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SEMICLASSICAL THEORY FOR MOLECULAR AUTOIONIZATION

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In the limit of high vibrational and electronic principal quantum numbers a semiclassical model for autoionization of diatomic molecules has been constructed. The molecular vibrations are treated as classical oscillators, whose parameters are chosen from a knowledge, which can be taken either from theory or experiment, of the positions of the quantal vibrational levels and the position and depth of the minimum of the adiabatic potential curve of the residual molecular ion. The theory is designed for the case where vibrational quantum numbers are greater than about 10. Electronic quantum numbers are restricted by the requirement that they be high enough so that the excited electron-core electron interaction can be represented by the monopole term in the region where the distance of the excited electron from either nucleus is always greater than the distance of the core electron and the excited electron-nuclear interactions can be represented by the monopole terms in all regions. An advantage of the theory over the perturbed stationary state theory is that its validity extends into the region of very high electronic quantum numbers ($n=100$) where the electron and nuclear velocities are comparable, and the Born-Oppenheimer theory is not valid. Numerical estimates for the autoionization rates are presented for several sample cases for vibrations in the neighborhood of $n'=10$ and excited electrons of $n=10$ to $n=20$, and for zero energy ejected electrons.

Introduction

A molecule can autoionize when one of its electrons is so highly excited that a transition from an excited vibrational or rotational level can supply enough energy to ionize the electron. The electron is almost decoupled from its parent molecular ion, and the process is almost the process of energy transfer between colliding systems. Typically a $n'=5$ to $n'=4$ vibrational transition supplies enough energy to ionize an $n=9$ electron. The process is observed experimentally in the neighborhood of threshold in the photoionization of H_2[1], in which there is photoexcitation of electrons to around $n=10$ and vibrations to $n'=5$ and then the production of photoelectric current by autoionization. In this region of energy an $n=10$ electron has an order of magnitude higher velocity than the relative nuclear velocity of a $n'=10$ vibration (estimated from the exact H_2^+ vibrational energies). The mechanism responsible for the transition is taken by Nielsen and Berry[2] (hereafter referred to as NB), in an application of the perturbed stationary state theory for heavy particle collisions[3], to be the nonadiabatic (vibronic) corrections on the adiabatic electronic states for the nuclear motion; thus the transition amplitude is proportional to $\nabla^2_{\vec{R}}\psi_i(\vec{r},\vec{R})$ and $\nabla_{\vec{R}}\psi_i(\vec{r},\vec{R})\cdot\nabla_{\vec{R}}\chi_i(\vec{R})$, where ψ_i and χ_i are the initial electronic and vibrational states and $\vec{r}$ and $\vec{R}$ are the position vectors of the electron in the molecule fixed frame and the relative nuclei respectively, integrated over the product with the final electronic and vibrational states. The first derivative term is dominant, and autoionization rates calculated by this theory are in qualitative agreement with the experimental estimates of Chupka and Berkowitz.[1]

The purpose of this paper is to formulate a theory in which autoionization rates can be predicted without an explicit knowledge of the vibrational states involved, which in its turn requires a knowledge of accurate adiabatic potential curves and surfaces, available for only the smallest molecules. Provided the vibrations are excited enough (about $n'=10$) so that they can be represented by classical oscillators, the information required about the vibrational levels involved in the internal conversion process can instead be taken from the extensive infrared spectroscopic measurements of vibrational quanta and experimental determinations of molecular binding energies. This semiempirical aspect should be especially useful for polyatomic molecules (not explicitly considered here). In addition the formulation is not made within the framework of the Born-Oppenheimer theory and thus avoids many of the numerical complications of this theory and more importantly extends into the region of comparable electron-nuclear velocities in which the BO theory is not valid. In the energy range considered by NB it is reasonable that non-adiabatic effects could be invoked to give a reliable first-order theory. However in the region in which $50<n<\infty$ the electron and nuclear velocities are comparable so that vibronic couplings are no longer perturbations on the Born-Oppenheimer system. A similar situation is encountered in H atom-H atom collisions above 1 keV incident projectile energy in which the ground state-ground state Heitler-London energy curve departs from its zero velocity limit below 1keV, distorts beyond recognition from 1 to 100 keV, and merges into a coulomb curve when the electron exchange interactions become negligible above 100 keV[4]

Autoionization from the higher levels (electronic and vibrational) may be important in H1 regions in interstellar space in which competing processes for electron supply are ionization of $n=100$ hydrogen atoms by collision with ground state hydrogen atoms and by background radiation from H2 regions. There has been recent astrophysical interest[5] in "anomalous" recombination radiation from H2 regions as a result of observation through H1 regions in which such processes are occurring. Molecular autoionization has not yet been proposed, although undissociated H_2 molecules are known to be present in dark dust clouds in H1 regions[6]

Theory

Consider the H_2 molecule in an highly excited electronic and vibrational state. We choose to treat the vibrational levels of the H_2^+ residual ion for $n' \geq 9$ as classical oscillators. This is a good approximation for the higher states since the classical distribution function can represent an average of the oscillatory quantum distribution over the stretch of the molecule[7]. Hence a knowledge from experiment or theory of the positions[8] of the quantum states and the depth, D_e, of the minimum of the adiabatic potential curve of the residual ion at R_e can be used to choose the parameters of the classical oscillator,, whose position and velocity are given by,

$$R_i(t) = R_e + D_i \sin \omega t$$

$$v_i(t) = D_i \omega \cos \omega t \qquad (1)$$

where $\omega = (k/\mu)^{\frac{1}{2}}$ where k is the stretch constant equal to $(\partial^2 V(R)/\partial R^2)_{R=R_e}$ and V(R) is the potential curve. The stretch constant is taken from the Morse model to be $2D_e a^2$ where a is a fitting parameter[9]. μ is the nuclear reduced mass. D_i is the amplitude of the i^{th} oscillator and is chosen by fitting the classical energies, $\frac{1}{2}kD_i^2$, to the quantum eigenvalues[7] where the bottom of the well, D_e, is chosen as the zero point. We use the Wentzel[10] correspondence relation which gives a classical velocity which is an average of the initial and final velocities resulting froma quantal absorption of energy,

$$v \quad (v_i v_f (v_i + v_f)/2)^{1/3} \tag{2}$$

This "symmetrization" seems especially justifiable as we approach the top of the potential well where the quantum states are almost degenerate. We do not symmetrize the trajectories, R_i, but choose the initial trajectory. In a more careful treatment the symmetrized trajectories could be obtained from an integration over the time of the correspondence given in (2).

The excited electron is in a state of high principal quantum number so that its average distance from the H_2^+ residual core is large (of order n^2). The existence of H_2^+ in a highly excited vibrational state means that the quantum mechanical average relative position of the nuclei can change over a very wide range of internuclear distances as determined by the modulus $|\chi_i(\vec{R})|^2$ of the vibrational wave function in distinction to the range for a low vibrational state whose modulus is peaked near R_e. Classically this means that there is a large vibrational amplitude, D_i, and that in the time, $(t_2-t_1)/2$, of a half period in which the molecular ion goes from its minimum to maximum stretch the sphere swept out by the nuclei in the space occupied by the excited electron has a large radius; hence the average electron distance from the core is effectively decreased (the electron, originally outside the core at $R=R_{min}$, has a greater chance of being inside the core where the ionizing interaction occurs over the period $T=t_2-t_1$). At t_1 we take the electron to be outside this sphere (outside the core, for which $r>R$), so that it moves in the potential,

$$-1/r - R^2/r^3 P_2(\hat{r}\cdot\hat{R}) - (\text{higher order poles}) \tag{3}$$

where the monopole term of the expansion in the region $r > r'$ (r' is the core electron coordinate) of the excited electron-core electron potential r_{12}^{-1} has been cancelled (complete screening) and the higher order poles dropped. The quadrupole term in (3) was first proposed by Berry[11] to be the dominant ionizing interaction, but calculations by Berry[11], Bardsley[12], and Russek et al[13] showed that it contributed only a few percent to the rates as measured by Chupka and Berkowitz[1]. Physically this is clear because the electron is always outside the molecular core ($r > R$), and vibronic effects are of higher order. We will there neglect the quadrupole term. Thus at $t = t_1$ the electron moves in a coulomb potential, and its states are hydrogenic. In the interval $t_1 \leq t \leq t_2$, the period of the vibration, the nuclei move from their minimum to maximum stretch and back to their minimum. The ionizing interaction occurs during this interval. Also, during this interval it is reasonable to treat the electron as a molecular electron, whose molecular orbital ψ_1 (in the simplest "Linear Combination of Atomic Orbitals" approximation) is given by,

$$\psi_1 = a_1(t)\left(\phi_{n\ell m}(\vec{r}_A)e^{i\vec{v}\cdot\vec{r}} \pm \phi_{n\ell m}(\vec{r}_B)e^{-i\vec{v}\cdot\vec{r}}\right)e^{-i(\varepsilon_n + v^2/2)t} \qquad (4)$$

where the states are bound hydrogenic states of energy ε_n on protons A and B, and the exponential factors result from the translational component of motion of the electron travelling with the classical protons moving in the directions of positive and negative velocities respectively[14] The upper and lower signs are taken for the gerade and ungerade molecular symmetries. The final molecular orbital ψ_2 is,

$$\psi_2 = a_2(t)\left(\phi_{k\ell m}(\vec{r}_A)e^{i\vec{v}\cdot\vec{r}} \pm \phi_{k\ell m}(\vec{r}_B)e^{-i\vec{v}\cdot\vec{r}}\right)e^{-i(k^2/2+v^2/2)t} \qquad (5)$$

where the states are the hydrogenic continuum states of energy $k^2/2$ on protons A and B. The total wave function is the sum of (4) and (5) (in the two-state approximation[15]). Substitution into the time-dependent Schrodinger equation and projection from the left with the molecular orbitals yields the usual set of coupled first-order differential equations in the time for the set of a(t)'s,

$$\underline{S}\ \underline{\dot{a}} = (i\hbar)^{-1}\underline{V}\ \underline{a} \qquad (6)$$

where $\underline{S}$ and $\underline{V}$ are the overlap and potential matrices respectively. During the time of ionization, the potential is just $-1/R(t) + 1/r$ in the region $r<R(t)$, $r>r'$ and zero in the region $r>R(t)$, $r>r'$ (zero in the region $r>R(t)$, $r>r'$ is consistent with the neglect of the quadrupole term in (3)), where we have kept only the monopole terms (as in (3)) of $|\vec{r} - \vec{R}|^{-1}$ and $|\vec{r} - \vec{r}'|^{-1}$ in the region $r<R(t)$, $r>r'$, and the monopoles have cancelled in the region $r>R(t)$, $r>r'$. Note that the excited electron is always taken to be in the region $r>r'$. This bears closer examination since $r<R(t)$ implies that the excited electron can move in the space of the core electron during the collision. Hence the integration over r extends only to R(t). We solve (6) by neglecting back-coupling and distortion[15], thereby reducing the set to the Born amplitude,

$$a(T,k) = (i\hbar)^{-1}\int_{t_1}^{t_2} dt\ e^{i(k^2/2-\epsilon_n)t}(\langle\phi_{k\ell m}(\vec{r}_A)|1/r_A - 1/R(t)|\phi_{n\ell m}(\vec{r}_A)\rangle$$

$$\pm \langle \phi_{k\ell m}(\vec{r}_A) | (1/r_A - 1/R(t)) e^{2i\vec{v}\cdot\vec{r}} | \phi_{n\ell m}(\vec{r}_B) \rangle) \qquad (7)$$

where we have neglected the continuum-continuum overlap. The momentum factors vanish by orthogonality except for the interference term which results because the exchange integral contains the atomic orbital components of opposite velocity direction of the molecular orbital (cross term). Since the time of a classical period is $2\pi/\omega$, and the modulus of $a(T,k)$ is the probability, which cannot be greater than unity, the semiclassical autoionization rate has an upper bound of $(2\pi/\omega)^{-1}$ $= 0.65865 \times 10^8\ \text{sec}^{-1}$.

Numerical Results and Discussion

To obtain numerical estimates of a(T,k) we make the following set of approximations. Since the electronic states are continuum and highly excited bound states, $r_A \rightleftarrows r_B$ to a good approximation, i.e. the two-center integration can be performed about a single center. We expand the continuum function in partial waves and keep only the $\ell=1$ wave ($\ell=1$ bound states are the initial states of interest in the photoionization experiment[1]; hence $\Delta\ell=0$ only are considered). The maximum velocity, k_{max}, of the ejected electron is small for the small energy transfers involved, so that we evaluate the rates for zero energy electrons only; the radial coulomb wave function normalized on the energy scale (coulomb functions normalized on the k scale multiplied by $k^{-\frac{1}{2}}$) is[16],

$$\phi_{0\ell} = (2/r)^{\frac{1}{2}} J_{2\ell+1}((8r)^{\frac{1}{2}}) \qquad (8)$$

Using (8) the rate per unit velocity is given by $|a(T,0)|^2/T$ at zero velocity. Assuming the probability to be nearly constant over the range $0 \leq k \leq k_{max}$, the total rate is estimated by taking the product $|a(T,0)|^2 k_{max}/T$. Numerical difficulties in evaluating the generalized Laguerre polynomials limit the calculation to about $n \leq 20$; continuum waves of very low k are likewise subject to the same numerical difficulties (convergence of the confluent hypergeometric function for large $n=-i/k$).

Table 1 gives sample values for the rates for $n'=9$, 10, 11, and 12 vibrations (all possible $\Delta n'$) and $10 \leq n \leq 20$. Some of these rates violate the upper bound given in the previous section because the probabilities are greater than unity. This error is inherent in the Born approximation, which does not conserve probability. It is strongly suspected that the larger than unity probabilities are due mainly to the overestimation of the two-center integral by the one-center approximation and (probably a more important source of error) the treatment of the probability as a constant over the interval $0 \leq k \leq k_{max}$, especially since only the $\Delta n' > 1$ rates show the violation of the bound and k_{max} increases with $\Delta n'$. This increase of rate with increase of $\Delta n'$ is also not in agreement with the NB rates, which decrease with $\Delta n'$. This incorrect behavior of the semiclassical rates seems to be due (with smaller contributions from the two sources of error above) to the dependence only on the initial trajectory; with increase in $\Delta n'$ the final trajectory (amplitude) has less and less stretch while the initial trajectory remains the same. Symmetrization of trajectories would therefore be indicated. The decrease with increase of n is in agreement with NB.

The upper bound of nearly 10^8 means that the semiclassical rates can never be as fast as the quantum rates of around 10^{12} for $\Delta n' = 1$ for vibrations $0 \leq n' \leq 5$ and $n \leq 10$ of Berry and Nielsen[2c]. Their values for $\Delta n' > 1$ are as slow as 10^5. Clearly the very fast rates are the result purely of the quantum effect of initial and final vibrational states whose overlap is strongly peaked in a very small region of internuclear distance. This effect could be mimicked classically if we allowed $0 < \omega T \leq 2\pi$; that is if we restricted the classical time to some very small region instead of allowing the ionization to occur over the entire period. Since there is no unique prescription for choosing such shorter times, the classical description of the nuclear motion must fail for these cases.

There is an intermediate region ($5 < n' < 12$) into which the calculation of NB does not extend, so that a direct comparison between quantum and semiclassical rates cannot be made. It would be useful if calculations based on the NB theory were made in this region.

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Table 1. $|a(T,0)|^2 x k_{max}/T \times 10^{-8}$ in sec^{-1} for n'_i and n'_f initial and final vibrational states, for electrons ionizing from the n^{th} bound state. x means energetically forbidden.

				n			
n'_i	n'_f	10	12	14	16	18	20
12	11	x	0.32	0.31	0.24	0.19	0.14
12	10	1.23	0.87	0.60	0.43	0.31	0.23
12	9	1.88	1.22	0.82	0.57	0.41	0.30
11	10	x	0.41	0.35	0.26	0.20	0.15
11	9	1.35	0.93	0.64	0.45	0.32	0.24
10	9	0.28	0.47	0.38	0.28	0.21	0.16