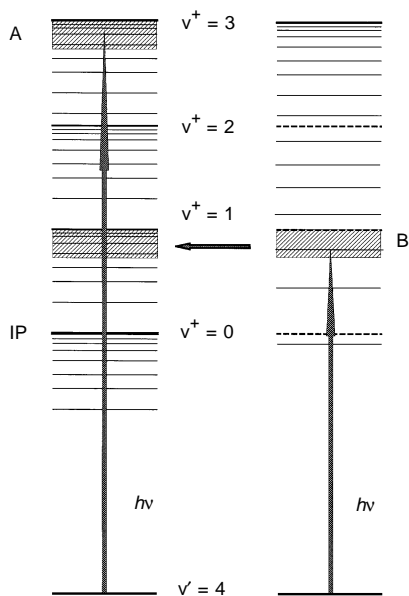

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Level scheme for the two classes in ZEKE spectroscopy. The region A corresponds to vertical transitions as seen in normal ZEKE spectroscopy. The region B represents class B transitions to lower Rydberg states. The higher n states then are produced by lateral channel coupling and can be detected as ZEKE states

class A apply to all the Rydberg series built upon the internal states of the core which are near in energy.

The richer or more complex is the internal structure of the core, the more states there can be in class B, so class B is more interesting for molecular Rydberg states and in atoms one will typically deal with states of class A, but this need not be invariably the case particularly so if one recognizes the possibility of electronic excitation of the atomic core.

We emphasize that the distinction between the two classes is not simply based on autoionization. States of both classes can autoionize. This is clear for states of class B. It is also the case for states of class A because such states are present, by definition, below every threshold. For any threshold but the lowest one, states of class A also have enough energy to ionize, because, just like the states of class B, they are built on excited states of the core. For both classes, at higher energies the states can, in principle, autoionize. The distinction is not in the total energy as states of both classes can coexist in the same energy range. The distinction is in how the total energy is partitioned between the core and the Rydberg electron. For states of class A so much energy is localized in the electron that with a very slight increment it will ionize. It does not require any energy from the core in order to do so. Rather than incrementing the energy of the Rydberg electron one can lower the threshold for ionization which is what is done by the delayed application of a field. In other words, states of class A are what can readily be detected by a ZEKE experiment.

States of class A lie just below the threshold for ionization and the principal quantum number n of the Rydberg electron is very high so that, at a slightly higher energy, the Rydberg electron will be in the continuum. Rather than increase the energy we can lower the oneset of the continuum by the application of an electrical field. Hence states of class A will be detected by a delayed pulsed field. Of course, one can apply a very weak delayed field or a slice of a field so that only a subset of states A are ionized thus greatly increasing resolution. In principle, one can also do the opposite, that is, apply such a large delayed field that it will ionize not only the states lying just below the threshold in question but also states which lie even below a lower treshold, assuming that there is one. This is quite practical if the finite spacing between the threshold is due to rotational states of the core. It is even practical for vibrational spacings if the core has low frequency van der Waals vibrational modes. It is not so practical for ordinary vibrational modes. As a matter of principle, increasing the delayed field so as to detect states in class B is important because such experiments show that this class is not empty, *i.e.*, that one can harvest additional bound states, states which are not in class A. In this paper we assume that this is not done. That what is detected are only states of class A. For future reference we do note that this is not necessarily the case and that one can tailor the detection so as to explore different classes of states.

Optical excitation of states of class B provides a back door entrance to the ZEKE region. It follows that if they are relevant at all, they must communicate with the isoenergetic states of class A, because otherwise their presence will not be detected. That they can be accessed is suggested by those experiments which show a "non class A behaviour". Examples include a non Franck–Condon distribution of the vibrational states of the ion examined quantitatively in Ag_2 (ref.[26], see Fig. 3), O_2 (ref.[27]), NO_2 (ref.[28]) and in Ar_2 (ref.[29]) but also seen quite dramatically in the ZEKE spectra of van der Waals bound dimers[30–32] where in some cases, all six "vibrational" modes of the van der Waals bond are active[33].

Optical excitation of states of class B provides for a now well known route to overcome the propensity rules of ordinary spectroscopy, although it must be emphasized that this apparent violation of selection rules has produced much confusion in the development of ZEKE spectroscopy. To be effective in this way, the coupling to states of
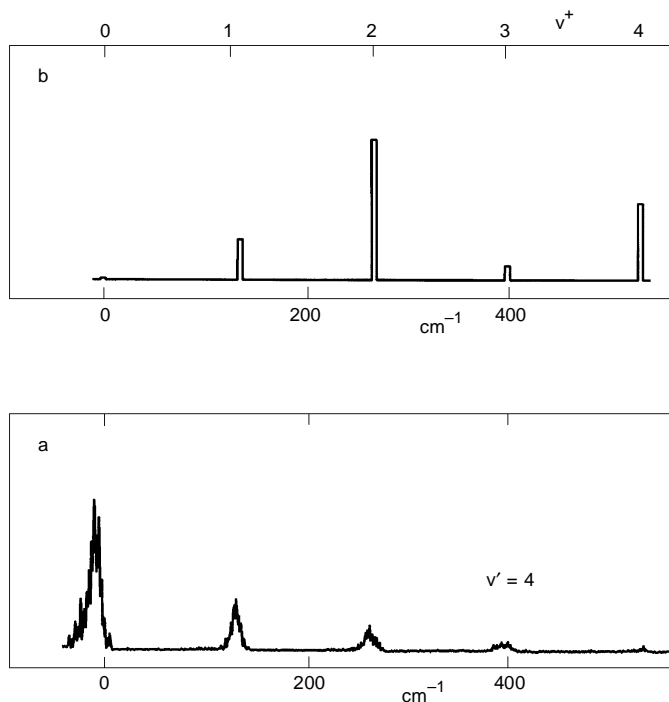

FIG. 3

Discrepancy between Franck–Condon calculations and observed ZEKE spectra of the silver dimer. The excitation is performed from the vibrational excited ($v' = 4$) intermediate state $B^1\Sigma_u$. The ZEKE signal from the vibrationless ionic state (lower panel **a**) is the strongest in contrast to the calculated Franck–Condon intensities (upper panel **b**) and is due to lateral channel coupling which makes this state visible *via* a "back door mechanism"

class A must not be too weak. This is facilitated when the levels of the ionic core are not too far apart in energy. Hence rotational states or low vibrations are particularly useful, since they also will have a correspondingly small discrepancy in the mismatch of the principal quantum number n, thus facilitating crossing to the high n ZEKE state. Accessing states of class B is facilitated by excitation of either the ground state of the neutral or of the intermediate resonant state (assuming that the excitation is by a two photon process).

This could provide for a new, yet unexploited road to spectroscopy of Franck–Condon forbidden transitions.

CONCLUSIONS

Two classes of entry into the ZEKE range are useful to be distinguished. Optical excitation into class A is the front route and thus the typical case in any spectroscopy. The states which will be readily detected by a delayed pulsed field ionization are thus the states that are being optically accessed here. These are the states which at a slightly higher photon frequency will be in the continuum and hence lead to prompt ionization, *i.e.*, they are Rydberg states built upon the same state of the core as the state of the ion produced (together with a photoelectron) at a slightly higher excitation energy. A ZEKE spectrum is then just a photoelectron spectrum but at a slightly lower energy, made possible by the lowering of the threshold for ionization by the delayed field.

The back route is excitation into isoenergetic states but where the state of the core is higer up in energy (and these necessarily have a lower energy for the electron). When the optical excitation is into states of class B, the state of the ion produced by the ZEKE spectrum will *not* be the same as the state initially reached. The selection (or propensity) rules will then appear "strange", because the relevant rules of spectroscopy apply to the optical stage. During the long time (often, many µs) between excitation and detection, the nearly good quantum numbers of the core are being mixed due to the interaction with the Rydberg electron, an interaction which can be modulated also by external fields. This provides for an interesting unexploited class B excitation method in ZEKE spectroscopy of reaching the Franck–Condon gap, a region typically not accessible in conventional spectroscopy. Purposely entering adjacent Rydberg series should be just one way to force these new transitions. Such experiments have not yet been undertaken.

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