

VIBRONIC AUTOIONIZATION AND PREDISSOCIATION IN HYDROGEN

S. E. NIELSEN

*Chemistry Laboratory III, H. C. Ørsted Institute,
University of Copenhagen, Copenhagen, Denmark*

and

R. S. BERRY

*Department of Chemistry and James Franck Institute,
University of Chicago, Chicago, Illinois 60637, USA*

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Recent high-resolution photoionization experiments on H_2 , HD and D_2 [1] have shown that 1) near the threshold for ionization, the dominant mechanism for ionization is autoionization; 2) the lifetimes for autoionization are 0.3×10^{-12} sec or longer; 3) although the vibrational propensity rule [$\tau(\Delta v = -1) < \tau(\Delta v = -2) < \dots$] is frequently obeyed, there are significant violations of this rule, and 4) predissociation is as fast as or faster than autoionization in some cases for which both are allowed. We report here a theoretical treatment which accounts for these phenomena. We also derive the effect of isotopic substitution on the autoionization and predissociation rates. In addition, the method is applied to associative ionization and dissociative recombination; this will be described elsewhere, with a fuller treatment of the present topics.

In brief the method is as follows. The rates are first calculated as a first-order perturbation arising from vibronic coupling of bound molecular Rydberg states H_2 ($n\rho\sigma$, π) with the continuum, $H_2^+(v, K) + e$ for autoionization or $H(3s, 3p, 3d) + H(1s)$ for predissociation. The coupling operator is the nuclear kinetic energy operator, which we further restrict to the vibrational or radial component in the present discussion. The electronic and vibrational basis functions are obtained in the Born-Oppenheimer approximation. For a given internuclear distance R , the effective static potential for the electrons is a truncated spherical harmonic series containing monopole Coulomb and exchange contributions and quadrupolar Coulomb terms. This potential and the static effect of internuclear distance on the electronic wave function $\psi(r, R)$ were described previously [2]. The eigenvalues of the static Hamiltonian for various R values give the effective potentials

for determining vibrational wave functions $\chi(R)$. The functions $\psi(r, R)$ and $\chi(R)$ were evaluated by Numerov integration for the bound and continuum states of interest.

Let us omit the angular part of the nuclear wave functions and the nuclear rotational kinetic energy operator, both for reasons discussed previously [3] and because of the nature of the dominant vibronic coupling term. This dominant term in the coupling matrix is the one proportional to

$$\langle \psi_f(r, R) \chi_f(R) | (d\chi_i/dR) (d\psi_i/dR) \rangle.$$

The dominant contributions from the electronic wave functions themselves are, in almost all cases, those due to variations with R in the finite-size *monopole* of the effective potential of the H_2^+ core. Previous formulations of vibronic autoionization [3-5] had omitted this term entirely, and had suggested that the R -dependence of the core quadrupole was normally the dominant term [3-5]. The quadrupolar part is second in importance, but for autoionization and predissociation, ordinarily contributes only a few percent to the total rates. The importance of the monopole term is not only its magnitude but also its ability to couple two s-like electronic states. However, we are concerned here primarily with the optically accessible $n\rho\sigma$ and $n\rho\pi$ states; these are also coupled primarily by the monopole.

From the Fermi Golden Rule, $\tau^{-1} = (2\pi/\hbar) |(i|\mathcal{H}|f)|^2$, the *direct* bound-free rates are obtained. Typical values are shown in tables 1 and 2. Only values for rotationless ($K = 0$) nuclei are given; since the rates are almost independent of K , at least to $K = 8$. Predissociation rates are very sensitive to the principal quantum number and, except for slow ($< 10^9$ sec $^{-1}$) predissociation, relatively insensitive to

Table 1
 Autoionization rates (without intermediate states)

$n\Delta$	ν_{initial}	$\nu_{\text{final}} (\text{H}_2^+)$	H_2	HD	D_2
$5p\sigma$	3	0	$3.9 \times 10^6 \text{ sec}^{-1}$	3.8×10^6	(closed)
	4	1	2.4×10^8	(closed)	(closed; 4-0: 3.4×10^7)
$6p\sigma$	2	0	1.5×10^9	1.0×10^9	(closed)
	3	1	5.1×10^9	3.5×10^9	(closed; 3-0: 7.3×10^6)
	4	2	1.5×10^{11}	(closed)	(closed)
$8p\sigma$	4	1	1.6×10^7	6.4×10^6	(closed; 5-1: 1.1×10^8)
	1	0	2.1×10^{11}	1.8×10^{11}	(closed)
	2	1	4.7×10^{11}	(closed; 2-0: 4.7×10^8)	(closed; 2-0: 3.2×10^9)
	3	2	7.9×10^{11} (expt. a): ca. 10^{11})	(closed; 3-1: 1.6×10^9)	(closed; 3-1: 9.4×10^9)
$6p\pi$	4	2	$5.8 \times 10^9 \text{ E}$)	3.8×10^9	2.3×10^9
	2	0	1.3×10^9	9.3×10^9	(closed; 3-0: 6.4×10^6)
$10p\pi$	6	4	5.4×10^{10}	(closed)	(closed; 6-3: 4.5×10^7)
	1	0	1.0×10^{11}	8.4×10^{10}	6.6×10^{10}
	6	5	9.7×10^{11}	7.8×10^{11}	5.8×10^{11}
	6	4	1.3×10^{10}	8.0×10^9	4.0×10^9

a) Measured from a copy of the drawing used in ref. [1]; we are indebted to Drs. Chupka and Berkowitz for providing this figure.

b) The channel $\Delta v = -1$ is not open in our model from $8p\sigma (\nu = 4)$. However the experimental width (ref. [1]) suggests that in reality, $8p\sigma$ does autoionize by a $\Delta v = -1$ transition.

 Table 2
 Predissociation rates

n_{initial}	ν_{initial}	n_{final}	(United atom: separated atom)	H_2	HD	D_2
$6p\sigma$	7	$5p\sigma$	$\sigma_u 3s$	6.2×10^{12}	(closed)	(closed)
	12			5.0×10^{12}	3.3×10^{12}	1.5×10^{12}
$7p\sigma$	7	$5p\sigma$	$\sigma_u 3s$	6.2×10^{11}	(closed)	(closed)
	15			4.3×10^{11}	1.8×10^{11}	3.6×10^{10}
$5p\sigma$	12	$5p\sigma$	$\sigma_u 3s$	9.8×10^{10}	2.6×10^{10}	1.5×10^9
$9p\sigma$	12	$5p\sigma$	$\sigma_u 3s$	2.7×10^{10}	3.5×10^9	2.8×10^8
$3p\pi$	12	$4p\pi$	$\pi_u 3c$	2.6×10^{12}	1.0×10^{12}	9.0×10^{10}
$7p\pi$	12	$4p\pi$	$\pi_u 3d$	2.1×10^{10}	5.7×10^9	4.7×10^8
$9p\pi$	9	$4p\pi$	$\pi_u 3d$	4.5×10^8	6.5×10^8	3.3×10^8
$4p\pi$	15	$3p\pi$	$\pi_u 3p$	7.8×10^9	2.1×10^{10}	1.9×10^9

vibrational quantum number. Autoionization rates increase rapidly with initial vibrational quantum number, up to the maximum ν for each n . (Principal quantum numbers n refer to the united atom state designation.) Autoionization rates decrease markedly with $\Delta\nu$, the number of vibrational quanta by which the initial H_2^+ and final H_2^+ states differ. The rate of increase of autoionization rate

with initial vibrational quantum number,

$$\delta(\tau_{\text{auto}})^{-1} / \delta\nu_{\text{initial}},$$

increases with $\Delta\nu$. The autoionization rates vary as $(n_{\text{initial}})^{-3}$; Bardsley [4] has shown that this dependence is a direct consequence of the normalization in the core and must hold for sufficiently large n . This dependence holds essentially per-

fectly for $n \geq 5$ and within a few percent for $n = 4$ in our calculations.

Comparison of autoionization and predissociation rates shows that predissociation is the faster for only a few values of n_{initial} . Predissociation in the σ -system, from $6p\sigma$ and $7p\sigma$ to $H(3s) + H(1s)$ (i.e. H_2^+ , $5p\sigma$) is always faster than autoionization, for all open channels, meaning for $v \geq 7$ for H_2^+ , ≥ 9 for HD^+ and ≥ 11 for D_2^+ . For $n = 8$, $6 \leq v \leq 11$ and for $n = 9$, $v = 7, 8$ (for H_2), the two processes have comparable rates. For the π system, for H_2 , states with $n = 5$, $v \geq 8$ predissociate rather than autoionize. For π states with $n = 6$, states with $v = 7, 8$ and 12 predissociate; both processes contribute for $v = 9, 10, 11, 13$ and 14 . The apparently erratic behavior of the rates is a function of which Δv channels are open for autoionization; for $n = 6$, $\Delta v = -3$ closes for $v_{\text{initial}} > 11$, allowing predissociation to take over.

The isotope effect is shown in tables 1 and 2. Predissociation rates are increasingly sensitive as v increases. The pattern of competition between autoionization and predissociation is not changed significantly by isotopic substitution, even though the rates themselves are strongly affected. Occasionally cancellations in the integration over R may produce isolated anomalies, as in the last two predissociations cited in table 2.

Finally, we have examined the effect of intermediate coupling between bound Rydberg states as a possible mechanism to explain violations of the vibrational propensity rule for autoionization [1,3]. The procedure for determining coupling matrix elements is the same as for autoionization and predissociation but now all the wave functions refer to bound states, electronic or nuclear. Such coupling allows a slowly-autoionizing or predissociating "zero-order" state to steal autoionizing capability very much as one state can steal oscillator strength from another. The quantitative details of the coupling are quite sensitive to the accuracy of the model because of the dependence of coupling on the energy separations of zero-order states. The off-diagonal matrix elements are at most 5×10^{-4} a.u. (100 cm^{-1}) and more commonly 10 - 30 cm^{-1} . This means that states couple strongly when their energy separations are of about this size. We could give reliable quantitative estimates for the effect of such coupling on rates only if we knew the zero-order vibrational-electronic state energies to this accuracy; our model is clearly not this accurate. However, we can pick out some general features and give some examples of large effects of intermediate couplings as they appear in our model.

The Π states are somewhat more affected than the Σ states and in particular the Π states of low n (4,5) couple effectively with states with $n = 8, 9, 10$. Furthermore we find that strong coupling occurs only between two, three or at most four states, so that one can readily estimate the contribution of "rate stealing" for most cases of interest. Here are the most prominent examples of rate stealing in our calculations for H_2 : (these are for $K = 0$, but the rates are nearly independent of rotational state) ($6p\sigma$, $v = 6$) with ($8p\sigma$, 5) which almost quadruples the ($6p\sigma$, 6) autoionization rate from 3×10^8 to $1.1 \times 10^9 \text{ sec}^{-1}$; the ($6p\pi$, 2) with the ($10p\pi$, 1), giving a total ($6p\pi$, 2) autoionization rate of 2×10^{10} compared with $1.3 \times 10^9 \text{ sec}^{-1}$ which one obtains without rate stealing, and, most dramatic of all, the ($5p\pi$, 10) coupling with ($7p\pi$, 8) state, which increases the autoionization rate of ($5p\pi$, 10) from $9 \times 10^7 \text{ sec}^{-1}$ to $1.9 \times 10^{10} \text{ sec}^{-1}$. We have not calculated couplings for the $3p\pi$ state because, for such low n , the Rydberg model for the electronic wave functions would be too unreliable. However we can say with some assurance that the observed high autoionization rate of the $R(L)$ line of the $D(3p\pi$, $v = 6)$ state need not surprise us, and that seemingly capricious violations of the vibrational propensity rule can probably be used to locate states with high autoionization rates but low intensity in absorption spectra.

In conclusion, we may mention the kinds of data with which one may expect to draw useful comparison between experimental and theoretical results on vibronic autoionization and predissociation. One can soon expect to compare absorption and autoionization line widths, and hopefully, relative intensities of broadened absorption and autoionization lines, in order to compare the relative rates of predissociation and autoionization. One can also look forward to using frequency perturbations in Rydberg spectral series to locate states and give experimental values for the strengths of some of the coupling terms.

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