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Ionization of H_2^+ in Intense Laser Fields

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INTRODUCTION

Recent calculations[1] of ionization rates for H_2^+ by an intense λ=228nm laser show a strong dependence of the rate constant on the internuclear distance R. We have performed comparable time-dependent calculations for H_2^+ in fields $I \leq 1 \times 10^{15} W/cm^2$ for a wide range of fixed R (2-8au) and wavelengths (228-1064 nm). Indeed we obtain excellent agreement with the results of Chelkowski etal[1] at λ=228nm. At large R we find the ionization rate for all wavelengths rapidly approaches that of H(1s). However, at R≈2au and especially for the longer wavelength lasers, such as the λ=769nm Ti:sapphire laser, the large ionization potential (29eV) of the molecule allows it to easily survive intensities up to $I=5 \times 10^{14} W/cm^2$ for typical short pulses of, say, 150 fsec.

Interestly, the ionization rates obtained from the exact numerical solution of the time-dependent Schroedinger equation conform beautifully with a very simple representation of H_2^+ which only involves its two lowest electronic states $1s\sigma_g$ and $2p\sigma_u$ and an optical potential to represent the ionization. Moreover, the two-state model only conforms to the exact

results using a length gauge coupling, and yields extremely poor results if the asymptotically pleasing velocity gauge coupling used in reference 2 is employed. These fully dynamic results confirm the conclusion inferred from quasi-energy variational calculations[3] in a periodic field that indeed a two-state length-gauge model is good in H_2^+ at least out to R≈6au.

The motivation for the present ionization calculations is to test the reliability of a recent study of H_2^+ photodissociation[4] which employed such a two electronic state model and neglected any competition with ionization. The photodissociation calculations indicate that in intense short pulsed laser fields appreciable populations of stable vibrational states can survive the pulse. This survival effect can be attributed to the trapping of portions of the initial vibrational wavepacket in transient laser-induced potential wells at intermediate R≈3-4au distances. Since the calulated ionization rates exhibit a marked decrease at short R, they already lend some credence to the vibrational trapping effect. Having accurate R-dependent rates enables us to estimate the competitive influence of the ionization on the stabilized population, and may ultimately allow us to predict the contribution of the Coulomb 'explosion' channel to observed proton kinetic energy distributions.

In this paper we will demonstrate the effectiveness of the two-state length gauge model in interpreting the ionization rates that we extract from the numerically exact solutions of the time-dependent Schroedinger Equation. A more elaborate presentation of the theory and the results for the full range of distances and wavelengths will be presented elsewhere.[7]

THEORY

We assume that H_2^+ has a fixed bond-length R with the bond oriented along the $\hat{z}$ axis, which coincides with the polarization vector of the linearly polarized electric field of the laser

$$\mathbf{E}(t) = E_{max} f(t) \sin(\omega t+\delta)\ \hat{z} = E(t)\ \hat{z}, \tag{1}$$

where f(t) defines the envelope of the laser pulse. This orientation preserves the cylindrical symmetry of the molecule[1,6] and allows us to perform calculations using finite difference methods in a two-dimensional cylindrical grid.[6] Of course we use the dipole approximation.

The numerically exact calculations are actually performed in the Coulomb (≈ velocity) gauge,

$$[\tfrac{1}{2}(\mathbf{p} + \tfrac{e}{c}\mathbf{A})^2 + V_{coul}](e^{-i\Lambda}\Psi) = i\hbar \frac{\partial}{\partial t}(e^{-i\Lambda}\Psi). \tag{2}$$

Using the following gauge transformation

$$\Lambda(t) = \frac{e}{c\hbar}\mathbf{A}(t)\cdot\mathbf{r} \qquad\qquad \hbar\frac{\partial\Lambda}{\partial t} = \mathbf{E}(t)\cdot(e\mathbf{r}) \tag{3}$$

where $\mathbf{r}$ is the electronic coordinate conjugate to $\mathbf{p}$, we obtain the usual time-dependent Schroedinger eq. in the length gauge,

$$[H_o + \mathbf{E}(t)\cdot(e\mathbf{r})]\,\Psi = i\hbar\frac{\partial}{\partial t}\Psi. \tag{4}$$

Obviously the field-free electronic Hamiltonian $H_o \equiv \tfrac{1}{2}(\mathbf{p}^2 + V_{coul})$ for H_2^+ is implicitly dependent on R. We calculate the ionization rates for the ground $H_2^+(1s\sigma_g)$ and the first excited $H_2^+(2p\sigma_u)$ states which are represented by the electronic wavefunctions φ_g and φ_u with R-dependent eigenvalues (potentials) $V_g(R)$ and $V_u(R)$ respectively. Identical numerical results are obtained from integrating either Eq. (2) or Eq. (4) for a given initial $\Psi(0)$, but only if one is very careful to include the proper gauge transformation factor $e^{-i\Lambda(t)}$. The same consideration applies when we discuss various projected probabilities in the Results Section. Actually φ_g and φ_u both dissociate to $H^+ + H(1s)$ and are asymptotically degenerate. At large R they correlate respectively with a $\pm$ combination $[\varphi_{1s}(\mathbf{r}-\mathbf{R}/2) \pm \varphi_{1s}(\mathbf{r}+\mathbf{R}/2)]/\sqrt{2}$ of atomic ground state wavefunctions φ_{1s} centered on either of the two protons. As expected, we find that their ionization rates at large R are identical and coincide with the rate for the isolated hydrogen atom.

Our concern in this paper is to understand the effect of radiative coupling between these two states which is induced by the transition dipole $\mu(R)_{gu} = \langle\varphi_g|(ez)|\varphi_u\rangle$. In the length gauge the radiative coupling is

$$\Omega_{gu}(R,t) = \langle\varphi_g|\mathbf{E}\cdot(e\mathbf{r})|\varphi_u\rangle = E(t)\mu_{gu}(R). \tag{5}$$

Because of the asymptotic degeneracy $\mu_{gu} \to eR/2$ and Ω_{gu} actually diverges as $R\to\infty$. In contrast, the asymptotic radiative coupling in the velocity gauge,

$$\Omega_{gu}^{vel}(R,t) = \langle\varphi_g|\mathbf{p}\cdot\tfrac{e}{c}\mathbf{A} + (\tfrac{e}{c}\mathbf{A})^2|\varphi_u\rangle \equiv \frac{(V_g - V_u)}{\hbar\omega}\,\Omega_{gu}(R,t), \tag{6}$$

vanishes since $(V_g - V_u)\to 0$ as $R\to\infty$. Thus, this gauge is often used in Floquet-type[2] calculations in order to avoid troublesome boundary conditions. Of course if a <u>complete</u> electronic basis is used then the solutions to (2) and (4) must give identical results. This is apparent in the interesting variational calculations of Muller[3] as well as in the present results.

If we chose to use only the two field-free electronic states φ_g and φ_u to diagonalize the time-dependent Hamiltonian in Eq. (4) we obtain a pair of adiabatic "field-following" dressed states, <u>using length gauge coupling</u>,

$$\varphi_s(\text{Length},t) = \cos\phi_L(t)\ \varphi_g - \sin\phi_L(t)\ \varphi_u \tag{7a}$$

$$\varphi_f(\text{Length},t) = \sin\phi_L(t)\ \varphi_g + \cos\phi_L(t)\ \varphi_u. \tag{7b}$$

The phase $\phi_L(t)$ is defined by the 2x2 orthogonal matrix obtained from the diagonalization of eq. (4), such that,

$$\langle\varphi_s(t)|H_o + \mathbf{E}\cdot(e\mathbf{r})|\varphi_s\rangle = V_s(t) \underset{\mathbf{E}\to 0}{\sim} V_g \tag{8a}$$

$$\langle\varphi_f(t)|H_o + \mathbf{E}\cdot(e\mathbf{r})|\varphi_f\rangle = V_f(t) \underset{\mathbf{E}\to 0}{\sim} V_u \tag{8b}$$

$$\langle\varphi_s(t)|H_o + \mathbf{E}\cdot(e\mathbf{r})|\varphi_f\rangle \equiv 0. \tag{8c}$$

These dressed states and their diagonalized potentials V_s and V_f are now implicit functions of t and adiabatically follow the time-dependent field $\mathbf{E}(t)$. In particular $\phi_L(t)$ is periodic over an optical cycle, and has been defined to insure that $\varphi_s \to \varphi_g$ and $\varphi_f \to \varphi_u$ whenever $\mathbf{E}(t) \to 0$. For any finite R the potential V_f always exceeds V_s and hence the ionization potential of φ_s always exceeds that of φ_f. The f,s notation is chosen to remind us that we can expect a 'faster' ionization rate for the φ_f state and a generally 'slower' rate for the φ_s state.

If we choose to use the same two "bare" electronic states φ_g and φ_u to diagonalize the velocity gauge Hamiltonian in Eq. (2), then we will obtain a <u>different</u> pair of field dressed states $\varphi_s(\text{Velocity},t)$ and $\varphi_f(\text{Velocity},t)$. Although these adiabatic states have the same form as Eq. (7), the phase $\phi_L(t)$ is now replaced by a distinctly difference phase $\phi_V(t)$ obtained from the orthogonal matrix which diagonalizes Eq.(2).

In either the length or velocity gauge representation the adiabatic states φ_f and φ_s are coupled by non-adiabatic terms involving $\partial\phi/\partial t$. In addition we can simulate the net effect of ionization by introducing an <u>adhoc</u> optical potential for each state in the pair of coupled equations. We have solved these coupled equations[7] using two alternative forms for the optical potentials, one defined by the projections of the diabatic or bare states φ_g and φ_u

$$V_{op} = -i\Gamma_g/2|\varphi_g\rangle\langle\varphi_g| - i\Gamma_u/2|\varphi_u\rangle\langle\varphi_u| \tag{9}$$

and a second involving the projections of the time-dependent adiabatic dressed states φ_s and φ_f

$$V_{op}(t) = -i\Gamma_s/2\ |\varphi_s\rangle\langle\varphi_s| - i\Gamma_f/2|\varphi_f\rangle\langle\varphi_f|. \tag{10}$$

If we further assume that the factors Γ are independent of time, then, for a given laser wavelength and intensity, the particular electronic state associated with Γ will decay as $e^{-\Gamma t/2\hbar}$, and molecules in this pure state will have an ionization rate constant equal to $\Gamma/\hbar$. The question is, do any of these simple two-state models, dressed either in the length gauge or the velocity gauge, and ionizing as prescribed by Eq. (9) or (10) come even close to simulating the ionization rates obtained for the exact solutions of Eq. (2)? In fact we have found[5] that simply using the two state solutions in the length gauge, and employing the optical potential in Eq. (10) yields a surprisingly good approximation to the exact results obtained from Eq. (2), and gives us confidence in extracting and interpreting state specific rate constants from the exact time-dependent wavepackets.

RESULTS

The time-dependent Schroedinger equation is solved in a box[6] of dimension $z=\pm 100$au in the field direction, and with transverse cylindrical coordinate $\sqrt{(x^2+y^2)} \leq 28$au. Beyond these distances a gradually absorbing boundary is installed which does not allow reflection of the wavefunction,[6] and hence simulates the loss of electron density due to ionization. The deviation of the norm within this box

$$P_{norm}(t) = \int_{box}|\Psi(t)|^2 dr \tag{11}$$

from its initial unit value at $t=0$ gives a measure of the total probability for ionization, $P_{ion}(t) = 1-P_{norm}(t)$. In addition to P_{norm} we evaluate the instantaneous contribution of various states φ_j to the exact wavefunction within the box

$$P_j(t) = |\langle e^{-i\Lambda}\varphi_j|e^{-i\Lambda}\Psi(t)\rangle|^2 = |\langle\varphi_j|\Psi(t)\rangle|^2. \tag{12}$$

Specifically the probabilities for the bare states $j=g,u$ and the field-dressed states $j=s,f$ in both the length and velocity gauge are obtained. Although we use particular states $\Psi(0)=\varphi_j$ to initialize the wavepacket at $t=0$, all the projections we present are made on the exact solutions, and we

are in no way imposing or using the two-state models discussed above. What we want to demonstrate is that the exact solutions do in fact conform nicely to one particular two-state model for times extending over many optical cycles. .

As a first example we present the probabilities for H_2^+ fixed at its equilibrium distance R=2au and exposed to a λ=769nm laser with intensity $I=2\times10^{14}W/cm^2$. In each case we start the solution of Eq.(2) with some prescribed initial state. In Fig. 1 we have the results for $\Psi(0)=\varphi_g$, and also for an initial field dressed state $\Psi(0)=\varphi_s(0)$ defined by Eq. (7a), using the length gauge coupling in Eq. (5). In all the examples we present the field is turned on as a step function at t=0, with f(t)=0 for t<0 and f(t)=1 for t≥0, in Eq. (1). Furthermore, the initial field is taken at its maximum with $\delta=\pi/2$ in Eq. (1), which produces the maximum dressing of the field-dressed states $\varphi_s(0)$ and $\varphi_f(0)$ in Eq.(7).

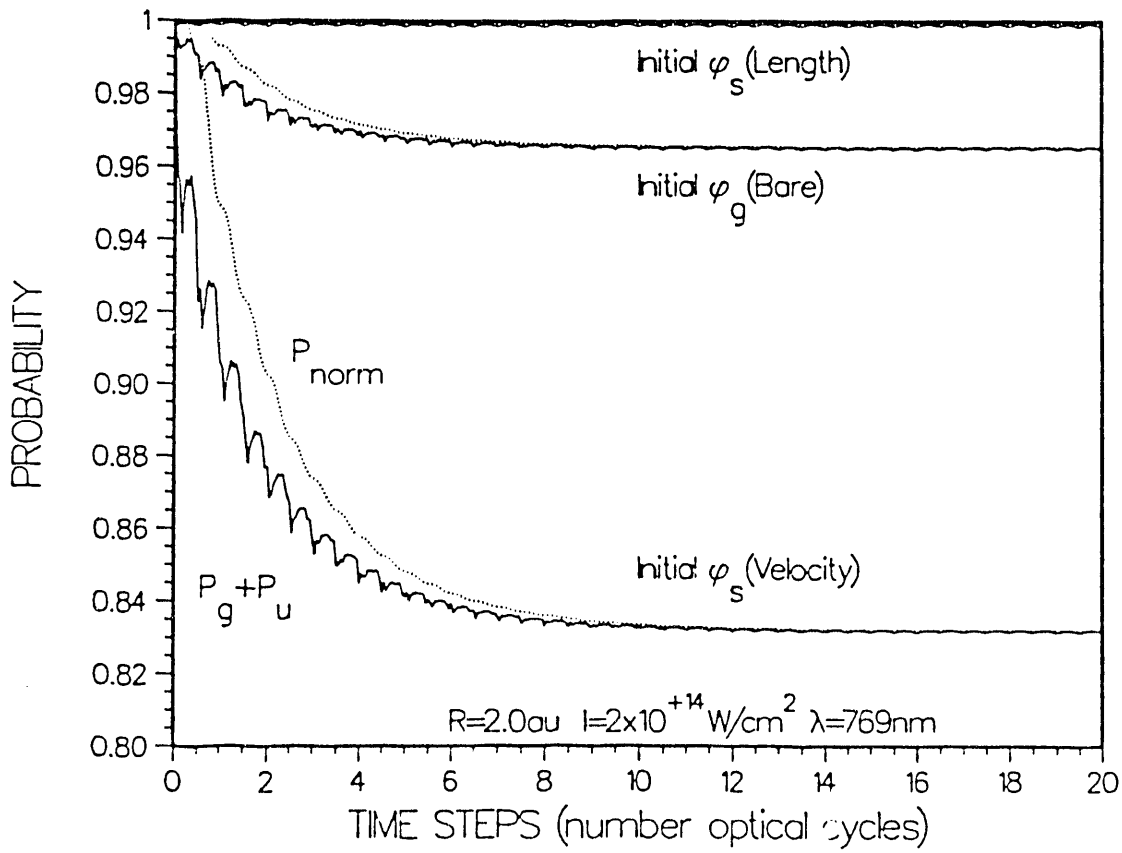

Figure 1. Decay of initially prepared φ_g, φ_s(Length) and φ_s(Velocity) states for λ=769nm, $I=2\times10^{14}W/cm^2$, at R=2.0au. Solid curves give the total probability $(P_g+P_u)$of the wavepacket being in either the φ_g or φ_u state. This sum is identical to(P_s+P_f). The dotted curves give P_{norm}. An initial φ_s(Length) state decays slowly and fairly exponentially, while an initial φ_g state always exhibits a rapidly decaying φ_f(Length) component. An initially prepared φ_s(Velocity) state contains aneven larger φ_f component.

We see that preparing the initial wavepacket in the φ_s(Length) state leads to a very slow, and very exponential decay of the packet over 20 optical cycles of time. In every example that follows wavepackets initially prepared in either the slow φ_s(Length) or the fast φ_f(Length) field-dressed state exhibits a nice, almost perfectly exponential decay. Thus they appear as almost pure "stationary states" of Eq. (4), which are uncoupled from each other, and separately experience direct ionization into the continuum. In contrast wavepackets initiating in the field-free or bare states, φ_g and φ_u invariably exhibit a fast and a slow decaying component which is well represented as a linear combination of decaying φ_s(Length) and φ_f(Length) states. It should be noted that if we adiabatically "turn on" the field, with f(t) rising gradually over a number of optical cycles in Eq. (1), the φ_g states predominantly forms the field-dressed φ_s(Length,t) state.

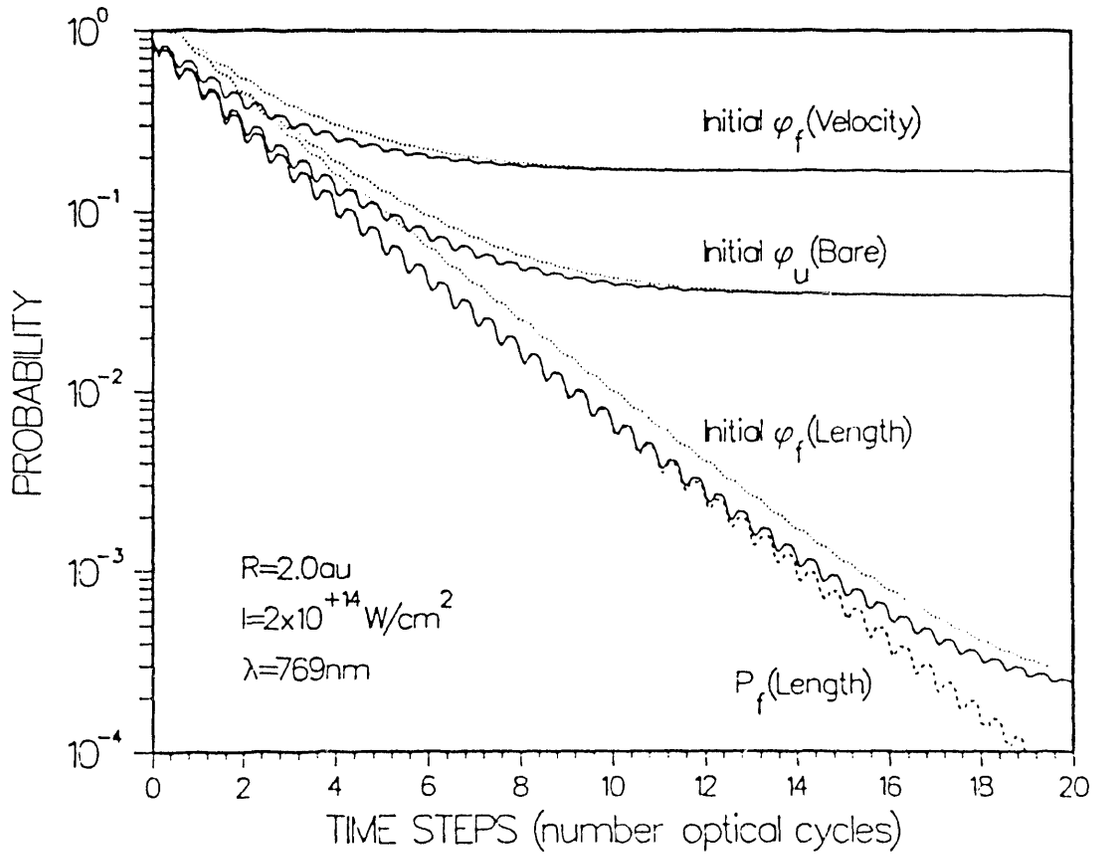

Figure 2. Same conditions as Fig. 1, but for initially prepared φ_u, φ_f(Length) and φ_f(Velocity) states. Again, an exponential decay for the field dressed φ_f state in the length gauge is observed, while φ_u and φ_f(Velocity) introduce various mixtures of fast and slow components. In contrast, note how P_f(Length) associated with the initial φ_f(Length) state remains exponential out to 20 optical cycles.

A striking feature of the figures we show for λ=769nm is that the sum $(P_g+P_u)=(P_s+P_f)$ closely follows P_{norm}, and the wavepacket within the 'box' is predominantly in the two lowest H_2^+ electronic states, φ_g and φ_u, or equivalently, φ_s and φ_f. There is a lag between (P_g+P_u) and P_{norm} due to the 'free' electron component of $\Psi(t)$ which has been ionized, but has not yet reached the absorbing boundary and is still included in P_{norm}. For shorter wavelengths, such as λ=228nm studied by Chelkowski etal[1] we indeed find a more pronounced discrepancy between (P_g+P_u) and P_{norm} which suggests that excited electronic states of H_2^+ might be contributing to $\Psi(t)$ as well.

In Fig. 1 we also include the decay of a wavepacket initially prepared in a velocity dressed φ_s(Velocity) state. Here we see that a very large φ_f(Velocity) component contributes to the decay, strongly confirming the validity of using the two-state length gauge model. This is exactly the same conclusion that we have extracted from the calculations of Muller[1] for λ=396nm. Even more dramatic confirmation is seen in Fig. 2 where the initial φ_f(Length) state remains beautifully exponential over three decades, while the initial φ_f(Velocity) state is strongly coupled to the slowly decaying φ_s(Velocity) state.

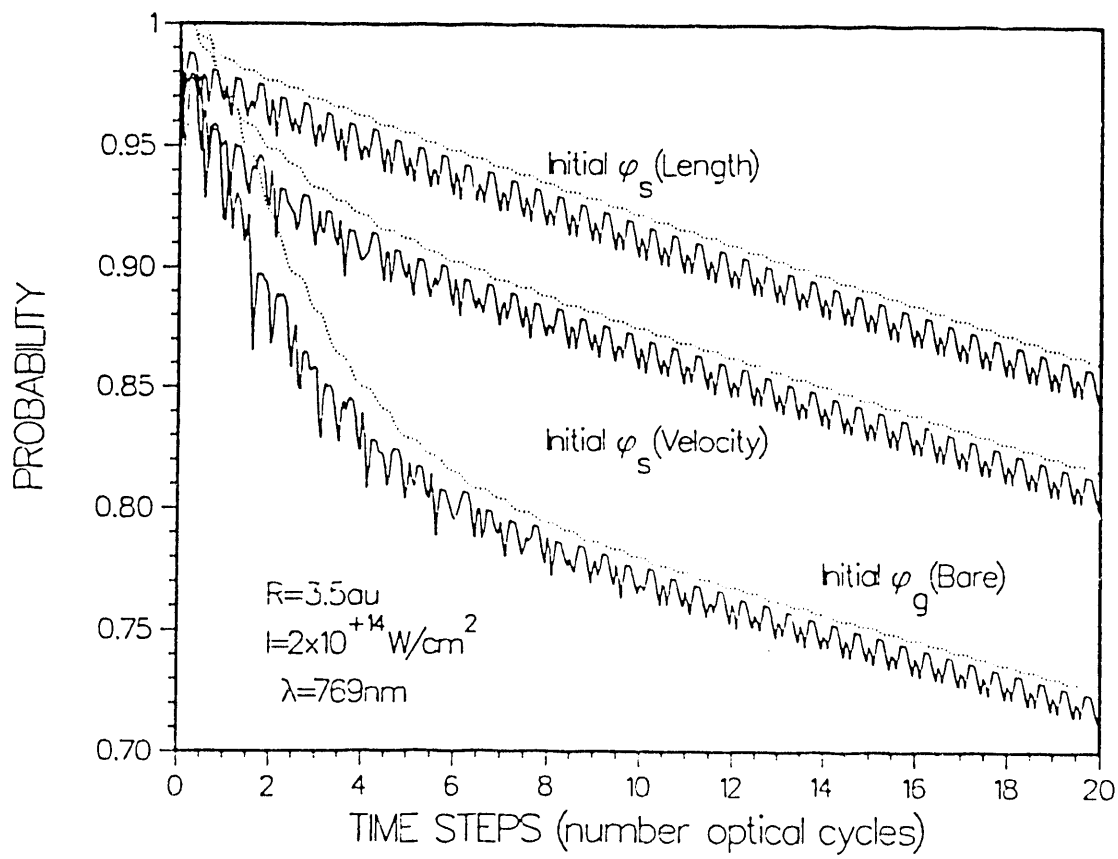

Figure 3. Identical conditions and notation as Fig. 1, but for a fixed internuclear distance of R=3.5au.

This same behavior is still prevalent at R=3.5au as seen in Fig. 3 and Fig. 4 again for λ=769nm and I=2x10^{14}W/cm^2. Once more, in the length gauge φ_s and φ_f are predominantly uncoupled, and decay exponentially, while φ_g and φ_u and now to a lesser extent the φ_s(Velocity) and φ_f(Velocity) states are still coupled to each other and represent poor "stationary states" in the laser field.

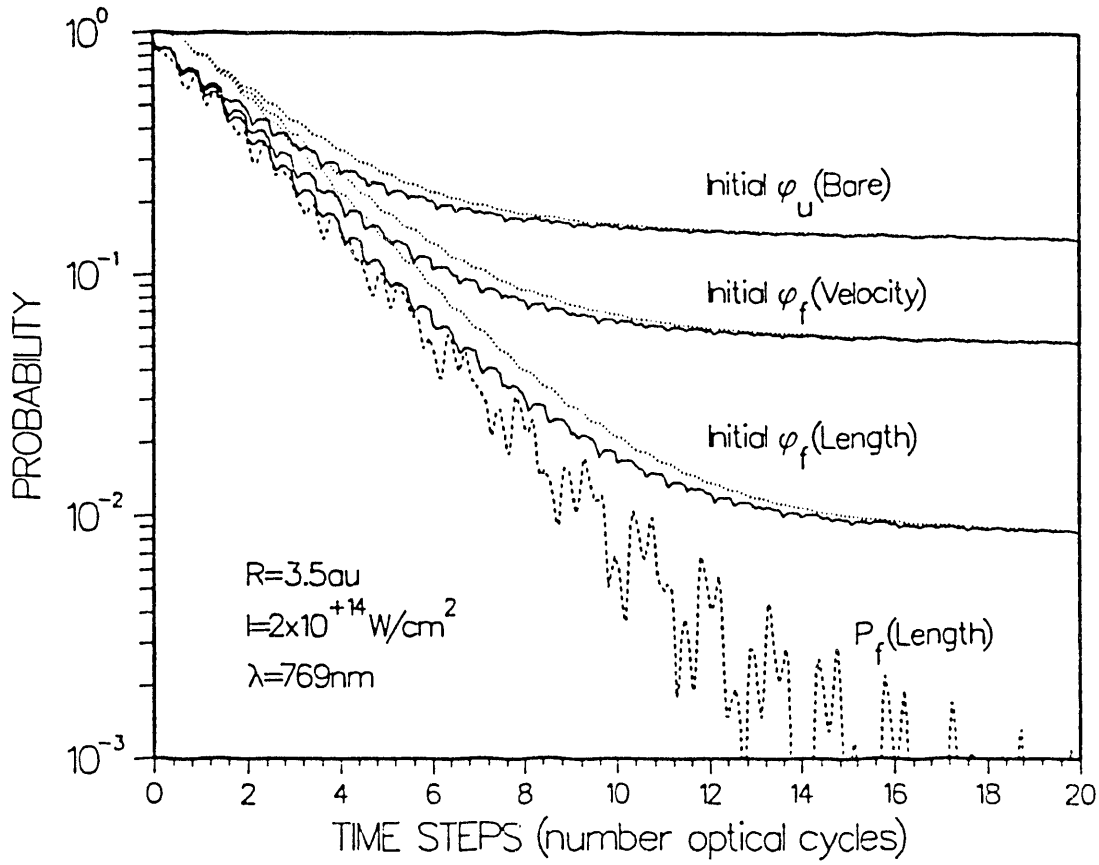

Figure 4. Identical conditions and notation as Fig. 2, but for a fixed internuclear distance of R=3.5au.

Table I gives a summary of some ionization rate constants that have been extracted from the observed exponential decay of the <u>exact</u> solution initially prepared in the φ_s(Length) state. If this rate constant is equated to $\Gamma_s/\hbar$ in Eq. (9), and if the comparable rate for $\Gamma_f/\hbar$ extracted from the exact solutions is also used, then indeed the solution of the simple two-state model does an excellent job of simulated the exact results. Hopefully an adiabatic turn-on of the laser field predominantly converts $\varphi_g \rightarrow \varphi_s$(Length) and these tabulated rates are a good measure of what we can expect in a real pulsed laser experiment. The question is what do these results tell us about the possibility of producing vibrationally stabilized populations of H_2^+ molecules[4] without having them destroyed by ionization?

Table 1. Calculated ionization rate constants ($fsec^{-1}$) for H_2^+ at fixed R. Rates are given for the slow φ_s(length) field-following dressed state which adiabatically correlates with the field-free φ_g state for $H_2^+(1s\sigma_g)$.

	Intensity (W/cm^2) for linearly polarized λ=769nm laser					
R(a.u)	$5x10^{13}$	$1x10^{14}$	$2x10^{14}$	$3x10^{14}$	$5x10^{14}$	$1x10^{15}$
2.0	-	-	$2x10^{-7}$	$2x10^{-5}$	0.0009	0.004
2.5	-	-	0.0002	0.0008		0.14
3.0		0.0001	0.0006	0.003	0.04	
3.5	0.0003	0.0010	0.003	0.016	0.36	
4.0		0.009	0.017			
4.5[a]		0.013	0.04			
5.0		0.012	0.06			
6.0[b]		0.014	0.10			
7.0[b]		0.022	0.10			
8.0[b]		0.023	0.14			

	Intensity (W/cm^2) for linearly polarized λ=228nm laser[c]					
R(a.u)	$5x10^{13}$	$1x10^{14}$	$2x10^{14}$	$3x10^{14}$	$3.9x0^{14}$	$5x10^{14}$
2.0	$2x10^{-5}$	0.0001	0.0004	0.004	0.018	0.028
3.0[a]	0.014	0.022	0.11	0.12	0.12	0.16

[a] At these distances $V_u - V_g = \hbar\omega$ and length and velocity couplings are equivalent.
[b] At large distances the φ_s(length) and φ_f(length) states give identical rates and approach the H(1s) rate defined by the dissociation limit H(1s) $+H^+$.
[c] Wavelength and distances chosen for comparison with comparable rates obtained by Chelkowski etal[1]. The two sets of calculations are in excellent.

The situation for λ=228 in Table 1 is as presented in reference 1. At R=2au the ionization rate is negligible for $I \leq 2x10^{14} W/cm^2$, but rapidly increases as R→3au. Indeed, at this wavelength vibrationally stabilized molecules are expected to be predominantly trapped in the vicinity of R≈3au[4], and this enhanced ionization rate puts a severe upper bound on how long such trapped molecules can survive without being ionized. In this case, as already emphasized by Chelkowski etal[1], either very short pulses, or peak intensities appreciable below $5x10^{13} W/cm^2$ are required if stabilized populations of H_2^+ are to survive without being ionized and experiencing the effect of Coulomb explosion.

The results for λ=769nm are much more encouraging. The population of vibrationally trapped H_2^+ molecules[3] for λ=769nm is predominantly located at R=3.5-4.0au. The results presented in Table 1 suggest that at I=2x10^{14}W/cm^2 and certainly for I=1x10^{14}W/cm^2 the stabilized molecules might survive a 150μsec pulse without appreciable ionization. For higher intensities the ionization of the trapped molecules will again lead to Coulomb explosion. Such processes are suggested by recent experiments with λ=769 radiation.[7] It is our hope that the ionization rates provided by these calculations can be used to predict the proton kinetic energy distribution associated with the explosion.

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