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ABSTRACT

Rates of autoionization of H_2 near threshold is calculated within an internal conversion model. The present calculation remedies the apparent inability of the model to predict desirable rates as calculated by previous authors. Results are obtained which compare fairly well with the experimental estimates of Chupka and Berkowitz and alternative calculations of Berry and Nielsen for $\Delta\nu_{if} = 1$ and 2. The results explicitly show the $\frac{1}{n^3}$ dependence of rates for increasing principal quantum numbers n and follows the socalled 'propensity rule' for vibrational quanta involved. Unlike other theoretical calculations the present model provides a simple formula from which the rates may easily be calculated. Limitations and possible refinements of the model are discussed and generalisations for diatomic molecules other than H_2, is indicated.

AUTOIONIZATION OF H_2 NEAR THRESHOLD

I. INTRODUCTION

In molecular hydrogen if one of the electrons is removed sufficiently away from the nuclei, it may be considered to move in an approximate Rydberg State around the residual H_2^+ ion. High resolution experiments[1,2,3] on photoionization and photoabsorption have not only confirmed the presence of such states for H_2 but also have yielded quantitative rates of autoionization from these states. The results further reveal that the autoionization process, in fact, dominates over the photoionization process in the neighborhood of the threshold of ionization. Several theoretical calculations[4,5,6,7] have already been done to estimate the autoionization rates from these states. The calculations may be divided into two kinds of models. (Recently Ritchie[8] has calculated rates of autoionization within a semiclassical method, which are in qualitative agreement with experimental estimates for high vibrational states with single quantum transitions.) In the first kind of calculations, initiated by Berry[4] the autoionization is assumed to be mediated by the nuclear kinetic energy terms which break down the Born-Oppenheimer separation by coupling the core vibrations with the electronic motion. We may call it the non-adiabatic model. In the second kind of model, first used for the present purpose by Russek et al.[5], the energy of vibrations is assumed to be mediated to the Rydberg electron directly through an internal conversion process, much used in nuclear problems before[9].

In their first applications both the theories[4,5] failed to produce the estimated experimental rates, by falling short of by an order of magnitude or more. Subsequently, however, the calculation of Berry and Nielsen[5] using elaborate non-adiabatic molecular calculations have improved the results to within a few times the experimental results. The experimental estimates[2] may be uncertain within a factor of two or so and it may be considered that the non-adiabatic model is adequate enough to describe the autoionization process. However, due to the very nature of the theory, extensive numerical calculations are necessary to arrive at the estimates. The internal conversion model, on the other hand, is attractive for its simplicity and would be useful if the model could be shown to yield the appropriate rates.

From results of calculations within non-adiabatic models[7] it has emerged that the monopole nuclear interaction is principally responsible for transmission of vibrational energy to the Rydberg electron. Previously it has been demonstrated by Russek et al.[5] that there is an essential equivalence between the non-adiabatic and the internal conversion models. In view of these two facts we re-examine the internal conversion model and show in this paper that the model is capable of yielding the desired results via the so-called "0-0 transition" case well known in the analogous process of nuclear conversions[9].

II. MATHEMATICAL FORMULATION

Atomic units are used throughout the present formulation. We assume that the total Hamiltonian of the system can be approximated by the sum of a Hamiltonian of the core and the Hamiltonian of the Rydberg electron, plus an effective interaction between the Rydberg electron and the ion-core. Thus we write

$$H_{tot} = H_{core}(\bar{R}) + H_0(\bar{r}) + V_{eff}(\bar{R},\bar{r}) \qquad (1)$$

where the core Hamiltonian may be given by

$$H_{core}(R) = -\frac{1}{2\mu}\nabla_R^2 + \frac{Z_1 Z_2}{R} + E(R) \qquad (2)$$

In (2) we neglect the rotational part of the Hamiltonian $\frac{J(J+1)}{I\,R^2}$ (we shall be concerned solely with vibrational autoionizations for transitions between ground $J = 0$ rotational states).

In the present first order theory we further confine ourselves to the ground electronic state of the core and neglect all other effects of the core electron besides its effect in generating the ground state potential energy $E(R)$ (which supports the nuclear vibrations).

The Hamiltonian of the Rydberg electron is defined by

$$H_0(\bar{r}) = -\frac{1}{2}\nabla_r^2 - \frac{1}{r} \qquad (3)$$

Thus the autoionizing states are characterized by the usual hydrogenic wave functions with quantum numbers nlm.

We, therefore, have the potential interaction

$$V(\bar{R},\bar{r}) = -\frac{Z_1}{\left|\bar{r} - \frac{\bar{R}}{2}\right|} - \frac{Z_2}{\left|\bar{r} + \frac{\bar{R}}{2}\right|} + \frac{1}{\left|\bar{r} - \bar{r}_c\right|} + \frac{1}{r} \qquad (4)$$

where the first two terms represent the interaction of the Rydberg electron with the nuclei (with charges Z_1 and Z_2) and the third term is the correlation interaction with the core-electron at $\bar{r}_c$. The last term $\frac{1}{r}$ should be included in equation (4) in order that the definition (3) of the Rydberg states is preserved throughout. It may be noted in this connection that in any decomposition of the total Hamiltonian, a part of the Hamiltonian that is included in defining the 'unperturbed' states of the system must not be present in the interaction (part) that mediates transitions between these states. By expanding (4) in Legendre Polynomials it is easily seen that for large r, there is no monopole term in the expansion and that the coupling between the nuclei and the Rydberg electron is of the quadrupole order (the dipole interaction disappears due to the fact that the core is homo-nuclear in nature). It is this quadrupole interaction

$$\frac{(R/2)^2 \, P_2(\hat{R} \cdot \hat{r})}{r^3}$$

which was considered by Russek et al.[5] to be responsible for autoionizing transitions. The contribution from the quadrupole interaction, however, turned out to be too small by one or two orders of magnitude[2]. One notes now that there is a second part of the interaction (4) that corresponds to $r < R/2$. Thus neglecting the correlation term (as assumed in the present model) and expanding we find

$$V(\bar{R}, \bar{r}) = -\frac{4}{R} + \frac{1}{r} + 0\left(\frac{r}{R^3}\right), \quad \text{when } r < R/2. \tag{5}$$

We shall consider only the leading terms in (5). Although at first sight it appears that the nuclear monopole terms being independent of coordinates of the Rydberg electron is incapable of producing the coupling required to mediate the transition; on closer examinations however, one finds the situation to be different. Thus we shall find that to the extent the 'tail' of the Rydberg electron penetrates the core and overlaps with the nuclear wave function, the monopole interaction provides a non-vanishing contribution to the transition matrix elements.

According to our decomposition of the total Hamiltonian we write down the first order wave function of the whole system to be

$$\psi_i(\bar{R},\bar{r}) = \chi_{\nu_i}(R)\, R_{n\ell}(r)\, Y_{\ell m}(\hat{r}) \tag{6}$$

where $\chi_{\nu_i}(R)$ are vibrational wave functions of the core, $R_{n\ell}(r)$ is the radial wave function of the Rydberg electron, and $Y_{\ell m}(\hat{r})$ are the normalized spherical harmonics for the angular wave functions of the electron. (In the present treatment we are interested in the vibrational autoionization process itself and therefore, have explicitly avoided introducing rotational wave functions of the core. In future we intend to publish the corresponding theory for rotational autoionizations involving appropriate frame-transformation properties of the system. At least one case of rotational autoionization in H_2 has already been observed[2]). In the final state, likewise, we assume the wave function to be

$$\psi_f(\bar{R},\bar{r}) = \chi_{\nu_f}(R)\, \varphi_{\bar{k}}(\bar{r}) \tag{7}$$

where $\varphi_{\bar{k}}(\bar{r})$ is the coulomb wave for the ionized electron moving in the direction of the final state momentum $\bar{k}$:[10]

$$\varphi_{\bar{k}}(\bar{r}) = \frac{1}{k}\sum_{\ell'=0}^{\infty} i^{\ell'} e^{-\sigma_{\ell'}}\, R_{k\ell'}(r)\, Y_{\ell' m'}(\hat{r})\, Y^{*}_{\ell' m'}(\hat{k}); \quad \sigma_{\ell'} = \text{coulomb phase.} \tag{8}$$

The functions $\varphi_{\bar{k}}(\bar{r})$ are normalized in momentum space by the relation

$$\int \phi_{\bar{k}}(\bar{r})\, \phi_{\bar{k}'}(\bar{r})\, d\bar{r} = \delta(\bar{k} - \bar{k}') \tag{9}$$

The transition probability for autoionization may now be given by[9]:

$$\frac{dT}{d\Omega_k} = 2\pi \left| < \psi_f \mid V_{eff} \mid \psi_i > \right|^2 \zeta(k) \tag{10}$$

where $\zeta(k)$ is the density of final states, which, in atomic units, is equal to the momentum k. The above expression corresponds to the probability of ejection in the differential solid angle $d\Omega_k$. Substituting the wave functions (6) and (7) and the interaction (5) in equation (10) and performing the angular integrations over $d\hat{r}$, we obtain

$$\frac{dT}{d\Omega_k} = 2\pi \left| \int_0^\infty dR \left[\chi_{\nu_f}(R) \left(-\frac{4}{R} \right) \chi_{\nu_i}(R) \times \int_0^{R/2} R_{n\ell}(r)\, R_{k\ell}(r)\, r^2 dr \right.\right.$$
$$\left.\left. + \int_0^\infty dR\, \chi_{\nu_i}(R) \times \int_0^{R/2} R_{n\ell}(r) \left(\frac{1}{r} \right) R_{k\ell}(r)\, r^2\, dr \right] \right|^2 \times \left(Y_{\ell m}(\hat{k})\, Y^*_{\ell m}(\hat{k}) \right) \tag{11}$$

We note that the penetration integrals over r in (11) range within a small region, between 0 to R/2. Thus the radial functions may be conveniently approximated by[10]:

$$R_{n\ell}(r) \approx \frac{2^{\ell+1}}{n^{2+\ell}} \cdot \frac{1}{(2\ell+1)!} \cdot \left\{ \frac{(n+\ell)!}{(n-\ell-1)!} \right\}^{1/2} r^\ell \tag{12}$$

Since all electrons considered are ejected with energy << 1 a.u., we may also approximate $R_{k\ell}(r)$ by the leading term of its small energy expansion[10]:

$$\mathrm{Lim}_{k\to 0}\, R_{k\ell}(r) \approx \left(\frac{2k}{r} \right)^{1/2} J_{2\ell+1}\left(\sqrt{8r} \right) \tag{13}$$

Substituting (12) and (13) in (11) and integrating over r , we find:

$$\frac{dT}{d\Omega_k} = 2\pi \cdot A_{n\ell} \left|S_{\nu_i \nu_f ; \ell}\right|^2 Y_{\ell m}(k)\, Y^*_{\ell m}(k) \tag{14}$$

with,

$$A_{n\ell} = \frac{(n+\ell)!}{(n-\ell-1)\, n^{2\ell+4}} \cdot \frac{1}{\{(2\ell+1)!\}^2} \tag{15}$$

$$S_{\nu_i \nu_f , \ell} = \int_0^\infty dR \left[\chi_{\nu_f}(R) \left\{ 2R^{\ell+1/2} J_{2\ell+3}(2\sqrt{R}) - R^{\ell+1} J_{2\ell+2}(2\sqrt{R}) \right\} \chi_{\nu_i}(R) \right] \tag{16}$$

The integrations over r are performed analytically by noting that[11]

$$\int^z dz\, z^\nu J_{\nu-1}(z) = z^\nu J_\nu(z) .$$

The total autoionization probability is readily obtained by integrating (14) over all angles of ejection:

$$T = 2\pi \cdot A_{n\ell} \cdot \left|S_{\nu_i \nu_f ; \ell}\right|^2 \quad (\text{a.u.})^{-1} \tag{17}$$

To obtain the rate per second we need only to divide (15) by the a.u. of time[12], $t_0 = 2.4189 \times 10^{-17}$ sec.

III. RESULTS AND DISCUSSIONS

From expression (15) and (17) we readily find that the rates of autoionization decrease as $\frac{1}{n^3}$ with increasing n (as was noticed by Bardsley[13]).

The vibrational integrals $\left|S_{\nu_i \nu_f} ; \ell\right|^2$ (which are independent of n) are evaluated numerically, using Morse functions (see Appendix) for the ion-core.

In Table I we compare our calculated rates with the theoretical results of Berry and Nielsen[7] and the experimental estimates of Chupka and Berkowitz[2]. We also quote for comparison purposes the contribution from the quadrupole term as calculated by Russek et al.[5]

In Table II we present some results corresponding to vibrational transitions involving two quantum transitions $\Delta\nu_{if} = 2$, and compare them with the available theoretical results of Berry and Nielsen[7]. We find in agreement with these authors that the rates for $\Delta\nu_{if} = 2$ are much smaller than those for $\Delta\nu_{if} = 1$, thus satisfying the 'propensity rule' proposed by Berry[4].

In Table III we present some results for high vibrational transitions with $\Delta\nu_{if} =$ 3 and 4. We find that unlike the $\Delta\nu_{if} = 1$ and 2 cases these results differ greatly for most cases with the results of Reference 7. ($\nu_i = 4 \rightarrow \nu_f = 0$ case seems to be an exception!) Although these rates continue to satisfy the 'propensity rule' the disagreement may well be due to sensitive dependence of multiple quantum transitions on the exactness of vibrational wave functions (which we have approximated here simply by Morse functions).

We note that formula (17) does not distinguish between σ and π states, but can yield rates of autoionization from states other than p-states (if populated by non-optical means). We also have noted that if one omits the term $\frac{1}{r}$ from the effective interaction (5) the rates turn out to be somewhat higher (as may be expected) and tend to agree more closely with the experimental rates given in Table I. However (as explained in Section II), for a satisfactory definition of the Rydberg states (equation (3)) we have retained the $\frac{1}{r}$ term in the effective interaction (equations (4) or (5)).

In a more detailed treatment (which may be necessary if the experimental determination of rates improve significantly in fugure) one could also take account of the core-electronic functions and the electron-electron correlation explicitly. We expect this refinement to reduce (due to the repulsive nature of electron-electron interaction) the present estimates to a certain extent, but leave the essential feature of the model unaffected.

Within the approximations introduced in the present paper the generalization of the method to diatomic molecules other than H_2 (e.g., N_2, CO, etc.) would consist simply in substituting appropriate vibrational functions (or Morse functions), for the respective molecular ions, in expression (16) for the vibrational matrix elements.

APPENDIX

The vibrational wave functions, $\chi_\nu(R)$, for diatomic molecules are given (usually quite accurately) by Morse functions[14, 15]

$$\chi_\nu(R) = N_\nu \, e^{-\frac{1}{2}z} \, z^{\frac{1}{2}(\alpha-2\nu-1)} \, F_\nu(z)$$

where

$$z = \lambda \, e^{-\beta(R-R_0)}$$

$$\lambda = \frac{2}{\beta}(2\mu D)^{\frac{1}{2}}$$

$$N_\nu = \frac{(\alpha-\nu-1)(\alpha-\nu-2)\ldots\ldots(\alpha-2\nu)}{\nu!\,\Gamma(\alpha-2\nu-1)} \cdot \beta$$

$$F_\nu(z) = \sum_{s=0}^{\nu} \frac{(-1)^s \binom{\nu}{s} z^s}{(s-2\nu)(\alpha-2\nu+1)\ldots\ldots(\alpha-2\nu+s-1)}$$

where β is the parameter in Morse potential for the molecule

$$V(R) = D\left[e^{-2\beta(R-R_0)} - 2\,e^{-\beta(R-R_0)}\right]$$

D is the dissociation energy, R_0 is the equilibrium separation and μ is the reduced mass of the core.

For H_2^+ a good choice[15] of parameters is

$\beta = 0.6678\ (\text{a.u.})^{-1}$

$R_0 = 2.00\ (\text{a.u.})$

$D = 0.10265\ (\text{a.u.})$

$\mu = 918.334\ (\text{a.u.})$

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Table I

Autoionization rate (sec^{-1}) of npλ Rydberg state of H_2. $\Delta\nu_{if}$ = 1; CB: Experimental estimates of Chupka and Beckowitz[2], BN: Theoretical calculations of Berry and Nielsen[7] and RPB: Theoretical calculations of Russek et al.[5] (quadrupole contribution), PC: Present Calculation (the rates for σ and π states are not distinguishable in the present model)

ν_i	ν_f	$n\ell\lambda$	CB	PC	BN	RPB
1	0	8pσ	4.0×10^{11}	1.9×10^{11}	2.1×10^{11}	1.02×10^{10}
		8pπ	(3.0×10^{11})	1.9×10^{11}	1.9×10^{11}	1.02×10^{10}
		9pπ	(3.0×10^{11})	1.0×10^{11}	1.5×10^{11}	
2	1	8pσ	1.3×10^{12}	5.0×10^{11}	4.7×10^{11}	1.02×10^{10}
		8pπ	(9.0×10^{11})	5.0×10^{11}	4.2×10^{11}	1.02×10^{10}
3	2	8pσ	2.7×10^{12}	9.6×10^{11}	7.9×10^{11}	
		16pσ	(1.3×10^{12})	1.2×10^{11}		
4	3	7pσ	(9.0×10^{11})	2.3×10^{12}	1.7×10^{12}	
		(8pσ)	(5.0×10^{12})	1.6×10^{12}	1.1×10^{12}	
		9pσ	2.7×10^{12}	1.1×10^{12}	8.15×10^{11}	
		10pσ	(2.0×10^{12})	8.4×10^{11}	5.8×10^{11}	
		13pσ	(2.3×10^{12})	3.8×10^{11}		
5	4	8p	2.0×10^{12}	2.6×10^{12}	1.6×10^{12}	1.02×10^{10}
		9pσ	5.8×10^{12}	1.8×10^{12}	1.1×10^{12}	
		(10pσ)	(1.7×10^{12})	1.3×10^{12}	8.0×10^{11}	0.53×10^{10}

Table II

Autoionization rate (sec^{-1}) of $np\sigma$ Rydberg states of H_2. $\Delta\nu_{if} = 2$. BN: Theoretical calculation of Berry and Nielsen[7] (the rate for π states are in general slightly smaller than for σ state). PC: Present Calculation (the rates for σ and π states are not distinguishable in the present model).

ν_i	ν_f	n = 6		n = 7		n = 8		n = 9		n = 10	
		BN	PC	BN	PC	BN	PC	BN	PC	BN	PC
2	0	1.5×10^9	2.1×10^9	9.5×10^8	1.32×10^9	6.4×10^8	8.9×10^8	4.6×10^8	6.3×10^8	3.3×10^8	4.6×10^8
3	1	5.1×10^9	5.3×10^9	3.3×10^9	3.4×10^9	2.2×10^9	2.3×10^9	1.6×10^9	1.6×10^9	1.15×10^9	1.2×10^9
4	2	1.2×10^{10}	1.3×10^{10}	8.7×10^9	5.2×10^9	5.8×10^9	3.5×10^9	4.1×10^9	2.5×10^9	3.0×10^9	1.8×10^9
5	3	3.1×10^{10}	0.9×10^{10}	2.0×10^{10}	0.6×10^{10}	1.3×10^{10}	3.9×10^9	9.3×10^9	2.7×10^9	6.8×10^9	2.0×10^9

Table III

Autoionization rate (sec^{-1}) of npσ states of H_2. $\Delta\nu_{if}$ = 3, 4. BN: Theoretical calculation of Berry and Nielsen[7] (rates for π states are in general slightly smaller than for σ states). PC: Present Calculation (the rates for σ and π states are not distinguishable in the present model).

			n = 8		n = 9		n = 10	
$\Delta\nu_{if}$ = 3	ν_i	ν_f	BN	PC	BN	PC	BN	PC
	3	0	5.9×10^5	6.9×10^7	3.9×10^5	4.9×10^7	2.8×10^5	3.6×10^7
	4	1	8.1×10^6	3.1×10^8	5.8×10^6	2.1×10^8	4.3×10^6	1.6×10^8
	5	2	5.9×10^7	8.3×10^8	4.2×10^7	5.8×10^8	3.1×10^7	4.3×10^8
$\Delta\nu_{if}$ = 4	4	0	2.0×10^6	3.0×10^6	1.4×10^6	2.1×10^6	1.0×10^6	1.5×10^6
	5	1	4.3×10^5	1.9×10^7	3.0×10^5	1.3×10^7	2.3×10^5	9.9×10^6