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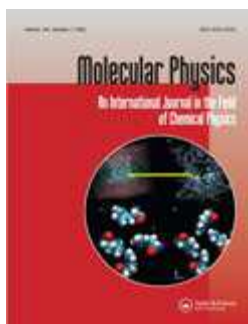
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**Dissociation and predissociation in the ns 1B1 and np 1A2 series of H₂O**

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Dissociation and predissociation in the $ns\ ^1B_1$ and $np\ ^1A_2$ series of H_2O .

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Abstract

It is shown how a carefully devised quantum defect function can be used to unify direct dissociation of the lowest member of a Rydberg series, with predissociation of the higher vibronic states. Results obtained by the techniques of multichannel quantum defect theory (MQDT) are compared with those of a simpler Fano golden rule approximation. A simplified model calculation for the $ns\ ^1B_1$ series of H_2O and D_2O yields results in good accord with experiment, and a dramatic isotope effect is explained. A similar application to the elusive $np\ ^1A_2$ series leads to the prediction of sharp rotational structure for the $np\ ^1A_2(000)$ bands with $n \geq 4$, despite the evidence of a very broad Franck-Condon profile for the dissociative $3p\ ^1A_2$ state. A band at 90051 cm^{-1} in the 2+1 REMPI spectrum is tentatively assigned to the 4p member of this 1A_2 series.

1 Introduction.

The Rydberg spectrum of H_2O is one of the best characterized of any polyatomic species (see [1] for a comprehensive reference list). However problems remain in the analysis of available high resolution spectra [2, 3, 4, 5], possibly because modern experiments rely on the detection of ions, which may be lost by relatively rapid predissociation into neutral fragments, which is known to pervades the entire spectrum [6]. A systematic study of the dissociation and predissociation dynamics is therefore desirable. The lowest energy dissociation pathways must ultimately proceed via excitation of one of the lone pair electrons to either the $4a_1^*$ or $2b_2^*$ antibonding molecular orbital [7], which ‘Rydbergize’ [8] in the spectroscopic region to the $3s a_1$ and $3p b_2$ orbitals respectively. The excitation $3s \leftarrow 1b_1$ gives rise to the $\tilde{A}\ ^1B_1$ state, which is bent at spectroscopically accessible geometries and directly dissociative to $H + OH(X\ ^2\Pi)$, while the $3s \leftarrow 3a_1\ \tilde{B}\ ^1A_1$ state is bound in the absence of molecular rotation, at energies below the $H + OH(A\ ^2\Sigma)$ dissociation threshold, except at linear geometries

where it undergoes a conical intersection with the ground state [9]. The dissociation dynamics of these two states, which includes an important Renner-Teller coupling mechanism [10], have been very fully characterized, both experimentally (see [11]) and theoretically (see [12]). Less attention has been given to the corresponding dynamics of the higher Rydberg states, except to note that similar Renner-Teller coupling between the so far unobserved bent dissociative $3pb_2 \leftarrow 1b_1 \ ^1A_2$ state and its linear $3pb_2 \leftarrow 3a_1 \ ^1B_2$ counterpart allows the observation of only the $K'_a = 0$ branches of the latter state [13, 14]. One also knows that bent $\tilde{D} \ ^1A_1$ and $\tilde{E}' \ ^1B_2$ states are strongly predissociated by configuration interaction with the linear $\tilde{B} \ ^1A_1$ and $3pb_2 \ ^1B_2$ states respectively [15, 16]. In addition quantum state selected predissociation rates for the bent $3pa_1 \tilde{C} \ ^1B_1$, $4s \tilde{D}' \ ^1B_1$ and $3db_2 \tilde{D}'' \ ^1A_2$ states have been reported [17, 18].

As a first step towards extension of the theory to higher members of the Rydberg series, this paper offers a theory for homogeneous predissociation from the $ns \ ^1B_1$ and $npb_2 \ ^1A_2$ states, which are not covered by the above Renner-Teller coupling and configuration interaction mechanisms. The central assumption is that s (or pb_2) quantum defect functions $\mu_s(Q)$ [or $\mu_{pb_2}(Q)$] can be defined in such a way that the family of potential functions

$$V_{n\lambda}(Q) = V^+(Q) - \frac{R_y}{[n - \mu_\lambda(Q)]^2} \quad (1)$$

includes the dissociative $n = 3$ potential surface, as well as the bound surfaces with $n \geq 4$. Within the spirit of MQDT theory [19], vibrational matrix element of $\sin \pi \mu(Q)$ and $\cos \pi \mu(Q)$ may then be used to compute the non-adiabatic coupling strength responsible for the predissociation. Since experiments on the $4s$ state [18] show that the homogeneous linewidth is independent of excitation in the modes, ν_1 and ν_2 , the vibrational coordinates Q in eqn (1) are reduced for simplicity to a single dissociation mode q . The computational method closely follows that used by Jungen [20] and Ross *et al* [21] to describe the competitive predissociation and autoionization of H_2 , although attention is restricted here to energies below the ionization threshold. Simpler golden rule estimates for the linewidths are also derived in order to bring out the physical origin of the dramatic difference between H_2O and D_2O . Implications for changes in the vibrational level structure within the relevant Rydberg series are also discussed.

The paper, starts in section 2, with a brief demonstration of the existence of a quantum defect function, with the desired properties. Section 3 then uses an MQDT treatment of non-adiabatic coupling leads to obtain a Wigner R matrix [22] from which both the $3s$ absorption profile and the higher ns predissociation linewidths may be deduced. Section 3 applies the theory to the ns series of H_2O and D_2O ; and the dramatic linewidth difference between H_2O and D_2O is found to be well reproduced. Golden rule linewidth estimates in Section 4 are shown to be in good agreement with the full MQDT theory, despite significant systematic errors in the resonance energy levels. Application of this perturbation approach to the $npb_2 \ ^1A_2$ indicates very narrow linewidths for the $4p \ ^1A_2(000)$ states of H_2O and D_2O , despite the existence of a very broad $3p \ ^1A_2$ Franck-Condon profile. The tentative assignment of a band attributable to this state in the

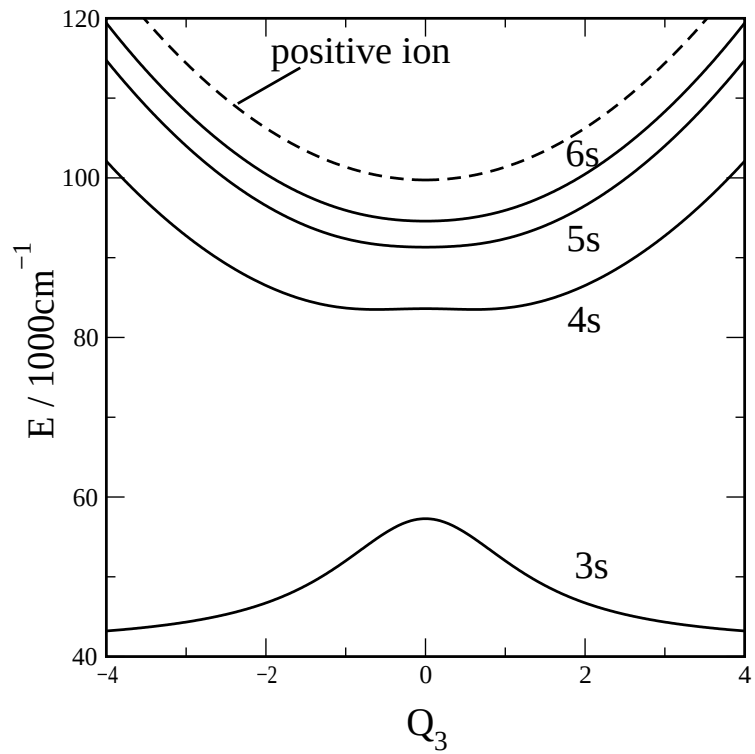


Figure 1: Schematic sections through the ns potential surfaces of H₂O in the direction of the antisymmetric stretching coordinate, Q_3 .

2+1 REMPI spectrum [23] is given. Finally section 6 summarizes the main conclusions, and gives pointers for future research.

2 Potential curves and a quantum defect functions.

Knowledge that the $3s \tilde{A}^1B_1$ state of H₂O is directly dissociative, with two equivalent H + OH products, while the $4s \tilde{D}''^1B_1$ state predissociates sufficiently slowly to allow the observation of resolved rotational structure [18], suggests that a typical section through the manifold of potential surfaces, in the direction of the dissociation mode, q , must take the form in Fig 1.

Such behavior is found to be consistent with eqn (1) if $V^+(q)$ and the quantum defect function $\mu_s(q)$ are taken in the forms

$$V^+(q) = V^+(0) + \frac{\omega}{2}q^2, \tag{2}$$

and

$$\mu_s(q) = 3 - \sqrt{\frac{R_y}{V^+(q) - V_{3s}(q)}} \quad (3)$$

with

$$V_{3s}(q) = A + \frac{B}{1 + \alpha q^2}. \quad (4)$$

The parameter values, which were used to construct Fig 1 are discussed in section 4.

It will be important later to recognize that although the sequence of excited potentials with $n \geq 4$ converges smoothly onto the positive ion potential as $n \rightarrow \infty$, the distorting influence of the quantum defect function, $\mu_s(q)$, has a significant influence on the vibrational level spacings, particularly for $n = 4$ and $n = 5$.

3 MQDT non-adiabatic coupling theory

The non-adiabatic coupling between the dissociative $3s \ ^1B_1$ state and its higher bound $n \geq 4$ counterparts is treated by the method pioneered for the competitive predissociation and auto-ionization of H_2 by Jungen [20] and Ross *et al* [21], except that only states below the ionization limit are treated at this stage, so that the autoionization does not come into play.

The first step is to construct a set of normalized vibrational basis functions $\psi_i(q)$, as eigenfunctions of the truncated positive ion Hamiltonian, taken here as

$$H_{vib} = I + \frac{\omega}{2} \left[\frac{1}{\mu} \hat{p}^2 + q^2 \right], \quad (5)$$

subject to the Sturm-Louville boundary conditions at $q = 0$ and $q = a$. Attention is restricted to the symmetric eigenfunctions, $\psi_i(-q) = \psi_i(q)$, which are optically accessible from the ground vibrational state, by requiring that the $\psi_i(q)$ should have zero derivative at both boundaries. The corresponding antisymmetric solutions would be obtained by setting $\psi_i(q) = 0$ at $q = 0$. The required solutions were obtained in practice by the numerical shooting method [24]. The resulting eigenvalues and boundary amplitudes are denoted as E_i and $\psi_i(a) = u_i$ respectively. Typically 60-80 elements of this basis are required for convergence of the full calculation.

The second step is to introduce the non-adiabatic coupling by trapezium quadrature for the matrix elements

$$C_{vv'} = \langle v | \sin \pi \mu_s(q) | v' \rangle \quad S_{vv'} = \langle v | \cos \pi \mu_s(q) | v' \rangle, \quad (6)$$

followed by solution of the MQDT quantization equations [19]

$$[C \sin \beta(E) + S \cos \beta(E)] Z = 0, \quad (7)$$

where $\sin \beta(E)$ and $\cos \beta(E)$ are a diagonal matrices, with elements given by

$$\beta_i(E) = \pi \nu_i(E) \quad \nu_i(E) = \sqrt{\frac{R_y}{E_i - E}}. \quad (8)$$

The eigenvalues, E_α , of eqn (7) are determined by the compatibility condition

$$\det [C \sin \beta(E) + S \cos \beta(E)] = 0; \quad (9)$$

and the elements of the amplitude vectors Z_α are rescaled and normalized in the form [19]

$$C_{\alpha i} = [\nu_i(E_\alpha)]^{3/2} Z_{\alpha i}, \quad \sum_i C_{\alpha i}^2 = 1, \quad (10)$$

in order to allow for the fact that MQDT is formulated in terms of energy normalized basis functions, whereas we are seeking a set of unit normalized vibronic basis functions, within the finite nuclear coordinate range $0 \leq q \leq a$. The first components, $C_{\alpha 1}$, of the vectors C_α are taken below to determine the Franck-Condon amplitudes for excitation from $v_3 = 0$, because the ground state wavefunction lies entirely within the quantization box..

The power of the theory is that solutions of eqns (7) and (9) in principle include truncated vibrational eigenfunctions of the entire Rydberg series, from $n = 3$ to arbitrarily high n values, although the search for roots of (9) was in practice limited to the energy range $E < V^+(0)$, in order to avoid the complication of the competing autoionization process. Different roots are associated with different principal quantum numbers n . Those belonging to vibrational levels of states with $n \geq 4$ are readily recognized, because one component $C_{\alpha i}$ of the vector C_α is very much larger than the others, and the effective quantum number, $\nu_i(E_\alpha)$, lies close to $n - \mu(0)$, where $\mu(0) = 1.5$, for the present set of parameter values in eqn (2)-(4) (see below). The remaining components of a given vector C_α reflect the strength of non-adiabatic coupling between the different series, a particular element, $C_{\alpha i}$, being assigned to the principal quantum numbers, $n(i)$, which is the closest integer to $\nu_i(E_\alpha) + \mu(0)$. There is also a relatively large residual set of roots, E_α , which are attributable to eigenvalues of the $n = 3$ continuum, truncated at $q = a$.

The third step in the theory is to construct an R matrix for the $n = 3$ continuum of the present model, by the formula

$$R(E) = \sum_\alpha \frac{w_\alpha^2}{E_\alpha - E} + R_b(E), \quad (11)$$

which relates the $n = 3$ continuum function, $\phi_3(E, q)$ to its derivative $\phi_3'(E, q)$, by the equation [22]

$$\phi_3(E, q) = R(E) \phi_3'(E, q). \quad (12)$$

Details of the derivation of eqn (11) and of the form of the Buttle correction, $R_b(E)$, which is introduced to correct for truncation of the continuum basis, are given in the appendix. The amplitudes w_α are obtained by combining the

boundary amplitudes of the vibrational basis, $u_i = \psi_i(a)$, with the components $C_{\alpha i}$ in the form

$$w_\alpha = \sum_{n(i)} C_{\alpha i} u_i, \quad (13)$$

where the prescription for $n(i)$ is given in the previous paragraph. A similar expression is derived in the appendix for the overlap amplitude, $S(E) = \langle \chi | \phi_3(E) \rangle$, between the internal part of $\phi_3(E, q)$ and some other function $\chi(q)$;

$$S(E) = \frac{\omega}{2} \sum_{\alpha} \frac{w_\alpha S_\alpha}{E_\alpha - E} \phi'_3(a) + S_b(E), \quad (14)$$

where, in the present model $S_\alpha = \langle \chi | \phi_\alpha \rangle = C_{\alpha 1} u_1$.

Expressions for the Buttle corrections are given in eqn (A.8) and (A.11) as particle in a box continuum contributions, summed from $N + 1$ to infinity. The cut-off index N was identified by comparing the energy spacing between the last two $n = 3$ continuum contributions to eqns (11), with the particle in a box spacing

$$E_N - E_{N-1} = (2N - 1) \frac{\pi^2 \omega}{2a^2}. \quad (15)$$

The value of N derived from the corresponding difference between the final two MQDT eigenvalues differed from an integer by typically only 5%.

The above results are combined with the energy normalized continuum function

$$\phi_3(E, q) = f(E, q) \cos \pi \tau(E) - g(E, q) \sin \pi \tau(E), \quad (16)$$

where $f(E, q)$ and $g(E, q)$ are defined in appendix B, to obtain the form of the $3s$ absorption profile. The eigenphase $\tau(E)$ is first obtained by combining eqns (11), (14) and (16) at $q = a$, to yield

$$\tan \pi \tau(E) = [g(E, a) - R(E)g'(E, a)]^{-1} [f(E, a) - R(E)f'(E, a)]. \quad (17)$$

The function $|S(E)|^2$ given by eqns (14) and (16) then give the $n = 3$ absorption profile, which is shown in the lower panel of Fig 2. Confirmation that $\int |S(E)|^2 dE \simeq 1$, to within a few percent, is good evidence for the reliability and convergence of the theory.

In addition, although the bound eigenfunctions, with $n \geq 4$, have negligible amplitude at $q = a$, their presence may be detected as local perturbations to $\tau(E)$, arising from the internal non-adiabatic coupling, which are taken into account by eqn (6)-(9). The resulting jumps in $\tau(E)$ are used to estimate the predissociation linewidths. As discussed above, the various poles, E_α , of the R matrix in eqn (11), are readily assigned either to the $3s$ continuum or to vibrational levels of the higher members of the series, which makes it convenient to define a resonant contribution, $\tau_{res}(E)$, as the difference between the term, $\tau(E)$, obtained from the full sum for $S(E)$ and that obtained from the sum over the poles belonging to the continuum. A typical jump in $\tau_{res}(E)$ by π is shown for the $4s(000)$ resonance in the upper left panel of Fig 2. The energy derivative

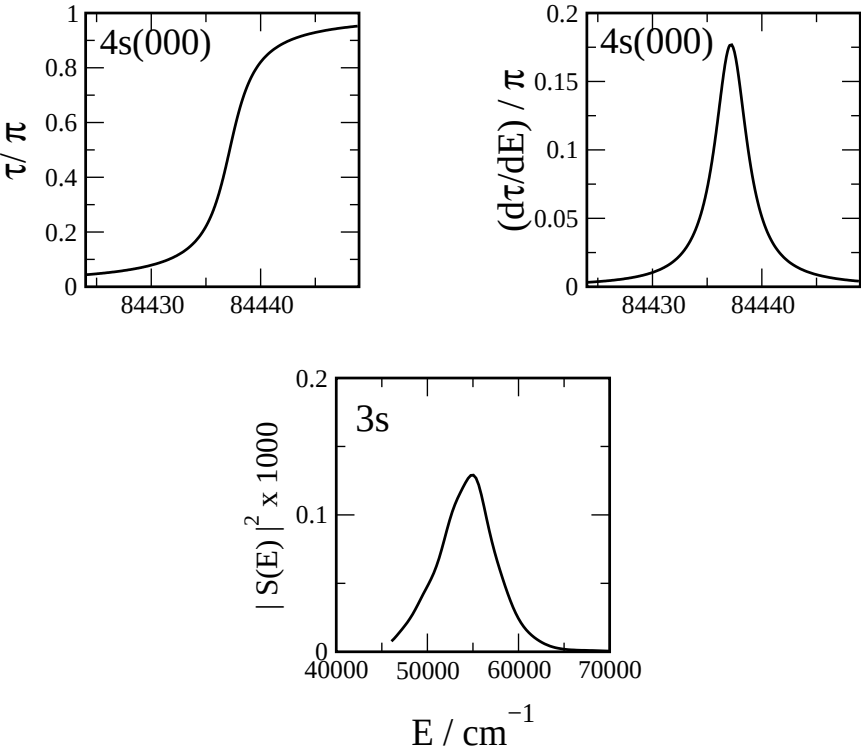


Figure 2: The 3s continuum absorption profile(lower) plus the resonant contribution to the eigenphase $\tau(E)$ (upper left) and its energy derivative (upper right) in the vicinity of the $4s\ ^1B_1(000)$ resonance of H_2O

	H ₂ O	D ₂ O	Ref
$G^X(000)$	4631	3386	[26]
$G^+(000)$	4068	2978	[27]
$G^{OX}(0)$	1848	1349	[28]
I	101766	101916	[29]
D_0	41244		[7]
Γ_{4s}	4.0	0.1	[18]
E_{4s}	84434	84646	[18]
G_{12}^{4s}	2051	1510	[18]

Table 1: Data in cm^{-1} used to determine the parameters of the model

of $\tau_{res}(E)$ then determines the predissociation lineshape, as shown in the right hand upper panel of Fig 2.

4 Application to the $nsa_1 \ ^1B_1$ series

The parameter values in eqns (2)-(4) were determined by reference to the spectroscopic properties of H₂O. With the energy zero taken at the minimum of the ground state potential function,

$$V^+(0) = I + G^X(000) - G^+(000) \quad (18)$$

and

$$A = D_0^{H_2O} + G^X(000) - G^{OH}(0), \quad (19)$$

where I is the ionization energy, D_0 is the dissociation energy and $G^X(000)$, $G^+(000)$ and $G^{OH}(0)$ are the ground state zeropoint energies of H₂O, H₂O⁺ and OH respectively. Numerical values for H₂O and D₂O are given in table 1. The harmonic frequency of the ion core was taken as $\omega = \nu_3 = 3259 \text{ cm}^{-1}$ [25], with the reduced mass in eqn (2) taken as $\mu = 1$ or 2 for H₂O or D₂O respectively. Finally, as discussed below, the parameters B and α in eqn (4) were adjusted to reproduce the absorption frequency and predissociation linewidth of the $4s(000)$ level of H₂O [18]. The resulting numerical values are $V^+(0) = 102329 \text{ cm}^{-1}$, $\omega = 3259 \text{ cm}^{-1}$, $A = 44025 \text{ cm}^{-1}$, $B = 14530 \text{ cm}^{-1}$ and $\alpha = 0.625$. The R matrix boundary radius for the scaled coordinate q was taken as $a = 7$, which corresponds to the turning point of the antisymmetric stretching state of H₂O⁺ with $v_3 = 24$. Typically 80 truncated even harmonic oscillator symmetric eigenfunctions, $\psi_i(q) = \psi_i(-q)$, were used to compute the sine and cosine matrices in eqn (6).

The most striking feature of the calculation is the sensitivity of the predissociation rate to the width parameter, α , of the model potential $V_{3s}(q)$. For

State	H ₂ O			
	MQDT		Golden rule	
	E/cm^{-1}	Γ/cm^{-1}	E/cm^{-1}	Γ/cm^{-1}
4s(000)	84438	4.1	84367	4.0
4s(002)	89271	11.8	89254	10.6
4s(004)	94862	10.6	94851	16.7
5s(000)	92895	0.2	92847	0.7
5s(002)	98799	0.8	98764	1.6
6s(000)	96332	0.1	96327	0.2
State	D ₂ O			
	MQDT		Golden rule	
	E/cm^{-1}	Γ/cm^{-1}	E/cm^{-1}	Γ/cm^{-1}
4s(000)	84671	0.1	84635	0.2
4s(002)	87882	0.7	87863	0.7
4s(004)	91702	4.3	91703	4.3
5s(000)	93049	0.05	93010	0.03
5s(002)	97185	0.3	97109	0.3
6s(000)	96429	0.008	96457	0.008

Table 2: Energy levels and resonance widths.

example the computed linewidth for the $4s \tilde{D}'^1B_1(000)$ state of H₂O increases from 0.02 cm^{-1} at $\alpha = 0.1$ to 0.8 cm^{-1} at $\alpha = 0.3$ and to the observed value [18] of 4 cm^{-1} at $\alpha = 0.625$. The width of the absorption profile also increases from 2900 cm^{-1} at $\alpha = 0.1$ to 4800 cm^{-1} at $\alpha = 0.3$ and 6700 cm^{-1} at $\alpha = 0.625$. The parameter B in eqn (4), which fixes the height of the $3s$ potential barrier in Fig 1 was adjusted to bring the computed $4s \tilde{D}'^1B_1(000)$ energy level into close agreement with the experimental value of 84434 cm^{-1} , after adding a term, $G_{12}(0,0)$, to account for zeropoint contributions from the neglected ν_1 and ν_2 modes. In the absence of other information, this latter term was taken as $G_{12}(0,0) = G^+(000) - \omega_3^+/2 - x_{33}^+/4$, where the superscript ‘+’ implies values for the positive ion - giving values of 2361 and 1704 cm^{-1} for H₂O and D₂O respectively.

The results of the calculation are presented in Fig 2 and table 2. It is seen from the lower panel of Fig 2 that the $3s$ absorption profile peaks at 55000 cm^{-1} with a width at half height of 6700 cm^{-1} , which may be compared with the experimental values of 60500 cm^{-1} and 7200 cm^{-1} [30]. The width is therefore well reproduced and the main contribution to the discrepancy in the peak positions

probably arises from the assumption of an energy independent quantum defect function, because *ab initio* estimates [31] of the vertical excitation energies between the 3s and 4s potential surfaces indicates a decrease in the quantum defect from $\mu = 1.31$ to 1.21, which is well in line with a calculated jump in the s quantum defect of NO by 0.1 units, attributable to core polarization effects at energies where the *d* channels open, an effect that is very well established for NO [32, 33].

The variations between the predissociation linewidths in Table 2 are the main focus of the paper. The parameters of the model were optimized to reproduce the experimentally observed value, $\Gamma = 4 \text{ cm}^{-1}$ for the 4s(000) state of H₂O [18], but it is striking that the very much smaller experimental value, $\Gamma = 0.05 \text{ cm}^{-1}$, for D₂O is also well reproduced. The physical origin of this dramatic isotope effect is examined in section 4 below. The fact that the calculated 4s(000) energy is higher than the experimental value of 84646 cm^{-1} by 25 cm^{-1} is attributable to neglect of any interaction between the ν_3 mode and the ν_1 and ν_2 degrees of freedom. One also sees that the predissociation linewidth typically increases with increasing excitation of the ν_3 mode, and decreases with increasing electronic excitation.

Another significant feature of table 2, with regard to future analysis of the spectrum, is that the lower, $n = 4$ and $n = 5$, bound potential curves are strongly anharmonic, as might be expected from the functional dependence of $V_{ns}(q)$ on the quantum defect in eqn (1). For example the ν_3 contributions to the zeropoint energy, deduced from potential minima, consistent with $\mu(0) = 1.5834$, increase roughly proportional to n^{-5} from 822 cm^{-1} at $n = 4$ to 1630 cm^{-1} for the positive ion, in the case of H₂O. The corresponding figures for D₂O are 477 cm^{-1} at $n = 4$ and 1152 cm^{-1} for the positive ion. Similarly the intervals between the 4s(000), (002) and (004) levels of H₂O take the values 4833 cm^{-1} and 5591 cm^{-1} , compared with a uniform interval of 6518 cm^{-1} for the positive ion.

5 Non-adiabatic perturbation theory

While the above MQDT based theory is fully non-perturbative, it is hard to trace the physical origin of resulting variations in predissociation linewidths and resonance energies. To obtain a more physically transparent picture, it is assumed that the nuclear wavefunctions, $\chi_i(q)$, are determined by the adiabatic potential functions, given by eqn (1), and that the linewidths are estimated by the following non-adiabatic golden rule formula:

$$\Gamma_i = 2\pi |H'_{ij}|^2, \quad (20)$$

where

$$H'_{ij} = \frac{\omega}{2\mu} \int_0^\infty \left[\chi_i(q) B_{ij}(q) \frac{d\chi_j}{dq} + \chi_j(q) B_{ji}(q) \frac{d\chi_i}{dq} \right] dq. \quad (21)$$

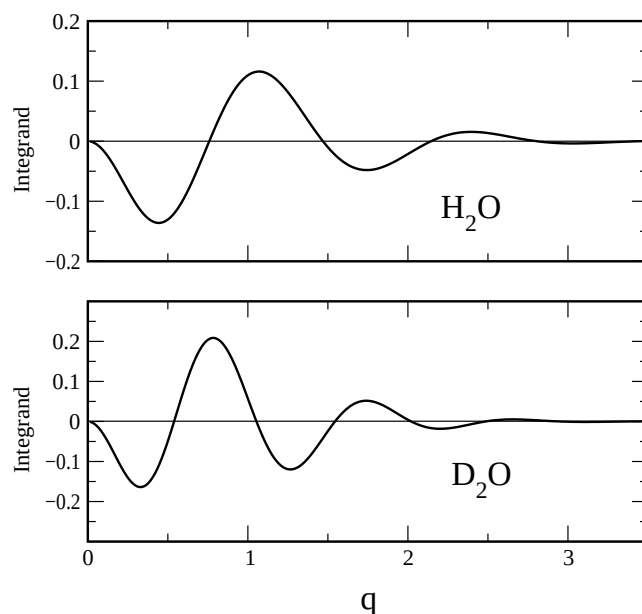


Figure 3: Integrands of eqn (21) for predissociation of the $4s \tilde{D}'(000) {}^1B_1$ states of H_2O and D_2O .

Following Stolyarov and Child [34] the electronic coupling terms are approximated as

$$B_{ij}(q) = -B_{ji}(q) \simeq \frac{2\mu'_s(q)\sqrt{\nu_i(q)\nu_j(q)}}{\nu_i(q)^2 - \nu_j^2(q)} \quad (22)$$

in which $\mu'_s(q)$ is the derivative of the quantum defect function in eqn (3) and $\nu_i(q) = n_i - \mu_s(q)$. The bound vibrational wavefunction, $\chi_i(q)$, is normalized to unity and the continuum function is taken to have the asymptotic form

$$\chi_j(q) \sim \sqrt{\frac{2\mu}{\pi\omega k}} \cos(kq + \delta), \quad k^2 = \frac{2\mu[E - V_{3s}(\infty)]}{\omega}, \quad (23)$$

which ensures normalization to an energy delta function.

Application to the $ns {}^1B_1$ series

It is seen from table 2 that the resulting golden rule linewidth estimates are in good order of magnitude agreement with the full MQDT model. One can also understand the dramatic difference between the linewidths of the two isotopologues, by plotting the integrands of eqn (21) in Fig 3. The essential difference is that the de Broglie wavelength of the continuum wavefunction is very much smaller for the heavier isotope, which leads to more complete cancellation of the integral. However, despite the good agreement with respect to the linewidths, one should notice that the golden rule eigenvalues, in the right hand column

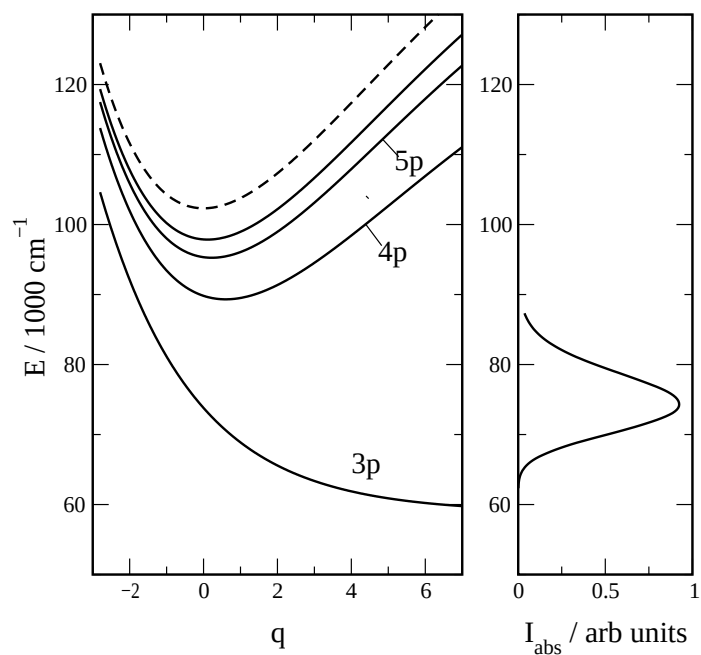


Figure 4: Schematic view of the adiabatic potential curves for the $npb_2 \leftarrow 1b_1$ 1A_2 series of H_2O . The right hand panel shows the $npb_2 \leftarrow 1b_1$ absorption profile. Energies are measured from the minimum of the ground state potential.

of table 2 show significant systematic differences from the full MQDT resonance energies because the perturbation approach neglects level shifts arising from non-adiabatic coupling to the 3s continuum, which leads to a systematic upward shift of the MQDT energies. In addition the MQDT method allows for vibronic perturbations between higher vibrational levels of a low electronic state and lower levels of a higher state, which are ignored in the perturbation approach.

Application to the $npb_2 \ ^1A_2$ series.

In the absence of experimental information, it is unjustified to apply the full MQDT method to the $npb_2 \leftarrow 1b_1 \ ^1A_2$ series, but the perturbation method may be used to illustrate some interesting points. In the first place the the Wigner-Witmer rules [7] require the lowest 1A_2 state to dissociate to $O(^1D) + H_2$ fragments. The dissociation mode, q , is therefore a combination of the symmetric stretching and bending degrees of freedom. Consequently the the Lorentzian form for the dissociative potential function in eqn (4) is replaced, for the purpose of illustration by a decaying exponential,

$$V_{3pb_2}(q) = A + Be^{-\alpha q}, \quad (24)$$

and the positive ion potential is taken in the scaled Morse form

$$V^+(q) = V^+(0) + \omega_1 d(1 - e^{-\beta q})^2, \quad (25)$$

with $\beta = 1/\sqrt{2d}$. With energies measured from the minimum of the ground state potential, the parameter values $A = 58900 \text{ cm}^{-1}$, $B = 14900 \text{ cm}^{-1}$, $\omega_1 = 49600 \text{ cm}^{-1}$ and $d = 21$ were chosen to be consistent with the $O(^1D) + H_2$ dissociation limit, the calculated [31] vertical excitation energy to the $3p \ ^1A_2$ state and the Morse parameters for the symmetric stretching mode of H_2O^+ [27]. Ideally one might have *ab initio* information on the exponent α in eqn (24) but Theodorakopoulos *et al* [35] follow only the first excited state of 1A_2 symmetry, along the $O(^1D) + H_2$ dissociation coordinate. In the absence of other information, the value $\alpha = 0.4$ was taken for illustrative purposes.

The resulting potential curves are shown in the left hand panel of Fig 4. Notice that the present model, implied by eqns (1), (3), (24) and (25) results in a significant distortion of the shapes of the lower $n \geq 4$ curves, from that of the parent ion. The right hand panel shows the computed the $3p \ ^1A_2$ Franck-Condon profile, which is seen to have a width of roughly 10000 cm^{-1} - even larger than for absorption to the $3s \ \tilde{A} \ ^1B_1$ state. The implied lifetime of 0.5 fs, in the Frank-Condon region, is fully consistent with the absence of any discernible $3p \ ^1A_2$ peak in the 3+1 MPI spectrum [18]. Any viable detection scheme would need to monitor either the $O(^1D)$ or the H_2 fragment.

The second point concerns the predissociation linewidths for $n \geq 4$, which are predicted to be substantially smaller than those for the $nsa_1 \ ^1B_1$ series. The estimate depends on the choice of α , with values of $2 \times 10^{-4} \text{ cm}^{-1}$ and $2 \times 10^{-5} \text{ cm}^{-1}$ for H_2O and D_2O respectively for $\alpha = 0.4$, rising to $2 \times 10^{-2} \text{ cm}^{-1}$ and $2 \times 10^{-3} \text{ cm}^{-1}$ respectively for $\alpha = 0.6$. Hence even if these estimates were

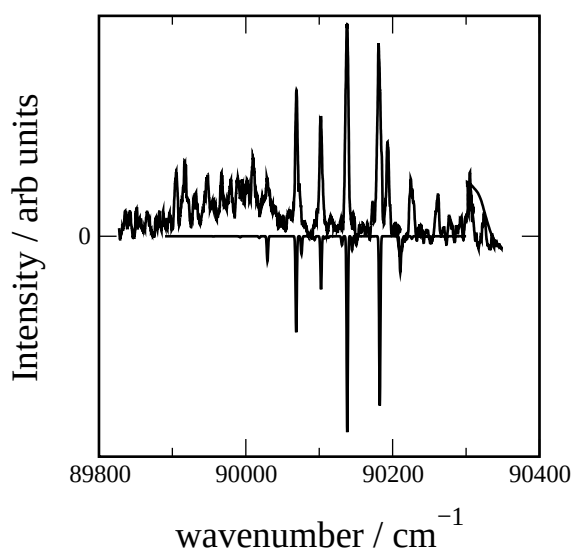


Figure 5: A fragment of the unassigned 2+1 REMPI spectrum of Dickinson *et al* [23], compared with the (inverted) $4p\ 1A_2 \leftarrow X\ ^1A_1$ simulation.

increased by two orders of magnitude, the bands, whose origins are predicted to lie in the range $90000\text{--}92000\text{ cm}^{-1}$ would be expected to show observable rotational structure. Inspection of the recent 2+1 REMPI spectrum, recorded by Dickinson *et al* [23], suggests a plausible candidate with an origin at 90051 cm^{-1} . A simulation based on the known rotational constants of H_2O [36] and H_2O^+ [25] is shown in Fig ?? . Although there are too few lines for a convincing analysis, further investigation of this spectral range would be of considerable interest, as the first indication of definitive information on this elusive $np\ A_2$ series.

6 Summary and conclusions

A model MQDT based theory of homogeneous predissociation throughout a given Rydberg series has been based on a quantum defect function of the nuclear coordinates, which encompasses both the lowest dissociative electronic state of the series and all higher bound members of the series. Test results for a one dimensional model of the $nsa_1\ ^1B_1$ series of H_2O correctly reproduce an observed [18] dramatic difference between the predissociation linewidths of the $4s(000)\ ^1B_1$ states of H_2O and D_2O , as well as the correct width of the $3s$ continuum absorption profile [30]. An important consequence of the model, for future spectroscopic analysis, is the prediction of much stronger vibrational anharmonicity in the lower $ns\ ^1B_1$ states, than in the positive ion, to which the

series converges.

A golden rule perturbation formula, which closely approximated the MQDT linewidths, was used to obtain a clearer physical understanding of the origin of the observed isotope effect. The shorter de Broglie wavelength of the continuum wavefunction of the heavier isotopic species was seen to be the deciding factor. The perturbation approach was also applied to the elusive $npb_2\ ^1A_2$ series. One important difference from the $ns\ ^1B_1$ case is that the dissociative $3p\ ^1A_2$ state correlates with $O(^1D) + H_2$ rather than $H + OH$ fragments. The Franck-Condon profile, which was predicted to be somewhat wider than that for the $3s\ ^1B_1$ state, implies a lifetime ~ 0.5 fs - much too short for detection by 3+1 MPI spectroscopy [18]. On the other hand the $4p(000)$ states of H_2O and D_2O , with band origins in the range 90000 - 92000 cm^{-1} , were predicted to show sharp rotational structure. A tentative candidate for this band at 90051 cm^{-1} was identified.

The strength of the present primitive model is that the R matrix, which carries information about the predissociation linewidths, can be computed for arbitrarily high energies by extending the theory to include the competitive autoionization process [20, 21]. The weaknesses are that it is currently formulated in a one dimensional approximation and that it applies only to homogeneous predissociation within a given Rydberg series. The extension to three vibrational dimensions is largely a matter of computational effort. The tacit assumption that the neglected symmetric stretching and bending modes of the $ns\ ^1B_1$ series are identical to those of H_2O^+ cannot be strictly valid, although the families of *ab initio* bending potentials [37, 38, 39] show no marked deviations from one state to the next. Strictly however one requires the full nuclear coordinate dependence of the quantum defect function, most likely from *ab initio* information on the lowest electronic state of the relevant symmetry, if eqn (3) is accepted. Systems involving two equivalent dissociation channels, such as the $ns\ ^1B_1$ series also raise questions about the nature of the dissociation coordinate, because the dissociation to $H + OH$ proceeds along a local mode coordinate, rather than the antisymmetric stretching mode. The difference may be small in practice, if one is concerned only with the predissociation rate, rather than the quantum state dependence of the fragments, but a proper formulation would be in terms of symmetrized local mode wavefunctions [40].

Extension of the theory to include Renner-Teller coupling is also planned for the future, although much work remains to be done. An accurate Renner-Teller treatment for the two lowest states of H_2O^+ , on well converged potential surfaces, was performed some years ago [41]. The strong K_a dependence of the coupling appears in the composition of the resulting two component wavefunctions, truncated versions of which would provide the vibrational basis for computation of sine and cosine matrices, analogous to those in eqn (6). The relevant expressions would however appear as 2×2 matrix contractions, rather than simple integrals. Construction of the dissociative R matrix and extraction of the predissociation linewidths would follow the lines of section 3, though no doubt with many complications of detail. It is also planned to use the present framework to handle configuration interaction and Coriolis induced predissoci-

ation.

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Appendices

A The R matrix and Buttle corrections

Derivation of the Wigner R matrix, that relates solutions $\phi_E(x)$ of the Schrodinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + V(q) \right] \phi_E = E \phi_E \quad (\text{A.1})$$

to their derivatives at $q = a$, involves a Green's function argument to obtain [22]

$$\phi_E(q) = \frac{\hbar^2}{2m} \sum_{\alpha} \frac{\phi_{\alpha}(a) \phi_{\alpha}(q)}{E_{\alpha} - E} \phi'_E(a) \quad 0 \leq q \leq a, \quad (\text{A.2})$$

where the sum is taken over a complete orthonormal set of $\phi_n(q)$ with vanishing derivatives at $q = a$. Specialization to the point $q = a$, together with the substitution $\hbar^2/2m \rightarrow \omega/2\mu$ to conform with the kinetic energy term in (5) leads to $\phi_E(a) = R(E) \phi'_E(a)$, with

$$R(E) = \frac{\omega}{2\mu} \sum_{\alpha} \frac{\phi_{\alpha}(a) \phi_{\alpha}(a)}{E_{\alpha} - E}. \quad (\text{A.3})$$

In addition the overlap of $\phi_E(q)$ with any other function $\chi(q)$ that vanishes for $q > a$ is given by

$$S(E) = \langle \chi | \phi_E \rangle = \frac{\omega}{2\mu} \sum_{\alpha} \frac{\phi_{\alpha}(a) \langle \chi | \phi_{\alpha} \rangle}{E_{\alpha} - E} \phi'_E(a). \quad (\text{A.4})$$

Buttle corrections

Eqn (A.3) and (A.4) are of limited practical value as they stand, because it is essential that the sums should be taken over a complete set. However, it frequently happens that the eigenvalue spectrum, for the final few members of the accessible finite set, approaches that of the 'particle in a box' eigenfunctions, with the same boundary conditions - taken for the present model as $\phi^{(0)'}(q) = 0$ at $q = 0$ and $q = a$. The relevant eigenfunctions are

$$\phi_0^{(0)}(q) = \sqrt{\frac{1}{a}} \quad \phi_n^{(0)}(q) = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi q}{a}\right), \quad (\text{A.5})$$

with energies

$$E_n^{(0)} = \frac{n^2 \pi^2 \omega}{2\mu a^2}; \quad (\text{A.6})$$

and it is easy to verify that

$$\begin{aligned} R^{(0)}(E_\nu) &= \frac{\omega}{2\mu} \sum_n \frac{\phi_n^{(0)}(a) \phi_n^{(0)}(a)}{E_n^{(0)} - E_\nu^{(0)}} \\ &= -\frac{a}{\nu\pi} \left[\frac{1}{\nu\pi} + \frac{2\nu}{\pi} \sum_{n=1}^{\infty} \frac{1}{\nu^2 - n^2} \right] \\ &= -\frac{a}{\nu\pi} \cot \nu\pi, \end{aligned} \quad (\text{A.7})$$

where the final line is taken from eqn 1.421.3 of Gradshteyn and Ryzhik [42]. The following Buttle correction may therefore be introduced, to add a tail contribution over $n = [N+1, \infty]$ to the truncated sum in eqn (A.3),

$$R_b(E_\nu) = \frac{\omega}{2\mu} \sum_{n=N+1}^{\infty} \frac{\phi_n^{(0)}(a) \phi_n^{(0)}(a)}{E_n^{(0)} - E_\nu^{(0)}} = \frac{a}{\nu\pi} \left[\frac{1}{\nu\pi} - \cot \nu\pi + \frac{2\nu}{\pi} \sum_{n=1}^N \frac{1}{\nu^2 - n^2} \right]. \quad (\text{A.8})$$

A similar argument may be used to obtain a Buttle-like correction to sum in eqn (A.4) for the overlap $S = \langle \chi | \phi_E \rangle$, in the case that $\chi(q)$ is the scaled harmonic oscillator zero-point eigenfunction, normalized over the interval $q = [0, \infty]$

$$\chi(q) = \left(\frac{4}{\pi} \right)^{1/4} \exp\left(-\frac{q^2}{2}\right). \quad (\text{A.9})$$

To the extent that $\chi(q)$ has negligible amplitude at $q = a$, the required elementary integrals are given by

$$\langle \chi | \phi_0^{(0)} \rangle = \sqrt{\frac{\pi}{a^2}} \quad \langle \chi | \phi_\nu^{(0)} \rangle = \sqrt{\frac{4\pi}{a^2}} \exp\left[-\frac{\nu^2 \pi^2}{2a^2}\right], \quad (\text{A.10})$$

from which a tail contribution to the sum in eqn (A.4) may be deduced as

$$\begin{aligned} S_b(E_\nu) &= \frac{\omega}{2\mu} \sum_{n=N+1}^{\infty} \frac{\phi_n^{(0)}(a) \langle \chi | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_\nu^{(0)}} \phi_E^{(0)'}(a) \\ &= \sqrt{\frac{4\pi}{a^2}} \left[e^{-\nu^2 \pi^2 / 2a^2} - \frac{\nu \sin \pi\nu}{\pi} \left\{ \frac{1}{\nu^2} + 2 \sum_{n=1}^N \frac{(-1)^n e^{-n^2 \pi^2 / 2a^2}}{\nu^2 - n^2} \right\} \right]. \end{aligned} \quad (\text{A.11})$$

Numerical tests readily confirm the validity of the underlying infinite series for $\exp[-\nu^2 \pi^2 / 2a^2]$.

B MQDT continuum basis functions

The basis functions, required to normalize the eigenfunctions of the $n = 3$ continuum to a delta function of energy, were taken as solutions of eqn (A.1), with $V(q) = V_{3s}(q)$ and $\hbar^2/2m = \omega/2\mu$. The two solutions were written in the phase-amplitude forms [43, 44]

$$\begin{aligned} f(E, q) &= \sqrt{(2\mu/\pi\omega)}\alpha(q)\sin\xi(q) \\ g(E, q) &= \sqrt{(2\mu/\pi\omega)}\alpha(q)\cos\xi(q), \end{aligned} \quad (\text{B.1})$$

where $\xi'(q) = [\alpha(q)]^{-2}$ and the factors under the square roots ensure normalization to an energy delta function in the present unit system. The function $f(E, q)$ was defined to have zero derivative at $q = 0$ and $\alpha(q)$ and $\xi(q)$ were determined by propagating $f(E, q)$ and $f'(E, q)$ out to a sufficiently large q value that $V(q)$ is constant. The connection between $\alpha(q)$ and $\xi'(q)$ is then assured by setting $\alpha(q) = [2\mu\{(E - V(q))/\omega\}]^{-1/2}$ and the required normalization factor is chosen to ensure that

$$[f^2(E, q)/\alpha^2(q)] + [f'(E, q)\alpha^2(q)] = 2\mu/\pi\omega, \quad (\text{B.2})$$

and

$$\tan\xi(q) = \frac{f(E, q)}{\alpha^2(q)f'(E, q)}. \quad (\text{B.3})$$

The functions $g(E, q)$ and $g'(E, q)$ were then constructed to be consistent with eqn (B.1). Finally $f(E, q)$, $g(E, q)$ and their derivatives were propagated back to $q = a$.

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Dissociation and predissociation in the $ns\ ^1B_1$ and $np\ ^1A_2$ series of H_2O .

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Abstract

It is shown how a carefully devised quantum defect function can be used to unify direct dissociation of the lowest member of a Rydberg series, with predissociation of the higher vibronic states. Results, for a one dimensional model, obtained by the techniques of multichannel quantum defect theory (MQDT) are compared with those of a simpler Fano golden rule approximation. A simplified model calculation for the $ns\ ^1B_1$ series of H_2O and D_2O yields results in good accord with experiment, and a dramatic isotope effect is explained. A similar application to the elusive $np\ ^1A_2$ series leads to the prediction of sharp rotational structure for the $np\ ^1A_2(000)$ bands with $n \geq 4$, despite the evidence of a very broad Franck-Condon profile for the dissociative $3p\ ^1A_2$ state. A band at 90051 cm^{-1} in the 2+1 REMPI spectrum is tentatively assigned to the $4p$ member of this 1A_2 series.

1 Introduction.

The Rydberg spectrum of H_2O is one of the best characterized of any polyatomic species (see [1] for a comprehensive reference list). However problems remain in the analysis of available high resolution spectra [2, 3, 4, 5], possibly because modern experiments rely on the detection of ions, which may be lost by relatively rapid predissociation into neutral fragments, which is known to pervades the entire spectrum [6]. A systematic study of the dissociation and predissociation dynamics is therefore desirable. The lowest energy dissociation pathways must ultimately proceed via excitation of one of the lone pair electrons to either the $4a_1^*$ or $2b_2^*$ antibonding molecular orbital [7], which ‘Rydbergize’ [8] in the spectroscopic region to the $3sa_1$ and $3pb_2$ orbitals respectively. The excitation $3s \leftarrow 1b_1$ gives rise to the $\tilde{A}\ ^1B_1$ state, which is bent at spectroscopically accessible geometries and directly dissociative to $H + OH(X\ ^2\Pi)$, while the $3s \leftarrow 3a_1\ \tilde{B}\ ^1A_1$ state is bound in the absence of molecular rotation, at energies

below the $\text{H} + \text{OH}(\text{A } ^2\Sigma)$ dissociation threshold, except at linear geometries where it undergoes a conical intersection with the ground state [9]. The dissociation dynamics of these two states, which includes an important Renner-Teller coupling mechanism [10], have been very fully characterized, both experimentally (see [11]) and theoretically (see [12]). Less attention has been given to the corresponding dynamics of the higher Rydberg states, except to note that similar Renner-Teller coupling between the so far unobserved bent dissociative $3\text{pb}_2 \leftarrow 1\text{b}_1 \text{ } ^1\text{A}_2$ state and its linear $3\text{pb}_2 \leftarrow 3\text{a}_1 \text{ } ^1\text{B}_2$ counterpart allows the observation of only the $K'_a = 0$ branches of the latter state [13, 14]. One also knows that bent $\tilde{\text{D}} \text{ } ^1\text{A}_1$ and $\tilde{\text{E}}' \text{ } ^1\text{B}_2$ states are strongly predissociated by configuration interaction with the linear $\tilde{\text{B}} \text{ } ^1\text{A}_1$ and $3\text{pb}_2 \text{ } ^1\text{B}_2$ states respectively [15, 16]. In addition quantum state selected predissociation rates for the bent $3\text{pa}_1 \tilde{\text{C}} \text{ } ^1\text{B}_1$, $4\text{s } \tilde{\text{D}}' \text{ } ^1\text{B}_1$ and $3\text{db}_2 \tilde{\text{D}}'' \text{ } ^1\text{A}_2$ states have been reported [17, 18].

As a first step towards extension of the theory to higher members of the Rydberg series, this paper offers a theory for homogeneous predissociation from the $\text{ns } ^1\text{B}_1$ and $\text{npb}_2 \text{ } ^1\text{A}_2$ states, which are not covered by the above Renner-Teller coupling and configuration interaction mechanisms. The central assumption is that s (or pb_2) quantum defect functions $\mu_s(Q)$ [or $\mu_{\text{pb}_2}(Q)$] can be defined in such a way that the family of potential functions

$$V_{n\lambda}(Q) = V^+(Q) - \frac{R_y}{[n - \mu_\lambda(Q)]^2} \quad (1)$$

includes the dissociative $n = 3$ potential surface, as well as the bound surfaces with $n \geq 4$. Within the spirit of MQDT theory [19], vibrational matrix element of $\sin \pi \mu(Q)$ and $\cos \pi \mu(Q)$ may then be used to compute the non-adiabatic coupling strength responsible for the predissociation. Since experiments on the 4s state [18] show that the homogeneous linewidth is independent of excitation in the modes, ν_1 and ν_2 , the vibrational coordinates Q in eqn (1) are reduced for simplicity to a single dissociation mode q . The computational method closely follows that used by Jungen [20] and Ross *et al* [21] to describe the competitive predissociation and autoionization of H_2 , although attention is restricted here to energies below the ionization threshold. Simpler golden rule estimates for the linewidths are also derived in order to bring out the physical origin of the dramatic difference between H_2O and D_2O . Implications for changes in the vibrational level structure within the relevant Rydberg series are also discussed.

The paper, starts in section 2, with a brief demonstration of the existence of a quantum defect function, with the desired properties. Section 3 then uses an MQDT treatment of non-adiabatic coupling leads to obtain a Wigner R matrix [22] from which both the 3s absorption profile and the higher ns predissociation linewidths may be deduced. Section 3 applies the theory to the ns series of H_2O and D_2O ; and the dramatic linewidth difference between H_2O and D_2O is found to be well reproduced. Golden rule linewidth estimates in Section 4 are shown to be in good agreement with the full MQDT theory, despite significant systematic errors in the resonance energy levels. Application of this perturbation approach to the $\text{npb}_2 \text{ } ^1\text{A}_2$ indicates very narrow linewidths for the $4\text{p } ^1\text{A}_2(000)$ states of H_2O and D_2O , despite the existence of a very broad $3\text{p } ^1\text{A}_2$ Franck-Condon

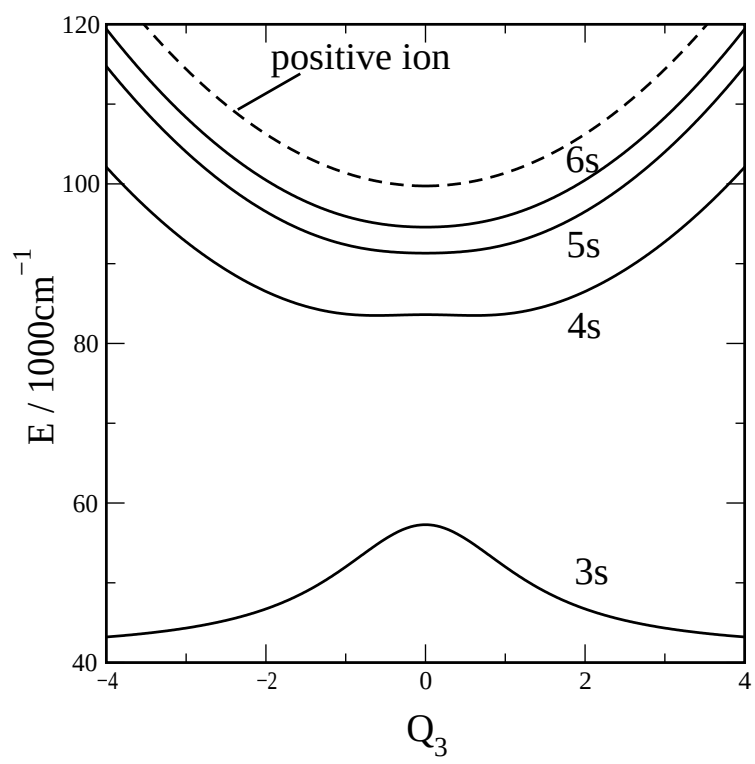


Figure 1: Schematic sections through the ns potential surfaces of H₂O in the direction of the antisymmetric stretching coordinate, Q_3 .

profile. The tentative assignment of a band attributable to this state in the 2+1 REMPI spectrum [23] is given. Finally section 6 summarizes the main conclusions, and gives pointers for future research.

2 Potential curves and a quantum defect functions.

Knowledge that the $3s \tilde{A}^1B_1$ state of H₂O is directly dissociative, with two equivalent H + OH products, while the $4s \tilde{D}''^1B_1$ state predissociates sufficiently slowly to allow the observation of resolved rotational structure [18], suggests that a typical section through the manifold of potential surfaces, in the direction of the dissociation mode, q , must take the form in Fig 1.

Such behavior is found to be consistent with eqn (1) if $V^+(q)$ and the quantum defect function $\mu_s(q)$ are taken in the forms

$$V^+(q) = V^+(0) + \frac{\omega}{2}q^2, \tag{2}$$

and

$$\mu_s(q) = 3 - \sqrt{\frac{R_y}{V^+(q) - V_{3s}(q)}} \quad (3)$$

with

$$V_{3s}(q) = A + \frac{B}{1 + \alpha q^2}. \quad (4)$$

The parameter values, which were used to construct Fig 1 are discussed in section 4.

It will be important later to recognize that although the sequence of excited potentials with $n \geq 4$ converges smoothly onto the positive ion potential as $n \rightarrow \infty$, the distorting influence of the quantum defect function, $\mu_s(q)$, has a significant influence on the vibrational level spacings, particularly for $n = 4$ and $n = 5$.

3 MQDT non-adiabatic coupling theory

The non-adiabatic coupling between the dissociative $3s \ ^1B_1$ state and its higher bound $n \geq 4$ counterparts is treated by the method pioneered for the competitive predissociation and auto-ionization of H_2 by Jungen [20] and Ross *et al* [21], except that only states below the ionization limit are treated at this stage, so that the autoionization does not come into play.

The first step is to construct a set of normalized vibrational basis functions $\psi_i(q)$, as eigenfunctions of the truncated positive ion Hamiltonian, taken here as

$$H_{vib} = I + \frac{\omega}{2} \left[\frac{1}{\mu} \hat{p}^2 + q^2 \right], \quad (5)$$

subject to the Sturm-Louville boundary conditions at $q = 0$ and $q = a$. Attention is restricted to the symmetric eigenfunctions, $\psi_i(-q) = \psi_i(q)$, which are optically accessible from the ground vibrational state, by requiring that the $\psi_i(q)$ should have zero derivative at both boundaries. The corresponding antisymmetric solutions would be obtained by setting $\psi_i(q) = 0$ at $q = 0$. The required solutions were obtained in practice by the numerical shooting method [24]. The resulting eigenvalues and boundary amplitudes are denoted as E_i and $\psi_i(a) = u_i$ respectively. Typically 60-80 elements of this basis are required for convergence of the full calculation.

The second step is to introduce the non-adiabatic coupling by trapezium quadrature for the matrix elements

$$C_{vv'} = \langle v | \sin \pi \mu_s(q) | v' \rangle \quad S_{vv'} = \langle v | \cos \pi \mu_s(q) | v' \rangle, \quad (6)$$

followed by solution of the MQDT quantization equations [19]

$$[C \sin \beta(E) + S \cos \beta(E)] Z = 0, \quad (7)$$

where $\sin \beta(E)$ and $\cos \beta(E)$ are a diagonal matrices, with elements given by

$$\beta_i(E) = \pi \nu_i(E) \quad \nu_i(E) = \sqrt{\frac{R_y}{E_i - E}}. \quad (8)$$

The eigenvalues, E_α , of eqn (7) are determined by the compatibility condition

$$\det [C \sin \beta(E) + S \cos \beta(E)] = 0; \quad (9)$$

and the elements of the amplitude vectors Z_α are rescaled and normalized in the form [19]

$$C_{\alpha i} = [\nu_i(E_\alpha)]^{3/2} Z_{\alpha i}, \quad \sum_i C_{\alpha i}^2 = 1, \quad (10)$$

in order to allow for the fact that MQDT is formulated in terms of energy normalized basis functions, whereas we are seeking a set of unit normalized vibronic basis functions, within the finite nuclear coordinate range $0 \leq q \leq a$. The first components, $C_{\alpha 1}$, of the vectors C_α are taken below to determine the Franck-Condon amplitudes for excitation from $v_3 = 0$, because the ground state wavefunction lies entirely within the quantization box..

The power of the theory is that solutions of eqns (7) and (9) in principle include truncated vibrational eigenfunctions of the entire Rydberg series, from $n = 3$ to arbitrarily high n values, although the search for roots of (9) was in practice limited to the energy range $E < V^+(0)$, in order to avoid the complication of the competing autoionization process. Different roots are associated with different principal quantum numbers n . Those belonging to vibrational levels of states with $n \geq 4$ are readily recognized, because one component $C_{\alpha i}$ of the vector C_α is very much larger than the others, and the effective quantum number, $\nu_i(E_\alpha)$, lies close to $n - \mu(0)$, where $\mu(0) = 1.5$, for the present set of parameter values in eqn (2)-(4) (see below). The remaining components of a given vector C_α reflect the strength of non-adiabatic coupling between the different series, a particular element, $C_{\alpha i}$, being assigned to the principal quantum numbers, $n(i)$, which is the closest integer to $\nu_i(E_\alpha) + \mu(0)$. There is also a relatively large residual set of roots, E_α , which are attributable to eigenvalues of the $n = 3$ continuum, truncated at $q = a$.

The third step in the theory is to construct an R matrix for the $n = 3$ continuum of the present model, by the formula

$$R(E) = \sum_\alpha \frac{w_\alpha^2}{E_\alpha - E} + R_b(E), \quad (11)$$

which relates the $n = 3$ continuum function, $\phi_3(E, q)$ to its derivative $\phi_3'(E, q)$, by the equation [22]

$$\phi_3(E, q) = R(E) \phi_3'(E, q). \quad (12)$$

Details of the derivation of eqn (11) and of the form of the Buttle correction, $R_b(E)$, which is introduced to correct for truncation of the continuum basis, are given in the appendix. The amplitudes w_α are obtained by combining the

boundary amplitudes, at $q = a$, of the vibrational basis, $u_i = \psi_i(a)$, with the components $C_{\alpha i}$ in the form

$$w_\alpha = \sum_{n(i)} C_{\alpha i} u_i, \quad (13)$$

where the prescription for $n(i)$ is given in the previous paragraph. A similar expression is derived in the appendix for the overlap amplitude, $S(E) = \langle \chi | \phi_3(E) \rangle$, between the internal part of $\phi_3(E, q)$ and some other function $\chi(q)$;

$$S(E) = \frac{\omega}{2} \sum_{\alpha} \frac{w_\alpha S_\alpha}{E_\alpha - E} \phi'_3(a) + S_b(E), \quad (14)$$

where, in the present model $S_\alpha = \langle \chi | \phi_\alpha \rangle = C_{\alpha 1} u_1$.

Expressions for the Buttle corrections are given in eqn (A.8) and (A.11) as particle in a box continuum contributions, summed from $N + 1$ to infinity. The cut-off index N was identified by comparing the energy spacing between the last two $n = 3$ continuum contributions to eqns (11), with the particle in a box spacing

$$E_N - E_{N-1} = (2N - 1) \frac{\pi^2 \omega}{2a^2}. \quad (15)$$

The value of N derived from the corresponding difference between the final two MQDT eigenvalues differed from an integer by typically only 5%.

The above results are combined with the energy normalized continuum function

$$\phi_3(E, q) = f(E, q) \cos \pi \tau(E) - g(E, q) \sin \pi \tau(E), \quad (16)$$

where $f(E, q)$ and $g(E, q)$ are defined in appendix B, to obtain the form of the 3s absorption profile. The eigenphase $\tau(E)$ is first obtained by combining eqns (11), (14) and (16) at $q = a$, to yield

$$\tan \pi \tau(E) = [g(E, a) - R(E)g'(E, a)]^{-1} [f(E, a) - R(E)f'(E, a)']. \quad (17)$$

The function $|S(E)|^2$ given by eqns (14) and (16) then give the $n = 3$ absorption profile, which is shown in the lower panel of Fig 2. Confirmation that $\int |S(E)|^2 dE \simeq 1$, to within a few percent, is good evidence for the reliability and convergence of the theory.

In addition, although the bound ns eigenfunctions, with $n \geq 4$, have negligible amplitude at $q = a$, their presence may be detected as local perturbations to $\tau(E)$, arising from the internal non-adiabatic coupling, which are taken into account by eqn (6)-(9). The resulting jumps in $\tau(E)$ are used to estimate the predissociation linewidths. As discussed above, the various poles, E_α , of the R matrix in eqn (11), are readily assigned either to the 3s continuum or to vibrational levels of the higher members of the series, which makes it convenient to define a resonant contribution, $\tau_{res}(E)$, as the difference between the term, $\tau(E)$, obtained from the full sum for $S(E)$ and that obtained from the sum over the poles belonging to the continuum. A typical jump in $\tau_{res}(E)$ by π is shown

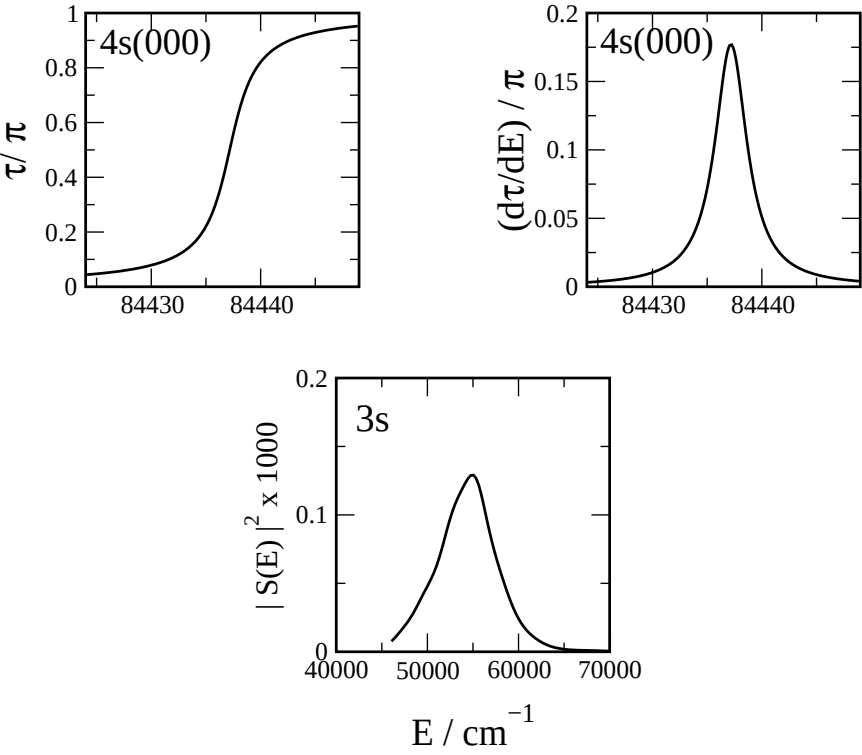


Figure 2: The 3s continuum absorption profile(lower) plus the resonant contribution to the eigenphase $\tau(E)$ (upper left) and its energy derivative (upper right) in the vicinity of the $4s\ ^1B_1(000)$ resonance of H_2O

	H ₂ O	D ₂ O	Ref
$G^X(000)$	4631	3386	[26]
$G^+(000)$	4068	2978	[27]
$G^{OX}(0)$	1848	1349	[28]
I	101766	101916	[29]
D_0	41244		[7]
Γ_{4s}	4.0	0.1	[18]
E_{4s}	84434	84646	[18]
G_{12}^{4s}	2051	1510	[18]

Table 1: Data in cm^{-1} used to determine the parameters of the model

for the $4s(000)$ resonance in the upper left panel of Fig 2. The energy derivative of $\tau_{res}(E)$ then determines the predissociation lineshape, as shown in the right hand upper panel of Fig 2.

4 Application to the $nsa_1 \ ^1B_1$ series

The parameter values in eqns (2)-(4) were determined by reference to the spectroscopic properties of H₂O. With the energy zero taken at the minimum of the ground state potential function,

$$V^+(0) = I + G^X(000) - G^+(000) \quad (18)$$

and

$$A = D_0^{H_2O} + G^X(000) - G^{OH}(0), \quad (19)$$

where I is the ionization energy, D_0 is the dissociation energy and $G^X(000)$, $G^+(000)$ and $G^{OH}(0)$ are the ground state zero-point energies of H₂O, H₂O⁺ and OH respectively. Numerical values for H₂O and D₂O are given in table 1. The harmonic frequency of the ion core was taken as $\omega = \nu_3 = 3259 \text{ cm}^{-1}$ [25], with the reduced mass in eqn (2) taken as $\mu = 1$ or 2 for H₂O or D₂O respectively. Finally, as discussed below, the parameters B and α in eqn (4) were adjusted to reproduce the absorption frequency and predissociation linewidth of the $4s(000)$ level of H₂O [18]. The resulting numerical values are $V^+(0) = 102329 \text{ cm}^{-1}$, $\omega = 3259 \text{ cm}^{-1}$, $A = 44025 \text{ cm}^{-1}$, $B = 14530 \text{ cm}^{-1}$ and $\alpha = 0.625$. The R matrix boundary radius for the scaled coordinate q was taken as $a = 7$, which corresponds to the turning point of the antisymmetric stretching state of H₂O⁺ with $v_3 = 24$. Typically 80 truncated even harmonic oscillator symmetric eigenfunctions, $\psi_i(q) = \psi_i(-q)$, were used to compute the sine and cosine matrices in eqn (6).

State	H ₂ O			
	MQDT		Golden rule	
	E/cm^{-1}	Γ/cm^{-1}	E/cm^{-1}	Γ/cm^{-1}
4s(000)	84438	4.1	84367	4.0
4s(002)	89271	11.8	89254	10.6
4s(004)	94862	10.6	94851	16.7
5s(000)	92895	0.2	92847	0.7
5s(002)	98799	0.8	98764	1.6
6s(000)	96332	0.1	96327	0.2
State	D ₂ O			
	MQDT		Golden rule	
	E/cm^{-1}	Γ/cm^{-1}	E/cm^{-1}	Γ/cm^{-1}
4s(000)	84671	0.1	84635	0.2
4s(002)	87882	0.7	87863	0.7
4s(004)	91702	4.3	91703	4.3
5s(000)	93049	0.05	93010	0.03
5s(002)	97185	0.3	97109	0.3
6s(000)	96429	0.008	96457	0.008

Table 2: Energy levels and resonance widths.

The most striking feature of the calculation is the sensitivity of the predissociation rate to the width parameter, α , of the model potential $V_{3s}(q)$. For example the computed linewidth for the $4s \tilde{D}'^1B_1(000)$ state of H_2O increases from 0.02 cm^{-1} at $\alpha = 0.1$ to 0.8 cm^{-1} at $\alpha = 0.3$ and to the observed value [18] of 4 cm^{-1} at $\alpha = 0.625$. The width of the absorption profile also increases from 2900 cm^{-1} at $\alpha = 0.1$ to 4800 cm^{-1} at $\alpha = 0.3$ and 6700 cm^{-1} at $\alpha = 0.625$. The parameter B in eqn (4), which fixes the height of the $3s$ potential barrier in Fig 1 was adjusted to bring the computed $4s \tilde{D}'^1B_1(000)$ energy level into close agreement with the experimental value of 84434 cm^{-1} , after adding a term, $G_{12}(0,0)$, to account for zeropoint contributions from the neglected ν_1 and ν_2 modes. In the absence of other information, this latter term was taken as $G_{12}(0,0) = G^+(000) - \omega_3^+/2 - x_{33}^+/4$, where the superscript ‘+’ implies values for the positive ion - giving values of 2361 and 1704 cm^{-1} for H_2O and D_2O respectively.

The results of the calculation are presented in Fig 2 and table 2. It is seen from the lower panel of Fig 2 that the $3s$ absorption profile peaks at 55000 cm^{-1} with a width at half height of 6700 cm^{-1} , which may be compared with the experimental values of 60500 cm^{-1} and 7200 cm^{-1} [30]. The width is therefore well

reproduced and the main contribution to the discrepancy in the peak positions probably arises from the assumption of an energy independent quantum defect function, because *ab initio* estimates [31] of the vertical excitation energies between the 3s and 4s potential surfaces indicates a decrease in the quantum defect from $\mu = 1.31$ to 1.21, which is well in line with a calculated jump in the s quantum defect of NO by 0.1 units, attributable to core polarization effects at energies where the *d* channels open, an effect that is very well established for NO [32, 33].

The variations between the predissociation linewidths in Table 2 are the main focus of the paper. The parameters of the model were optimized to reproduce the experimentally observed value, $\Gamma = 4 \text{ cm}^{-1}$ for the 4s(000) state of H₂O [18], but it is striking that the very much smaller experimental value, $\Gamma = 0.05 \text{ cm}^{-1}$, for D₂O is also well reproduced. The physical origin of this dramatic isotope effect is examined in section 4 below. The fact that the calculated 4s(000) energy is higher than the experimental value of 84646 cm^{-1} by 25 cm^{-1} is attributable to neglect of any interaction between the ν_3 mode and the ν_1 and ν_2 degrees of freedom. One also sees that the predissociation linewidth typically increases with increasing excitation of the ν_3 mode, and decreases with increasing electronic excitation.

Another significant feature of table 2, with regard to future analysis of the spectrum, is that the lower, $n = 4$ and $n = 5$, bound potential curves are strongly anharmonic, as might be expected from the functional dependence of $V_{ns}(q)$ on the quantum defect in eqn (1). For example the ν_3 contributions to the zeropoint energy, deduced from potential minima, consistent with $\mu(0) = 1.5834$, increase roughly proportional to n^{-5} from 822 cm^{-1} at $n = 4$ to 1630 cm^{-1} for the positive ion, in the case of H₂O. The corresponding figures for D₂O are 477 cm^{-1} at $n = 4$ and 1152 cm^{-1} for the positive ion. Similarly the intervals between the 4s(000), (002) and (004) levels of H₂O take the values 4833 cm^{-1} and 5591 cm^{-1} , compared with a uniform interval of 6518 cm^{-1} for the positive ion.

5 Non-adiabatic perturbation theory

While the above MQDT based theory is fully non-perturbative, it is hard to trace the physical origin of resulting variations in predissociation linewidths and resonance energies. To obtain a more physically transparent picture, it is assumed that the nuclear wavefunctions, $\chi_i(q)$, are determined by the adiabatic potential functions, given by eqn (1), and that the linewidths are estimated by the following non-adiabatic golden rule formula:

$$\Gamma_i = 2\pi |H'_{ij}|^2, \quad (20)$$

where

$$H'_{ij} = \frac{\omega}{2\mu} \int_0^\infty \left[\chi_i(q) B_{ij}(q) \frac{d\chi_j}{dq} + \chi_j(q) B_{ji}(q) \frac{d\chi_i}{dq} \right] dq. \quad (21)$$

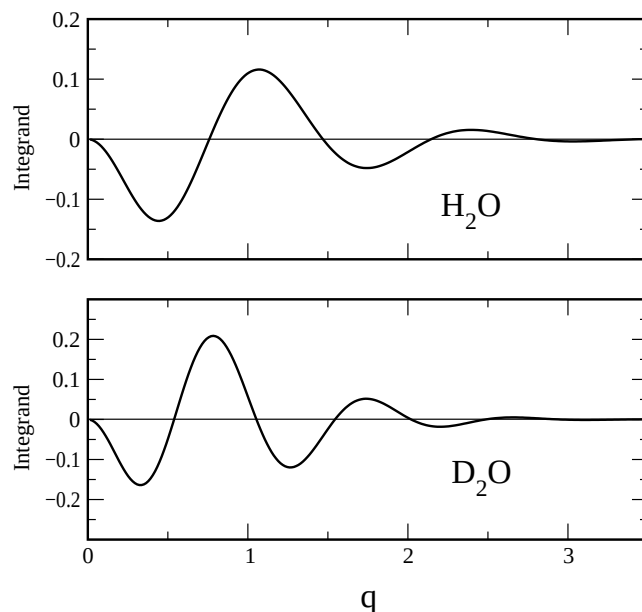


Figure 3: Integrands of eqn (21) for predissociation of the $4s \tilde{D}'(000) {}^1B_1$ states of H_2O and D_2O .

Following Stolyarov and Child [34] the electronic coupling terms are approximated as

$$B_{ij}(q) = -B_{ji}(q) \simeq \frac{2\mu'_s(q)\sqrt{\nu_i(q)\nu_j(q)}}{\nu_i(q)^2 - \nu_j^2(q)} \quad (22)$$

in which $\mu'_s(q)$ is the derivative of the quantum defect function in eqn (3) and $\nu_i(q) = n_i - \mu_s(q)$. The bound vibrational wavefunction, $\chi_i(q)$, is normalized to unity and the continuum function is taken to have the asymptotic form

$$\chi_j(q) \sim \sqrt{\frac{2\mu}{\pi\omega k}} \cos(kq + \delta), \quad k^2 = \frac{2\mu[E - V_{3s}(\infty)]}{\omega}, \quad (23)$$

which ensures normalization to an energy delta function.

Application to the $ns {}^1B_1$ series

It is seen from table 2 that the resulting golden rule linewidth estimates are in good order of magnitude agreement with the full MQDT model. One can also understand the dramatic difference between the linewidths of the two isotopologues, by plotting the integrands of eqn (21) in Fig 3. The essential difference is that the de Broglie wavelength of the continuum wavefunction is very much smaller for the heavier isotope, which leads to more complete cancellation of the integral. However, despite the good agreement with respect to the linewidths, one should notice that the golden rule eigenvalues, in the right hand column

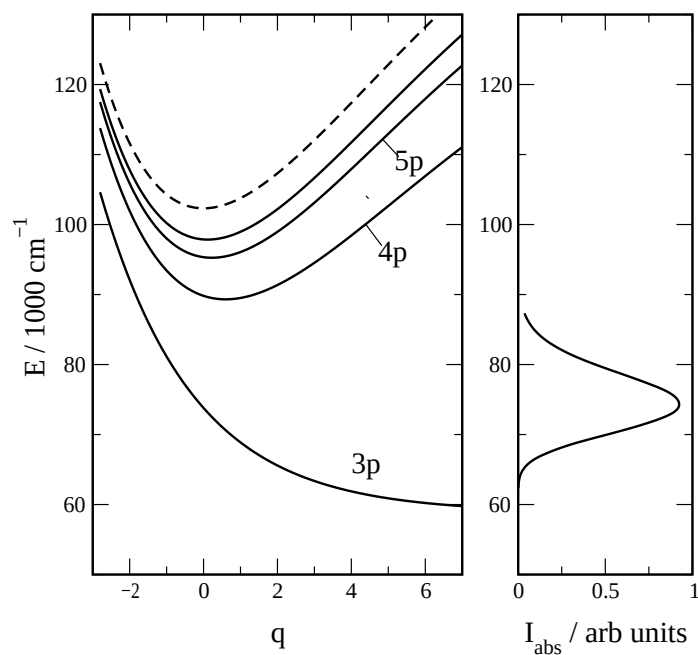


Figure 4: Schematic view of the adiabatic potential curves for the $npb_2 \leftarrow 1b_1$ 1A_2 series of H_2O . The right hand panel shows the $npb_2 \leftarrow 1b_1$ absorption profile. Energies are measured from the minimum of the ground state potential.

of table 2 show significant systematic differences from the full MQDT resonance energies because the perturbation approach neglects level shifts arising from non-adiabatic coupling to the 3s continuum, which leads to a systematic upward shift of the MQDT energies. In addition the MQDT method allows for vibronic perturbations between higher vibrational levels of a low electronic state and lower levels of a higher state, which are ignored in the perturbation approach.

Application to the $npb_2 \ ^1A_2$ series.

In the absence of experimental information, it is unjustified to apply the full MQDT method to the $npb_2 \leftarrow 1b_1 \ ^1A_2$ series, but the perturbation method may be used to illustrate some interesting points. In the first place the the Wigner-Witmer rules [7] require the lowest 1A_2 state to dissociate to $O(^1D) + H_2$ fragments. The dissociation mode, q , is therefore a combination of the symmetric stretching and bending degrees of freedom. Consequently the the Lorentzian form for the dissociative potential function in eqn (4) is replaced, for the purpose of illustration by a decaying exponential,

$$V_{3pb_2}(q) = A + Be^{-\alpha q}, \quad (24)$$

and the positive ion potential is taken in the scaled Morse form

$$V^+(q) = V^+(0) + \omega_1 d(1 - e^{-\beta q})^2, \quad (25)$$

with $\beta = 1/\sqrt{2d}$. With energies measured from the minimum of the ground state potential, the parameter values $A = 58900 \text{ cm}^{-1}$, $B = 14900 \text{ cm}^{-1}$, $\omega_1 = 49600 \text{ cm}^{-1}$ and $d = 21$ were chosen to be consistent with the $O(^1D) + H_2$ dissociation limit, the calculated [31] vertical excitation energy to the $3p \ ^1A_2$ state and the Morse parameters for the symmetric stretching mode of H_2O^+ [27]. Ideally one might have *ab initio* information on the exponent α in eqn (24) but Theodorakopoulos *et al* [35] follow only the first excited state of 1A_2 symmetry, along the $O(^1D) + H_2$ dissociation coordinate. In the absence of other information, the value $\alpha = 0.4$ was taken for illustrative purposes.

The resulting potential curves are shown in the left hand panel of Fig 4. Notice that the present model, implied by eqns (1), (3), (24) and (25) results in a significant distortion of the shapes of the lower $n \geq 4$ curves, from that of the parent ion. The right hand panel shows the computed the $3p \ ^1A_2$ Franck-Condon profile, which is seen to have a width of roughly 10000 cm^{-1} - even larger than for absorption to the $3s \ \tilde{A} \ ^1B_1$ state. The implied lifetime of 0.5 fs, in the Frank-Condon region, is fully consistent with the absence of any discernible $3p \ ^1A_2$ peak in the 3+1 MPI spectrum [18]. Any viable detection scheme would need to monitor either the $O(^1D)$ or the H_2 fragment.

The second point concerns the predissociation linewidths for $n \geq 4$, which are predicted to be substantially smaller than those for the $nsa_1 \ ^1B_1$ series. The estimate depends on the choice of α , with values of $2 \times 10^{-4} \text{ cm}^{-1}$ and $2 \times 10^{-5} \text{ cm}^{-1}$ for H_2O and D_2O respectively for $\alpha = 0.4$, rising to $2 \times 10^{-2} \text{ cm}^{-1}$ and $2 \times 10^{-3} \text{ cm}^{-1}$ respectively for $\alpha = 0.6$. Hence even if these estimates were

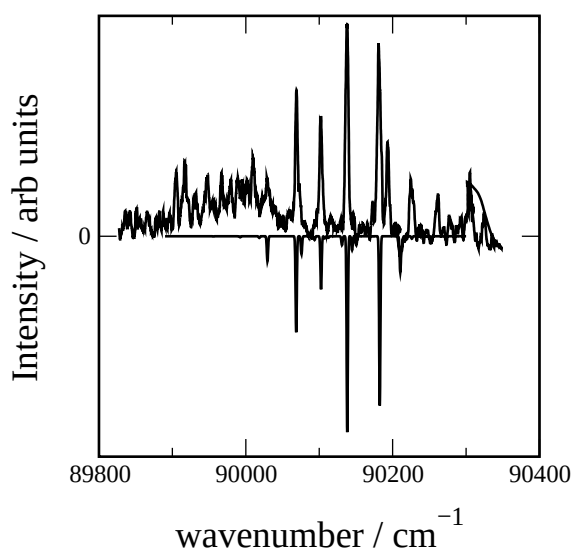


Figure 5: A fragment of the unassigned 2+1 REMPI spectrum of Dickinson *et al* [23], compared with the (inverted) $4p\ 1A_2 \leftarrow X\ 1A_1$ simulation.

increased by two orders of magnitude, the bands, whose origins are predicted to lie in the range $90000\text{--}92000\text{ cm}^{-1}$ would be expected to show observable rotational structure. Inspection of the recent 2+1 REMPI spectrum, recorded by Dickinson *et al* [23], suggests a plausible candidate with an origin at 90051 cm^{-1} . A simulation based on the known rotational constants of H_2O [36] and H_2O^+ [25] is shown in Fig 5. Although there are too few lines for a convincing analysis, further investigation of this spectral range would be of considerable interest, as the first indication of definitive information on this elusive $np\ A_2$ series.

6 Summary and conclusions

A model MQDT based theory of homogeneous predissociation throughout a given Rydberg series has been based on a quantum defect function of the nuclear coordinates, which encompasses both the lowest dissociative electronic state of the series and all higher bound members of the series. Test results for a one dimensional model of the $nsa_1\ 1B_1$ series of H_2O correctly reproduce an observed [18] dramatic difference between the predissociation linewidths of the $4s(000)\ 1B_1$ states of H_2O and D_2O , as well as the correct width of the $3s$ continuum absorption profile [30]. An important consequence of the model, for future spectroscopic analysis, is the prediction of much stronger vibrational anharmonicity in the lower $ns\ 1B_1$ states, than in the positive ion, to which the

series converges.

A golden rule perturbation formula, which closely approximated the MQDT linewidths, was used to obtain a clearer physical understanding of the origin of the observed isotope effect. The shorter de Broglie wavelength of the continuum wavefunction of the heavier isotopic species was seen to be the deciding factor. The perturbation approach was also applied to the elusive $npb_2\ ^1A_2$ series. One important difference from the $ns\ ^1B_1$ case is that the dissociative $3p\ ^1A_2$ state correlates with $O(^1D) + H_2$ rather than $H + OH$ fragments. The Franck-Condon profile, which was predicted to be somewhat wider than that for the $3s\ ^1B_1$ state, implies a lifetime ~ 0.5 fs - much too short for detection by 3+1 MPI spectroscopy [18]. On the other hand the $4p(000)$ states of H_2O and D_2O , with band origins in the range 90000 - 92000 cm^{-1} , were predicted to show sharp rotational structure. A tentative candidate for this band at 90051 cm^{-1} was identified.

The strength of the present primitive model is that the R matrix, which carries information about the predissociation linewidths, can be computed for arbitrarily high energies by extending the theory to include the competitive autoionization process [20, 21]. The weaknesses are that it is currently formulated in a one dimensional approximation and that it applies only to homogeneous predissociation within a given Rydberg series. The extension to three vibrational dimensions is largely a matter of computational effort. The tacit assumption that the neglected symmetric stretching and bending modes of the $ns\ ^1B_1$ series are identical to those of H_2O^+ cannot be strictly valid, although the families of *ab initio* bending potentials [37, 38, 39] show no marked deviations from one state to the next. Strictly however one requires the full nuclear coordinate dependence of the quantum defect function, most likely from *ab initio* information on the lowest electronic state of the relevant symmetry, if eqn (3) is accepted. Systems involving two equivalent dissociation channels, such as the $ns\ ^1B_1$ series also raise questions about the nature of the dissociation coordinate, because the dissociation to $H + OH$ proceeds along a local mode coordinate, rather than the antisymmetric stretching mode. The difference may be small in practice, if one is concerned only with the predissociation rate, rather than the quantum state dependence of the fragments, but a proper formulation would be in terms of symmetrized local mode wavefunctions [40].

Extension of the theory to include Renner-Teller coupling is also planned for the future, although much work remains to be done. An accurate Renner-Teller treatment for the two lowest states of H_2O^+ , on well converged potential surfaces, was performed some years ago [41]. The strong K_a dependence of the coupling appears in the composition of the resulting two component wavefunctions, truncated versions of which would provide the vibrational basis for computation of sine and cosine matrices, analogous to those in eqn (6). The relevant expressions would however appear as 2×2 matrix contractions, rather than simple integrals. Construction of the dissociative R matrix and extraction of the predissociation linewidths would follow the lines of section 3, though no doubt with many complications of detail. It is also planned to use the present framework to handle configuration interaction and Coriolis induced predissoci-

ation.

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Appendices

A The R matrix and Buttlet corrections

Derivation of the Wigner R matrix, that relates solutions $\phi_E(x)$ of the Schrodinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + V(q) \right] \phi_E = E \phi_E \quad (\text{A.1})$$

to their derivatives at $q = a$, involves a Green's function argument to obtain [22]

$$\phi_E(q) = \frac{\hbar^2}{2m} \sum_{\alpha} \frac{\phi_{\alpha}(a) \phi_{\alpha}(q)}{E_{\alpha} - E} \phi'_E(a) \quad 0 \leq q \leq a, \quad (\text{A.2})$$

where the sum is taken over a complete orthonormal set of $\phi_n(q)$ with vanishing derivatives at $q = a$. Specialization to the point $q = a$, together with the substitution $\hbar^2/2m \rightarrow \omega/2\mu$ to conform with the kinetic energy term in (5) leads to $\phi_E(a) = R(E) \phi'_E(a)$, with

$$R(E) = \frac{\omega}{2\mu} \sum_{\alpha} \frac{\phi_{\alpha}(a) \phi_{\alpha}(a)}{E_{\alpha} - E}. \quad (\text{A.3})$$

In addition the overlap of $\phi_E(q)$ with any other function $\chi(q)$ that vanishes for $q > a$ is given by

$$S(E) = \langle \chi | \phi_E \rangle = \frac{\omega}{2\mu} \sum_{\alpha} \frac{\phi_{\alpha}(a) \langle \chi | \phi_{\alpha} \rangle}{E_{\alpha} - E} \phi'_E(a). \quad (\text{A.4})$$

Buttlet corrections

Eqn (A.3) and (A.4) are of limited practical value as they stand, because it is essential that the sums should be taken over a complete set. However, it frequently happens that the eigenvalue spectrum, for the final few members of the accessible finite set, approaches that of the 'particle in a box' eigenfunctions, with the same boundary conditions - taken for the present model as $\phi^{(0)'}(q) = 0$ at $q = 0$ and $q = a$. The relevant eigenfunctions are

$$\phi_0^{(0)}(q) = \sqrt{\frac{1}{a}} \quad \phi_n^{(0)}(q) = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi q}{a}\right), \quad (\text{A.5})$$

with energies

$$E_n^{(0)} = \frac{n^2 \pi^2 \omega}{2\mu a^2}; \quad (\text{A.6})$$

and it is easy to verify that

$$\begin{aligned} R^{(0)}(E_\nu) &= \frac{\omega}{2\mu} \sum_n \frac{\phi_n^{(0)}(a) \phi_n^{(0)}(a)}{E_n^{(0)} - E_\nu^{(0)}} \\ &= -\frac{a}{\nu\pi} \left[\frac{1}{\nu\pi} + \frac{2\nu}{\pi} \sum_{n=1}^{\infty} \frac{1}{\nu^2 - n^2} \right] \\ &= -\frac{a}{\nu\pi} \cot \nu\pi, \end{aligned} \quad (\text{A.7})$$

where the final line is taken from eqn 1.421.3 of Gradshteyn and Ryzhik [42]. The following Buttle correction may therefore be introduced, to add a tail contribution over $n = [N+1, \infty]$ to the truncated sum in eqn (A.3),

$$R_b(E_\nu) = \frac{\omega}{2\mu} \sum_{n=N+1}^{\infty} \frac{\phi_n^{(0)}(a) \phi_n^{(0)}(a)}{E_n^{(0)} - E_\nu^{(0)}} = \frac{a}{\nu\pi} \left[\frac{1}{\nu\pi} - \cot \nu\pi + \frac{2\nu}{\pi} \sum_{n=1}^N \frac{1}{\nu^2 - n^2} \right]. \quad (\text{A.8})$$

A similar argument may be used to obtain a Buttle-like correction to sum in eqn (A.4) for the overlap $S = \langle \chi | \phi_E \rangle$, in the case that $\chi(q)$ is the scaled harmonic oscillator zero-point eigenfunction, normalized over the interval $q = [0, \infty]$

$$\chi(q) = \left(\frac{4}{\pi} \right)^{1/4} \exp\left(-\frac{q^2}{2}\right). \quad (\text{A.9})$$

To the extent that $\chi(q)$ has negligible amplitude at $q = a$, the required elementary integrals are given by

$$\langle \chi | \phi_0^{(0)} \rangle = \sqrt{\frac{\pi}{a^2}} \quad \langle \chi | \phi_\nu^{(0)} \rangle = \sqrt{\frac{4\pi}{a^2}} \exp\left[-\frac{\nu^2 \pi^2}{2a^2}\right], \quad (\text{A.10})$$

from which a tail contribution to the sum in eqn (A.4) may be deduced as

$$\begin{aligned} S_b(E_\nu) &= \frac{\omega}{2\mu} \sum_{n=N+1}^{\infty} \frac{\phi_n^{(0)}(a) \langle \chi | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_\nu^{(0)}} \phi_E^{(0)'}(a) \\ &= \sqrt{\frac{4\pi}{a^2}} \left[e^{-\nu^2 \pi^2 / 2a^2} - \frac{\nu \sin \pi\nu}{\pi} \left\{ \frac{1}{\nu^2} + 2 \sum_{n=1}^N \frac{(-1)^n e^{-n^2 \pi^2 / 2a^2}}{\nu^2 - n^2} \right\} \right]. \end{aligned} \quad (\text{A.11})$$

Numerical tests readily confirm the validity of the underlying infinite series for $\exp[-\nu^2 \pi^2 / 2a^2]$.

B MQDT continuum basis functions

The basis functions, required to normalize the eigenfunctions of the $n = 3$ continuum to a delta function of energy, were taken as solutions of eqn (A.1), with $V(q) = V_{3s}(q)$ and $\hbar^2/2m = \omega/2\mu$. The two solutions were written in the phase-amplitude forms [43, 44]

$$\begin{aligned} f(E, q) &= \sqrt{(2\mu/\pi\omega)}\alpha(q)\sin\xi(q) \\ g(E, q) &= \sqrt{(2\mu/\pi\omega)}\alpha(q)\cos\xi(q), \end{aligned} \quad (\text{B.1})$$

where $\xi'(q) = [\alpha(q)]^{-2}$ and the factors under the square roots ensure normalization to an energy delta function in the present unit system. The function $f(E, q)$ was defined to have zero derivative at $q = 0$ and $\alpha(q)$ and $\xi(q)$ were determined by propagating $f(E, q)$ and $f'(E, q)$ out to a sufficiently large q value that $V(q)$ is constant. The connection between $\alpha(q)$ and $\xi'(q)$ is then assured by setting $\alpha(q) = [2\mu\{(E - V(q))/\omega\}]^{-1/2}$ and the required normalization factor is chosen to ensure that

$$[f^2(E, q)/\alpha^2(q)] + [f'(E, q)\alpha^2(q)] = 2\mu/\pi\omega, \quad (\text{B.2})$$

and

$$\tan\xi(q) = \frac{f(E, q)}{\alpha^2(q)f'(E, q)}. \quad (\text{B.3})$$

The functions $g(E, q)$ and $g'(E, q)$ were then constructed to be consistent with eqn (B.1). Finally $f(E, q)$, $g(E, q)$ and their derivatives were propagated back to $q = a$.

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