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Differential Decay of States Excited in Zero-Kinetic-Energy Spectroscopy

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Anomalous intensity in zero-kinetic-energy pulsed-field-ionization (ZEKE-PFI) spectroscopy caused by differential decay of excited states during and immediately after pulsed excitation and before *l*-mixing, is considered. Changes by more than a factor of 2 or so are shown to be impossible under typical experimental conditions.

I. Introduction

There are a number of reasons why relative intensities, typically of rotational and vibrational structure, differ for photoelectron spectra (PES) and zero-kinetic-energy pulsed-field-ionization (ZEKE-PFI) spectra. Most reasons that have been previously explored and invoked rely on the fact that a particular ZEKE "slice" of high Rydberg states is very often overlayed by a band or line belonging to a series converging to a higher limit. The "channel interaction" between the band or line and the high *n* members of the ZEKE "slice" may result mainly in changes of the oscillator strength of that ZEKE slice, thus leading to changes in the intensity of the corresponding ZEKE spectrum.[1,2]

We wish to explore another factor which can affect relative intensities of ZEKE signals, even in the absence of perturbing interlopers and even in the presence of such electric fields and other external perturbations which should increase the lifetimes of the ZEKE states to values much greater than the typical ionizing pulse delay time of a microsecond or so. This other factor is the unavoidable decay that must occur during and at very short times after the optical pulse which forms the ZEKE states. If significant differential (i.e., of different core states) decay occurs during this time, the original relative populations of ZEKE states will be changed. We assume that sufficiently strong stray or applied electric fields are present, and the average value of *n* of the ZEKE slice is sufficiently high so that these fields are equal to or above the Inglis−Teller value, thus ensuring essentially complete *l*-mixing in the Stark manifolds. In addition, we assume that other fields (e.g., magnetic), field inhomogeneities (e.g., due to the presence of charged particles such as ions), and/or time dependent effects such as collisions or the motion of charged particles are sufficiently strong so as to ensure that m_l-mixing is essentially complete on a time scale considerably shorter than the lifetimes which have been lengthened by *l*-mixing. Thus, we assume that pulsed excitation of ZEKE states occurs directly to a Stark manifold (as is generally the case for conditions of typical ZEKE experiments), and that conditions for complete m_l-mixing may be present also. We further assume that the excitation oscillator strength is carried by one value of *l* and that only states with that value of *l* decay (e.g., by predissociation) with significant rate. This condition is well-approximated by many ZEKE studies (of NO, for example[1,2]). The results of the present treatment are also useful in considering more complex cases.

II. Short Pulse Excitation

We assume that pulsed excitation of the ZEKE manifolds is achieved by an optical pulse so short in time that its Fourier frequency transform spans each Stark manifold and excites each member of the *n*th manifold with equal probability. (While few if any ZEKE experiments are carried out with such short transform-limited pulses, the commonly used multimode pulsed laser operates on a number of unstable cavity modes so that each "macro" pulse consists of a train of "micro" pulses varying in separation and phase so that the present model is of relevance.) Such coherent excitation produces an initial non-stationary state, *nl*, which then evolves in time in a well-known fashion described by the equation

$$P_{nl}(t) = \left| \sum_{k=-(n-1)}^{+(n-1)} \frac{1}{n} \exp(-iE_k t) \right|^2 \tag{1}$$

where E_k is in atomic units ($\hbar = 1$) and is given by

$$E_k = \frac{1}{n^2} + \frac{3}{2}Fnk \tag{2}$$

where F is the electric field strength in au and $k = n_1 - n_2$ where n_1 and n_2 are parabolic quantum numbers. We also assume $m = 0$ for which $k = n - 1, n - 3, n - 5, ... -(n - 1)$. The time evolution of $P_{nl}(t)$ was given earlier[3] by approximating the Stark manifold as a continuum. This gave the result

$$P_{nl}(t) = \left[\frac{\sin\left(\frac{3}{2}Fn^2 t\right)}{\frac{3}{2}Fn^2 t} \right]^2 \tag{3}$$

An exact expression can be obtained,[4] namely

$$P_{nl}(t) = \left[\frac{\sin\left(\frac{3}{2}Fn^2 t\right)}{n\sin\left(\frac{3}{2}Fnt\right)} \right]^2 \tag{4}$$

This latter equation properly exhibits both the complete and partial recurrences expected from eqs 1 and 2. However, eq 3 is an excellent approximation for the range of parameters of interest here and will be used in what follows. As mentioned

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earlier,[3] the higher recurrences given by eq 4 will be dissipated and eliminated under typical ZEKE experimental conditions.

We now wish to determine the amount of decay of a ZEKE manifold as the original nonstationary l-state dephases into l-space forming the ZEKE states whose lifetimes are decreased, in our model by the factor n^{-1}. If the pure nl state decays by process i with the rate constant k_{inl} with mean lifetime $\tau_{i\mathrm{nl}} = k_{inl}{}^{-1}$, it can be shown easily that the ratio of the amount "decayed" by process i to the amount decayed by pure l-dephasing is given by

$$R_{inl} = \int_{t=0}^{\infty} P_{nl}(t) k_{inl}\, \mathrm{d}t \qquad (5)$$

If we use eq 4 for $P_{nl}(t)$, this integral obviously diverges because of the infinity of recurrences. Therefore, we use eq 3 which is an excellent approximation for the large values of n ($\geq$ 100) and typical ZEKE experimental conditions of interest here. Using eq 3 we obtain

$$R_{inl} = \pi k_{inl}/(3Fn^2) \qquad (6)$$

We note that the l-dephasing decay of $P_{nl}(t)$ is not even approximately exponential and therefore cannot be assigned a conventional rate constant. However, nearly all of the decay occurs before the first zero value of $P_{nl}(t)$ at $t = \tau_{n0} = 2\pi/(3Fn^2)$, and it is convenient to express eq 6 in terms of τ_{n0} as well as $\tau_{inl} = k_{inl}{}^{-1}$. The resulting expression is

$$R_{inl} = \frac{1}{2}\frac{\tau_{n0}}{\tau_{inl}} \qquad (7)$$

This result can obviously be generalized to several decay channels whereby the ratio of amounts decayed by any two channels is given by the ratio of the respective rate constants. In this connection, it can be seen that $(\tau_{n0}/2)^{-1} = 2/\tau_{n0}$ can be used as an "effective rate constant" for l-dephasing. In the present context, we note that significant differential decay during l-dephasing can occur only if at least one of the decay channels has an inverse rate constant k^{-1}, which is a significant fraction of τ_{n0}.

We now consider some typical rates of various modes of decay of Rydberg states. It is convenient to use reduced quantities as well as atomic units. Thus we will use reduced widths $\Gamma_\mathrm{r} = \Gamma_n\, n^3$ where all widths are fwhm. For an ideal Rydberg series, Γ_r remains constant for any specific decay channel and a specific series. We note that the spacing between adjacent members ($\Delta n = 1$) of a specific series is equal to n^{-3} au (1 au = 2Ry). Obviously reduced widths must be some fraction of unity. We note that the Bohr orbital period, τ_B, $= 2\pi n^3 = 6.28n^3$ au and the reduced Bohr period, τ_Br, = 6.28 au. We shall see that some of the fastest decays of well-developed and clearly recognized Rydberg series have reduced widths as large as $\Gamma_\mathrm{r} \cong 0.4$ or so and corresponding reduced lifetimes $\tau_\mathrm{r} = \Gamma_\mathrm{r}{}^{-1} = 2.5$ au or a fraction of the Bohr period.

A small sample of autoionization line widths of diatomic molecules is given in Table 7.2 of the monograph by Lefebvre-Brion and Field.[5] Conversion of some of the values given in cm^{-1} to reduced atomic units yields the following values. Rotational autoionization of the $v = 1$, $J = 1$, np2 series of H_2, $\Gamma_\mathrm{r} = 0.184$ au; vibrational autoionization of the $v = 2$, $J = 1$, npσ series of H_2, $\Gamma_\mathrm{r} = 0.0226$ au; spin–orbit ionization of the series converging to the $^2\Pi_{1/2}$ state of HI, $\Gamma_\mathrm{r} = 0.32$ au. The rotational autoionization example is fairly representative for a penetrating orbital. However, vibrational autoionization can be significantly stronger than the example given above. For example, the sum of all autoionization widths for nsσ, ndσ, and ndπ series converging to the most effective (symmetric stretch) vibrational excitation (100) of NO_2 give $\Gamma_\mathrm{r} = 0.22$,[6] while values for the other two vibrational modes are much less, which could lead to significant differential decay. Electronic configuration interaction processes (e.g., electronic autoionization, predissociation, internal conversion) vary greatly in strength and no useful typical values can be given. Of special importance is the fact that predissociation can be very strongly dependent on vibrational state, especially for small molecules, leading to significant differential decay of the relevant ZEKE states.

Now we wish to examine the magnitude of effects expected from a rather extreme case of such differential decay. We assume decay of a particular rovibrational ZEKE state via decay by some process i with $\Gamma_{\mathrm{r}i} = 0.4$ and thus $\tau_{i\mathrm{r}} = 2.5$, while all other rovibrational states belonging to the same electronic Rydberg series have negligible decay rates.

Since ZEKE experiments are usually carried out with stray or applied electric fields which are greater, usually by some small factor, than the Inglis–Teller value, $F_\mathrm{IT} = (1/3)n^{-5}$ au, the field at which adjacent Stark manifolds just begin to overlap, it is convenient to express the electric field in units of that field. Thus this "reduced" field is given by $F_\mathrm{r} = F \times 3n^5$ au. Then $\tau_{n0} = 2\pi n^3/F_\mathrm{r}$ and $\tau_{inl} = \Gamma_{il\mathrm{r}} \times n^3$, and we obtain the very convenient form

$$R_{il} = \frac{1}{2}\frac{\tau_{n0}}{\tau_{inl}} = \pi\Gamma_{i\mathrm{r}}/F_\mathrm{r} \qquad (8)$$

In the typical work of Reiser et al.,[7] the average value of n was found to be ~200 and the stray field was determined to be 0.20 mV cm^{-1}, a factor of 4 greater than the Inglis–Teller value of 0.05 mV cm^{-1}. Therefore, for our assumed value of $\Gamma_{i\mathrm{r}} = 0.4$, $R_{il} = 0.4\pi/4 = 0.314$, and the fraction of initially formed ZEKE states which decomposed before complete l-dephasing is given by $R/(\mathrm{R} + 1) = 0.314/1.314 = 0.24$. Thus, the corresponding ZEKE peak would be depleted to 0.76 of the value expected if no decay occurred before l-dephasing is complete. Even using a maximum value of $\Gamma_\mathrm{r} = 1.0$ with $F_\mathrm{r} = 4$ yields $R = 0.79$, the fraction decayed = 0.44, and thus depletion to 0.56. Values of F_r much lower than ~4 are not usually encountered in ZEKE spectroscopy in which the high-energy edge of the ZEKE slice is determined by destruction by field ionization and similar external effects, while the low-energy edge is determined by pulsed-field ionization with pulse amplitude chosen for optimum resolution with acceptable intensity. However, it is certainly possible to operate with much smaller values of F_r and with sufficiently short delays in order to test the validity of the present model. Nevertheless, the above calculations indicate that changes of ZEKE intensities by more than a factor of 2 or so are unlikely to be due only to the decay phenomenon discussed here, at least under the most common experimental conditions. Note that our assumption that the optical pulse frequency transform is much broader than the Stark manifold implies that the pulse is much shorter in time than t_{n0} and therefore we may neglect the decay occurring during the pulse.

Actual ZEKE spectra are usually taken with experimental conditions such that several Stark manifolds are spanned by the laser bandwidth. This should not affect very significantly the considerations above. If the manifolds interact negligibly, they can be considered separately. There is some formation of a radial wave packet which rapidly dephases as a result of the nonequality of energy spacing between adjacent manifolds and, in any case, does not affect lifetime significantly. If the manifolds interact strongly, the effects can introduce nonuniformity of spacing and of widths of individual lines of the Stark manifolds[8] so that l-dephasing decay is nonuniform and no clear zeros are reached at τ_0 or at subsequent values as given by eq 3. However, the average lifetime remains approximately the same. Another factor to be revisited is the matter of m_l-spoiling which leads to an additional lifetime lengthening factor of approximately n. If the experimental conditions, such as charged particle (ions and/or electrons, e.g.) densities, presence of other generators of nonaxially symmetric electric fields, magnetic fields not coaxial with electric fields, etc., are such that the excitation oscillator strength of the "initial l-state" is approximately uniformly distributed among all m_l states, the dephasing time remains the same as the l-dephasing time of the Stark manifold of a single value of m_l (and well approximated by eq 3), except that now dephasing occurs into the complete l and m_l space, and lifetimes after this dephasing would be increased by approximately the factor n^2 over that for the isolated unperturbed molecule. In the case that conditions are such that only l-mixing occurs on the time scale given by eq 3, the resulting increase in lifetime, by approximately the factor n, may allow considerable m_l-mixing by such stochastic processes as "collisions" with neutral species or very dilute, but moving, charged particles, etc. While it is very difficult, in the typical ZEKE experiment, to avoid efficient l-mixing by stray or applied electric fields (although this can be done deliberately by choosing a ZEKE slice or even a single state of sufficiently low value of n), the occurrence of efficient m_l-mixing can be more difficult to predict and, in its absence, state- and time-dependent ZEKE intensities can be expected. Of course, sufficiently low values of n for ZEKE states can result in such dependence if the lifetime lengthening factor of even n^2 is still too small for the chosen time delay.

The conclusion which can be reached from the present study is the following: Under typical conditions of ZEKE spectroscopy (of not-too-large molecules[9]), specifically with electric fields greater than the Inglis−Teller value and $n \geq 100$ or so, and pulse delays of about 1 μs or less, excitation occurs directly to Stark states in such a way that isolated-state (i.e., no collisional destruction) decay cannot deplete ZEKE states by more than a factor of 2 or so. Anomalous ZEKE intensities varying by much more than that factor must be due, at least in part, to other factors and/or inadequate m_l-mixing so that lifetime lengthening by only n is insufficient to prevent a large amount of decay during pulse delay.

Appendix

For mathematical convenience, we rewrite eq 2 in terms of a new parameter, j, defined as $j = (k + n + 1)/2$ where j now has the values $j = 1, 2, 3, ... n$ to get

$$E_j = -1/n^2 - 1/n^2 - \frac{3}{2}Fn^2 + \frac{3}{2}Fn(2j - 1) \tag{2'}$$

For simplicity we also make the substitution $x = 3/2Fnt$ and note that we can drop the first two constant terms in eq 2′ in rewriting eq 1 as

$$\begin{aligned} P_l(t) &= \left|\sum_{j=1}^{n} \frac{1}{n}\exp[-ix(2j - 1)]\right|^2 \\ &= \left|\sum_{j=1}^{n} \frac{1}{n}\cos x(2j - 1) + i\sum \frac{1}{n}\sin x(2j - 1)\right|^2 \end{aligned} \tag{1'}$$

We then use the following two equations:[10]

$$\sum_{j=1}^{n} \cos(2j - 1)x = \frac{1}{2}\sin 2n\, x \operatorname{cosec} x = \frac{1}{2}\sin 2nx/\sin x$$

$$\sum_{j=1}^{n} \sin(2j - 1)x = \sin^2 n\, x \operatorname{cosec} x = \sin^2 nx/\sin x$$

and obtain

$$\begin{aligned} P_l(t) &= \left|\frac{1}{2n}\sin 2nx/\sin x + \frac{i}{n}\sin^2 nx/\sin x\right|^2 = \\ &\qquad \frac{1}{4n^2\sin^2 x}(\sin^2 2nx + 4\sin^4 nx) \\ &= \frac{1}{4n^2\sin^2 x}[4\sin^2 nx(\cos^2 nx + \sin^2 nx)] = \frac{\sin^2 nx}{n^2\sin^2 x} \end{aligned}$$

Writing this out in original quantities, we obtain eq 4

$$P_l(t) = \left[\frac{\sin\left(\frac{3}{2}Fn^2t\right)}{n\sin\left(\frac{3}{2}Fnt\right)}\right]^2 \tag{4}$$

Note that for $3/2Fnt \ll \pi$ we may use $\sin x \cong x$ in the denominator and obtain the approximate eq 3, which can be recognized as the first term given by the Euler−Maclaurin summation formula,[11] and is an excellent approximation for conditions of interest in this work.

Equation 4 properly exhibits complete recurrence for $t = \tau_{\text{rec}} = 2\pi/3Fn$ and its first zero value at $t = \tau_0 = 2\pi/3Fn^2 = (1/n)\tau_{\text{rec}}$. The first maximum after τ_0 occurs for $t = \pi/Fn^2 = (3/2)\tau_0$ (approximately), at which the value of P_l is 0.04506 by eq 6 and 0.04503 by eq 3 for $n = 100$. Since we are concerned with values of $n = 100$ or greater, eq 3 will be more than adequate for our purposes. Over the entire range of interest eq 3 differs from eq 6 by <1 part in 10^3 for $n \geq 100$. The accuracy of eq 3 supports the expectation that treatment of the Stark manifold as a continuum (for large n and not-too-large F) will provide useful accuracy for other intensity distributions at $t = 0$, e.g., Gaussian or Lorentzian, the latter yielding an exponential decay. Equation 4 may find some use in cases of low n or other sparse, equally spaced, states.

References and Notes

(1) Müller-Dethlefs, K.; Schlag, E. W. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1346.

(2) Schlag, E. W. *ZEKE Spectroscopy*; Cambridge University Press: Cambridge, U.K., 1998. This book and the review article cited in reference 1 give many examples of the effects of channel interactions.

(3) Chupka, W. A. *Chem. Phys.* **1993**, *98*, 4520.

(4) See Appendix.

(5) Lefebvre-Brion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic Press: New York, 1986.

(6) Chupka, W. A.; Grant, E. W. *J. Phys. Chem. A* **1999**, *103*, 6127.

(7) Reiser, G.; Habenicht, W.; Müller-Dethlefs, K.; Schlag, E. W. *Chem. Phys. Lett*. **1988**, *152*, 119.

(8) Sakimoto, K. *J. Phys. B: At. Mol. Opt. Phys.* **1989**, *22*, 2727. Figure 4 and private communication of calculations at higher electric fields above F_{IT}.

(9) Very large molecules can decay, with large values of Γ_r, for several, or even many values of l, so that lifetime lengthening can be by a much smaller factor than n. Fast decay by predissociation and/or especially internal conversion can be very prevalent in such molecules.

(10) Gradshteyn, I. S.; Ryzhik, I. M. *Tables of Integrals, Series, and Products*, 4th ed.; Academic Press: New York, 1965; p 30.

(11) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1965; p 16.