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Photodissociation of H_2^+ upon Exposure to an Intense Pulsed Photonic Fock State[†]

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Producing and controlling nonclassical light states are now the subject of intense experimental efforts. In this paper we consider the interaction of such a light state with a small molecule. Specifically, we develop the theory and apply it numerically to calculate in detail how a short pulse of nonclassical light, such as the high intensity Fock state, induces photodissociation in H_2^+. We compare the kinetic energy distributions and photodissociation yields with the analogous results of quasi-classical light, namely a coherent state. We find that Fock-state light decreases the overall probability of dissociation for low vibrational states of H_2^+ as well as the location of peaks and line shapes in the kinetic energy distribution of the nuclei.

I. Introduction

The interaction of strong short laser pulses with molecular systems is a field of considerable activity, with applications in atomic physics,[1] molecular physics,[2] laser cooling,[3] laser technology,[4] coherent control[5] and basic quantum mechanics. Among the many types of laser-molecule interaction, molecular interaction with intense (>100 TW/cm^2), ultrashort pulses have been drawing prolonged interest over the years.[6] Exposure of molecules to strong fields is invariably associated with a delicate interplay of electronic and nuclear dynamics. Thus the understanding of fundamental dynamics induced in small molecules by light has been the focus of numerous experimental[7] and theoretical studies.[8,9]

A classical electromagnetic field can be closely approached by the quantum coherent photon state, which is a specific linear combination of Fock states $|N\rangle$ (where N is the number of photons) having the minimal allowed uncertainty $\Delta N \Delta\phi = \hbar/2$ (where ϕ is the photon phase).[10] As we show in the next section, the special constant phase difference relations between successive Fock states in the coherent state of light enables the combined molecule-photon wave function to be rigorously written as a product between the molecular state and the coherent light state and entanglement between the two is rigorously avoided. This shows that the standard "semiclassical" treatment is rigorously applicable as a quantum solution and the photons affect the molecule only through the expectation value of the electric field $\vec{E}$. This forms the basis for almost all published treatments of strong laser-molecule interactions originating in the mid 70s and early 80s.[11,12]

However, this "semiclassical" approach is accurate only for ideal coherent states of light with the perfect specialized phase relations mentioned above. The effect of deviations from coherency on molecular dynamics has not been, to our knowledge, considered in a detailed theoretical way. Although such distortions can arise due to cavity imperfections, laser threshold effects, or aberrations of the laser beam as it is released from the cavity, they can also be produced in a controlled way.[13] Furthermore, experimental techniques are close to the stage where specialized quantum states of light can be readily produced[13,14] with high intensities and ultrafast switching capabilities. It is therefore interesting to study theoretically the effects such fields can have on molecules and compare them with the standard coherent-state results.

It is the purpose of this paper to study in detail the photodissociation of H_2^+ following interaction with a nonclassical light source. We select to work with a Fock state $|N\rangle$ having exactly N photons of frequency ω. The Fock state is as different as can be from a classical electromagnetic field because the phase uncertainty is formally infinite. In section II we present our general formalism for strong laser fields with a prescribed quantum photon state. We then discuss coherent states showing they lead to the usual semiclassical equations. We develop a Born–Oppenheimer (BO) framework suitable for applying the formalism to study dynamical molecular processes under various conditions. Various methods for solving equations of this or similar type exist[15] and here we use a method which we describe in detail in section III. Using this framework we investigate the photodissociation of H_2^+ under a high N Fock state comparing it with the results of a coherent-state calculation. The results are reported in section IV and the conclusions are summarized and discussed in section V.

II. Theory

A. Basics. In the long wave limit the electric field operator of a cavity of volume Ω and a laser mode of frequency ω is[10]

$$\hat{E} = i\mathscr{E}_0(\hat{a} - \hat{a}^\dagger) \qquad (1)$$

where $\mathscr{E}_0 = (\hbar\omega/2\varepsilon_0\Omega)^{1/2}$, where $\hbar$ is Planck's constant and ε_0 is the permittivity of the vacuum. We will be interested in

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photonic states with an average large number of photons $\bar{N}$. We write the free-field Hamiltonian of a single mode of frequency ω as

$$\hat{H}_R = \left(\hat{a}^\dagger\hat{a} + \bar{N} + \frac{1}{2}\right)\hbar\omega = \left(\hat{n} + \bar{N} + \frac{1}{2}\right)\hbar\omega \tag{2}$$

A general photonic state is a linear combination of the N-photon states $|n\rangle$, where $n = N - \bar{N}$ and

$$\begin{aligned} \hat{a}^\dagger|n\rangle &= \sqrt{\bar{N} + n + 1}|n + 1\rangle \\ \hat{a}|n\rangle &= \sqrt{\bar{N} + n}|n - 1\rangle \\ \hat{n}|n\rangle &= (\bar{N} + n)|n\rangle \end{aligned} \tag{3}$$

and obviously, $\langle n|n'\rangle = \delta_{nn'}$. Any photonic state is a linear combination of Fock states:

$$\Psi_{\mathrm{phot}} = \sum_n \gamma_n|n\rangle \tag{4}$$

The summation includes all possible n's:

$$n = -\bar{N}, ..., \infty \tag{5}$$

Now we couple the photons with a collection of M particles of charge q_m and 3D vectors $\mathbf{r}_m$, $m = 1,..., M$. The molecular field-free Hamiltonian is denoted $\hat{H}_M$, and we will discuss its exact form later. Obviously, it operates only on the particle coordinates. If we assume linear polarization along the x axis, the combined particle-laser Hamiltonian is[10]

$$\hat{H} = \hat{H}_M + \hat{H}_R + \hat{E}\hat{\mu} \tag{6}$$

where $\hat{\mu}$ is the x-component of the total dipole moment of the particles:

$$\hat{\mu} = \sum_{m=1}^{M} q_m\hat{x}_m \tag{7}$$

On the basis of eq 4, we take the total wave function as

$$\Psi(t) = \sum_n \Phi_n(\mathbf{r},t)|n\rangle \tag{8}$$

where $\mathbf{r} \equiv (\mathbf{r}_1, ..., \mathbf{r}_M)$. The values of the coefficients $\Phi_n(\mathbf{r},t{=}0)$ define the initial state of the system. For example, when the system is initially in the molecular state $\Phi_{\mathrm{ini}}(\mathbf{r})$ and the laser is in a state given by eq 4, then

$$\Psi(t{=}0) = \Phi_{\mathrm{ini}}(\mathbf{r})\sum_n \gamma_n|n\rangle \tag{9}$$

So in this case

$$\Phi_n(\mathbf{r},t{=}0) = \Phi_{\mathrm{ini}}(\mathbf{r})\gamma_n \tag{10}$$

We intend to consider this initial condition in more detail later. Let us define

$$\rho_{nn'}(t) = \int \Phi_n^*(\mathbf{r},t)\,\Phi_{n'}(\mathbf{r},t)\,\mathrm{d}^{3M}r \tag{11}$$

Normalization of Ψ demands

$$\sum_n \rho_{nn}(t) = 1 \tag{12}$$

The expectation value of the number of photons is

$$\langle\hat{N}\rangle_t = \bar{N} + \sum_n \rho_{nn}(t)n \tag{13}$$

The expectation value of the electric field is

$$\begin{aligned} \langle\hat{E}\rangle_t &= i\mathcal{E}_0\sum_{nn'} \rho_{nn'}\langle n|(\hat{a} - \hat{a}^\dagger)|n'\rangle \\ &\approx i\frac{1}{2}E\sum_{nn'}(\rho_{nn'-1} - \rho_{nn'+1}) \end{aligned} \tag{14}$$

where we define E as

$$\frac{1}{2}E = \mathcal{E}_0\sqrt{\bar{N}} = \sqrt{\frac{\hbar\omega\bar{N}}{2\varepsilon_0\Omega}} \tag{15}$$

Note that E as defined has the dimensions of an electric field, but it is not in itself necessarily equal to the *expectation value* of the electric field (eq 14). In fact, in a perfect Fock state $|n\rangle$ the expectation value of the electric field is zero although the photonic state includes many (i.e., $n + \bar{N}$) photons. The definition in eq 15 is perfectly in accord with the standard definition of quantum electric-field energy-density[10] $(\varepsilon_0/2)E^2$ as the volume-density of the photonic-energy $\hbar\omega\bar{N}/\Omega$. Note that the effective electric field E can be strengthened either by increasing $\bar{N}$ or by decreasing the cavity volume Ω. E is the on/off control and is a function of time having an experimentally adjustable form. In this work we impose the following form for $E(t)$:

$$E(t) = \begin{cases} E_0\sin^2\left(\dfrac{\pi}{\tau_{\mathrm{p}}}t\right) & t \in [0, \tau_{\mathrm{p}}] \\ 0 & \text{otherwise} \end{cases} \tag{16}$$

where E_0 is the amplitude and τ_{p} the pulse duration. The Schrodinger equation for the combined molecule-light state is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(t) = \hat{H}\Psi(t) \tag{17}$$

This can be projected onto the Fock state $\langle n|$, yielding equations for the unknown coefficients $\Phi_n(\mathbf{r},t)$:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Phi_n(\mathbf{r},t) = (\hat{H}_M + n\hbar\omega)\,\Phi_n(\mathbf{r},t) + \frac{\mathrm{i}}{2}E(t)\,\hat{\mu}(\Phi_{n-1}(\mathbf{r},t) - \Phi_{n+1}(\mathbf{r},t)) \tag{18}$$

Equation 18 is a very general explicitly time-dependent equation of motion for the total photon-particle combined state. Because we have chosen the Fock states as a basis the equation pertains only to the *coefficients* $\Phi_n(\mathbf{r},t)$. These coefficients however offer full information concerning both the molecule and the photonic state coupled to it.

B. Application to Molecules Using a Born−Oppenheimer Approach. We simplify eq 18 for molecules using the Born−Oppenheimer approach. The particles of the system are separated to electrons and nuclei, writing $\mathbf{r} = (\mathbf{s},\mathbf{R})$, where $\mathbf{s}$ are the coordinates (including spin) of the electrons and $\mathbf{R}$ are those of the nuclei. The material Hamiltonian is written as

$$\hat{H}_M = \hat{T}_N + \hat{H}_{\mathrm{e}}(\mathbf{R}) \tag{19}$$

where $\hat{T}_N$ is the kinetic energy of the nuclei and $\hat{H}_e(\mathbf{R})$is the so-called electronic Hamiltonian, which depends parametrically on the nuclear position, including the kinetic energy of the electrons and all the potential energies of the Coulomb interaction between the charged particles of the molecule. The adiabatic states $\zeta_j(\mathbf{s};\mathbf{R})$ are eigenstates of the electronic Hamiltonian, with eigenvalues $u_j(\mathbf{R})$:

$$\begin{aligned} &\hat{H}(\mathbf{R})\,\zeta_j(\mathbf{s};\mathbf{R}) = u_j(\mathbf{R})\,\zeta_j(\mathbf{s};\mathbf{R}) \\ &\langle\zeta_j|\zeta_{j'}\rangle = \delta_{jj'} \qquad j' = 1, 2, ... \\ &u_1(\mathbf{R}) \le u_2(\mathbf{R}), ... \end{aligned} \tag{20}$$

We now expand the coefficient functions $\Phi_n(\mathbf{r},t)$ of eq 8 as linear combinations of the electronic adiabatic states, leading to new time-dependent coefficient functions $\psi_{nj}(\mathbf{R},t)$ that depend on the photon index n, the electron level index j, and explicitly on the nuclear degrees of freedom:

$$\Phi_n(\mathbf{s},R,t) = \sum_j \zeta_j(\mathbf{s};\mathbf{R})\, \psi_{nj}(\mathbf{R},t) \tag{21}$$

Plugging eq 21 into the general eq 18 and projecting onto state ζ_j by integration on the electronic coordinates, we obtain, after neglect of nonadiabatic couplings:

$$i\hbar \frac{\partial}{\partial t} \psi_{nj}(\mathbf{R},t) = (\hat{T}_N + u_j(\mathbf{R}) + n\hbar\omega)\, \psi_{nj}(\mathbf{R},t) + (V_{jj'}(\mathbf{R},t)\, \psi_{n-1,j'}(\mathbf{R},t) + V^*_{jj'}(\mathbf{R},t)\, \psi_{n+1,j'}(\mathbf{R},t)) \tag{22}$$

Here, a summation over the repeated index j' is implied (Einstein's convention) and $V_{jj'} = iE(t)\, \hat{\mu}_{jj'}(\mathbf{R})$ where

$$\mu_{jj'}(\mathbf{R}) = \int \zeta_j(\mathbf{R},\mathbf{s})^\dagger\, \hat{\mu}_e(\mathbf{R},\mathbf{s})\, \zeta_{j'}(\mathbf{R},\mathbf{s})\, d^3\mathbf{s} + \delta_{jj'}\mu_N(\mathbf{R}) \tag{23}$$

are the total dipole moment electronic matrix elements, with $\hat{\mu}_e$ and $\hat{\mu}_N$ the electronic and nuclear dipole moment operators.

C. Coherent Photonic State and the "Semiclassical" Solution. As explained above, the dynamics of the combined molecular-photon system depends on the equation of motion, eq 18 and the initial state of both the photons (eq 4) and molecule $\Phi_{\text{ini}}(\mathbf{r})$ (eq 9). If our system starts from the coherent photonic state $|\alpha\rangle$, then the coefficients for eq 10 are

$$\gamma_n = e^{-1/2|\alpha|^2} \frac{\alpha^{\bar{N}+n}}{\sqrt{(\bar{N}+n)!}} \qquad \alpha = \sqrt{\bar{N}}e^{i\theta} \tag{24}$$

where θ is a constant phase that characterizes the coherent state and will be will be discussed later. Note that due to normalization and because $\sum_n|\gamma_n|^2 = 1$ for eq 24, we must have also

$$\int |\Phi_{\text{ini}}(\mathbf{r})|^2\, d^{3M}r = 1 \tag{25}$$

Next we apply the approximation $\bar{N} + n \approx \bar{N}$ (which is valid for $\bar{N} \gg n$) so that a phase relation between two successive coefficients of the Fock states is formed in the coherent state:

$$\gamma_{n+1} \approx e^{i\theta}\gamma_n \tag{26}$$

As will be shown next, this phase relation is crucial for deriving the semiclassical expression. The solution of eq 18 fulfilling the initial conditions eqs 9 and 24 can be written as

$$\Phi_n(\mathbf{r},t) = \gamma_0 e^{in(\theta-\omega t)}\Phi(\mathbf{r},t) \tag{27}$$

where $\Phi(\mathbf{r},t{=}0) = \Phi_{\text{ini}}(\mathbf{r})$ and the equation for $\Phi(\mathbf{r},t)$ for $t > 0$ is obtained by plugging eq 27 into eq 18. Following a few simple manipulations and division by $e^{in(\theta-\omega t)}$, we find that $\Phi(\mathbf{r},t)$ is a solution of the equation

$$i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r},t) = [\hat{H}_M + E(t)\hat{\mu} \sin(\omega t - \theta)]\Phi(\mathbf{r},t) \tag{28}$$

This equation is recognized as the "semiclassical equation of motion", where the molecular system interacts with a classical electromagnetic field having an envelope $E(t)$ and a time-sinusoidal oscillatory part at the photon frequency ω.

We find that when the laser-molecule initial state is given by eq 9 and γ_n are given by eq 24, i.e., when we have an EM field initially in a coherent state, the solution of eq 28 is exactly equivalent to the solution of the full quantum equation eq 18.

The structure of the exact wave function in this case, namely, eq 27 shows that the light-matter wave function is a product function at all times (and not only at time $t = 0$). Thus the two entities stay separate in this special case and no correlation or entanglement between them develops. This is different than the general case (eq 21).

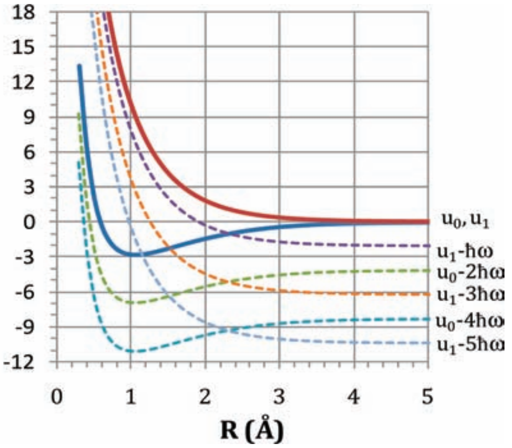

Figure 1. Ground $u_0(R)$ and the excited $u_1(R)$ adiabatic potentials (full lines). First potentials on the diagonal of the potentials matrix $W(R)$ of eq 33 formed from photon-displaced adiabatic potentials u_0 and u_1 (dashed lines).

Equation 28 can be applied to molecular systems using the Born−Oppenheimer approach.[12,16] Indeed, in this case, the semiclassical wave function is written as

$$\Phi(\mathbf{s},R,t) = \sum_j \zeta_j(\mathbf{s};\mathbf{R})\, \tilde{\psi}_j(\mathbf{R},t) \tag{29}$$

Comparing with eq 21, we see similarity, but there is no dependence on the photonic state, because Φ includes implicitly all possible photon absorption processes. After plugging eq 29 into eq 28, neglecting nonadiabatic couplings, we obtain the standard semiclassical-Born−Oppenheimer equations:

$$i\hbar \frac{\partial}{\partial t} \tilde{\psi}_j(\mathbf{R},t) = [\hat{T}_N + u_j(\mathbf{R}) + V_{jj'}(t) \sin(\omega t - \theta)]\tilde{\psi}_j(\mathbf{r},t) \tag{30}$$

III. Application: Photodissociation of H_2^+

In this section we discuss application of the formalism to the photodissociation of H_2^+, where the products are a proton (p) and a ground-state hydrogen atom. The photodissociation process is caused by a strong 100 TW/cm^2 pulse of wavelength 600 nm with envelop given in eq 16 and pulse duration τ_p = 40 fs. We assume alignment of the H_2^+ molecular axis with the direction of light polarization and treat dynamically only the internuclear distance R. As we are interested with photoproducts in their ground states, we limit our study to the two basic adiabatic potential curves $u_0(R)$ and $u_1(R)$ corresponding to the bonding $1\sigma_g$ and antibonding $1\sigma_u$ states shown as full line curves in Figure 1. We have also performed a few pilot runs referring to additional four excited states of H_2^+, We found that the presence of these states did not significantly affect the results. In addition, the ionization rate for this pulse is not high and this justifies neglecting this effect in first approximation.[17]

The adiabatic surfaces and transition dipole moments $\mu_{01}$for this calculation were obtained from ab initio calculations employing the 6-311++G(3df,3pd) basis set using the Hartree−Fock option of MOLPRO[18] (this is a 1-electron system so correlation is unnecessary). The calculated potentials compare well with the analytical results of ref 19. They are depicted in Figure 1. At large internuclear distance R the two curves coalesce as they both describe a proton and H atom in its ground state. The H_2^+ is assumed to be initially in the vth ($v = 0, 1, 2, ...$) vibrational eigenstate of $u_0(R)$. The energy difference $u_1(R_0) - u_0(R_0)$, where R_0 is the minimum of $u_0(R)$, is much larger than the photon energy ($\hbar\omega \sim 2.1$ eV) so photodissociation via transitions into the dissociative surface is efficient only for intense pulses.

A. Simplifications of the Equations. The first simplifying assumption is to neglect the possibility of emitting photons to positive n states. This assumption is correct for $v \leq 11$ because the vibrational excitation energy is then smaller than the photon energy. This assumption is similar to Rabi's *rotating wave approximation*, neglecting antiresonant terms in the solution, known to be widely applicable.

The coupling matrix $V_{jj'}$ has only nondiagonal elements. The state ψ_{00} will thus couple only to $\psi_{-1,1}$. Similarly, ψ_{-11} will couple to ψ_{00} and to ψ_{-20}. Further consideration shows that ψ_{-20} couples to ψ_{-11} and to ψ_{-31}. The emerging pattern is $\psi_{-n,j}$ couple to $\psi_{-n'j'}$ only if $j - n$ and $j' - n'$ are both even or both odd. Thus, there are two uncoupled manifolds. Because our initial condition is the state ψ_{00} the "odd" manifold is never occupied and can be discarded. Under these conditions it is only necessary to consider the following equation:

$$i\hbar \frac{\partial}{\partial t}\Theta(R,t) = \hat{T}\Theta(R,t) + W(R,t)\,\Theta(R,t) \tag{31}$$

where Θ is the "even" column vector given by

$$\Theta = (\psi_{0,0} \quad \psi_{-1,1} \quad \psi_{-2,0} \quad \psi_{-3,1} \quad \cdots)^{\mathrm{T}} \tag{32}$$

and $W_{jj'}(R,t)$ is given by

$$W = \begin{pmatrix} u_0 & V_{01} & & & & \\ V_{10}^{*} & u_1 - \hbar\omega & V_{01} & & & \\ & V_{10}^{*} & u_0 - 2\hbar\omega & V_{01} & & \\ & & V_{10}^{*} & u_1 - 3\hbar\omega & V_{01} & \\ & & & V_{10}^{*} & \ddots & \ddots \\ & & & & \ddots & \ddots \end{pmatrix} \tag{33}$$

This greatly simplifies the treatment of the equations. Note the interesting structure of the equations: for the system to be in the σ_g electronic state (u_0 potential) it must have absorbed an even (including zero) number of photons whereas for it to be in the σ_u electronic state (u_1) it must have absorbed an odd number of them.

The initial state at time $t = 0$ is the v vibrational eigenstate-state $\varphi_v(R)$ on the ground potential u_0 of H_2^+:

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2} + u_0(R)\right]\varphi_v = \varepsilon_v\varphi_v \tag{34}$$

where M is the reduced nuclear mass equal to half a mass unit. Thus the initial state is described by the coefficient spinor:

$$\Theta(R,t{=}0) = (0, 0, ..., \varphi_v(R), 0, 0, ...)^{\mathrm{T}} \tag{35}$$

To evolve the wave function using eq 31, we define vector-wave function $\Lambda(R,t)$ by

$$\Theta(R,t) = \Lambda(R,t) + \Theta(R,0)e^{-i\varepsilon_v t/\hbar} \tag{36}$$

where $\Theta(R,t)$ is the desired solution of eq 31. The response $\Lambda(R,t)$ can be shown to obey the equation

$$i\hbar \frac{\partial}{\partial t}\Lambda(R,t) = \hat{T}\Lambda(R,t) + W(R,t)\,\Lambda(R,t) + \tilde{\Theta}(R,t) \tag{37}$$

with

$$\tilde{\Theta}(R,t) = (0 \quad V_{10}^{*}(R,t)\,\varphi_v(R)e^{-i\varepsilon_v t/\hbar} \quad 0 \quad 0 \quad \cdots)^{\mathrm{T}} \tag{38}$$

Equation 37 is evolved with $\Lambda = 0$ taken at $t = 0$. For the numerical calculation, we use a grid consisting of 2048 points spanning the range $0.3 < R/\text{Å} < 12$. At the asymptote an absorbing potential is placed, guaranteeing efficient absorption of the photodissociated amplitude before reflection off the grid boundaries.[20] We included in all calculations 6 photonic states (i.e., there were 12 electro-photon states altogether). The propagation of the vector wave equation uses the fast Fourier (FFT)[21] and the Lanczos short-time iteration techniques.[22]

B. Adiabatic Electro-Photonic Potentials. One basic question is the number of photon states that have to be included in the calculation. It is evident from the explicit form of the matrix W in eq 33 that as its dimension $\tilde{N}$ increases the high (j, j) diagonal terms $W_{j,j}$ become dominated by $-j\hbar\omega$ whereas the off diagonal terms are independent of j but are proportional to the amplitude of the electric field envelope E_0. For the coupling to be ineffective the diagonal term must become much larger than the coupling:

$$\tilde{N}\hbar\omega \gg E_0\mu_{01} \tag{39}$$

In the present calculation we assume a field-intensity of $E_0 = 0.053$ au, corresponding to a pulse maximal intensity of 100 TW/cm^2. The transition dipole moment is of the order of $1a_0e$ and for a photon of 2.1 eV we obtain that the number $\bar{N}$ must be much larger than 1. We demonstrate this by comparing the eigenvalues of the matrix $W(R,t)$, here called "adiabatic electro-photonic" or "dressed" potentials[23] at the peak electric field in Figure 2. The eigenvalues for $\tilde{N} = 2$, 4, and 6 are shown. It is clear that the first (highest) two eigenstates are converged

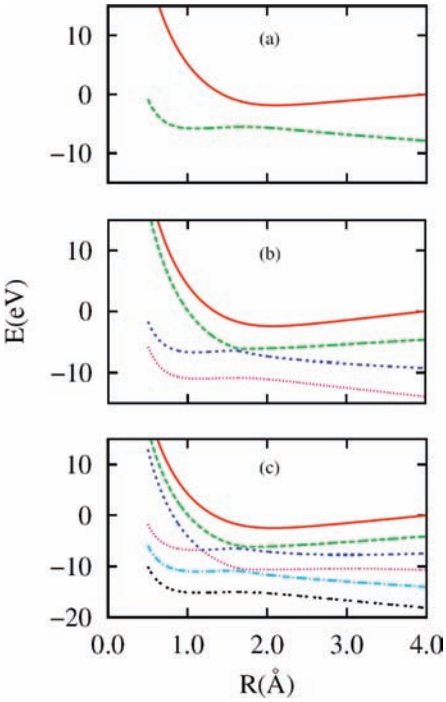

Figure 2. Eigenvalues of the matrix W, the so-called "electro-photonic" adiabatic potentials of eq 33, as a function of internuclear distance, for three matrix dimensions $\tilde{N} = 2$ (a), 4 (b), and 6 (c). Notice that the top two potentials are well converged already at $\tilde{N} = 4$.

TABLE 1: Photodissociation Probabilities for Three Initial Vibrational States

initial molecular state	initial light state Fock	 coherent
v=2	0.12	0.20
v=3	0.31	0.67
v=6	0.95	0.94

already at $\tilde{N} = 4$. This shows that adding photons much beyond this value will minimally affect the results. This is confirmed by the dynamical calculations.

C. Kinetic Energy Distribution. For a given initial vibrational state $\phi_{v_i}(R)$ the probability for dissociation on the (nj) electro-photonic is equal to the integrated flux outward of the association region. For convenience a certain asymptotic point R_a can be assigned, just before the absorbing potential starts, not too far from this region but far enough so that flux hardly ever comes back once passing it, and all time-dependent probabilities can be computed with reference to this point. The total dissociation probability from an initial state v_i up to time t is then the some over all states:

$$\begin{aligned} P(t|v_i) &= \sum_{nj} P_{nj}(t|v_i) \\ &= \sum_{nj} \int_0^t \langle \psi_{nj}(t'|v_i)|\, \hat{j}(R_a)\, |\psi_{nj}(t'|v_i)\rangle \, \mathrm{d}t' \end{aligned} \tag{40}$$

where the $\psi_{nj}(t|v_i)$ are the wave functions propagated by eq 31 with the initial state $\phi_{v_i}(R)$ of eq 35 and

$$\hat{j}(R_a) = (2M)^{-1}[\delta(\hat{R} - R_a)\hat{p} + \hat{p}\delta(\hat{R} - R_a)] \tag{41}$$

is the flux operator, where M is the reduced mass. To calculate the distribution of kinetic energy, we need to extract it from

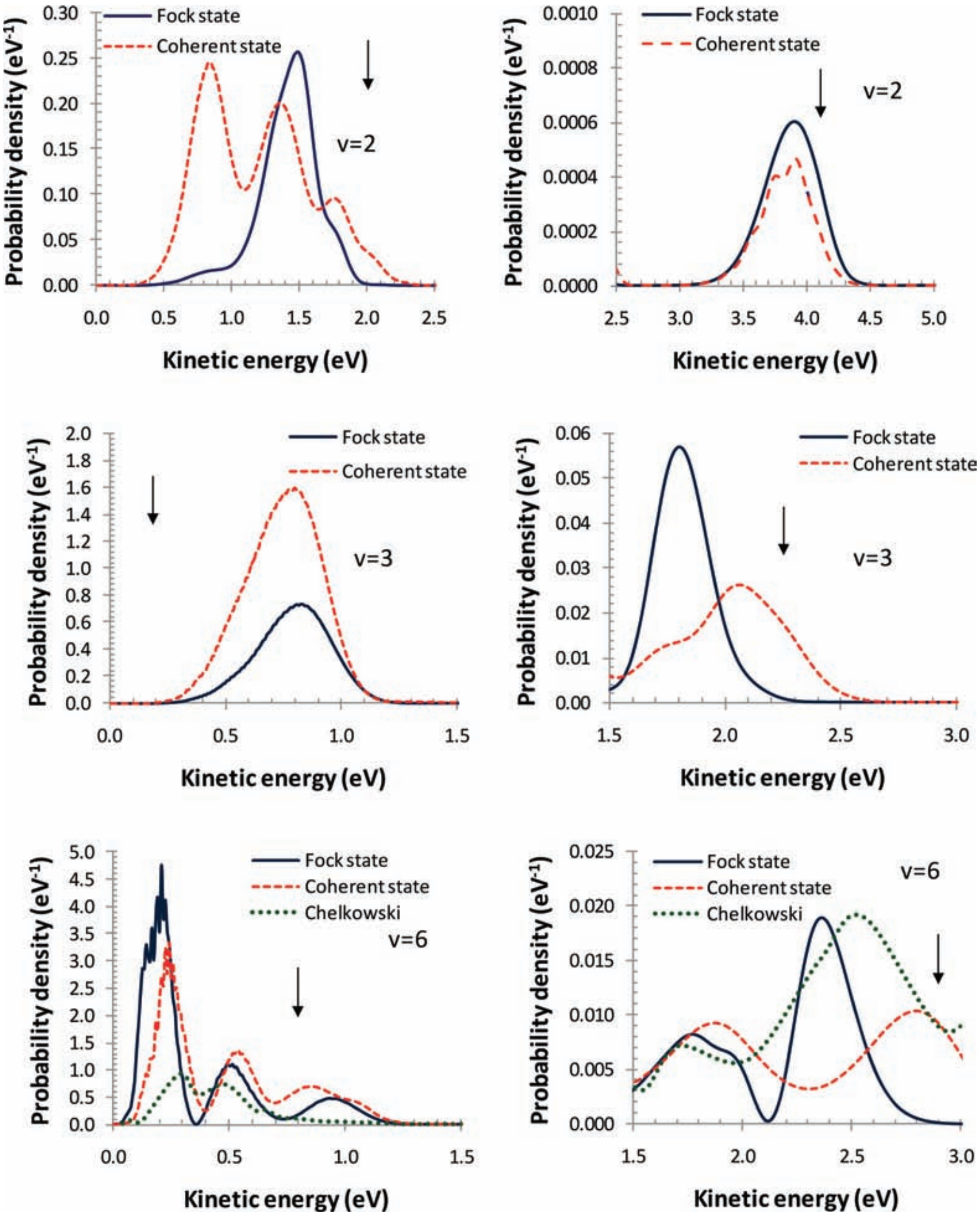

Figure 3. Kinetic energy distribution of H_2^+ as it photodissociates after exposure to a 40 fs pulse of Fock (continuous line) and coherent (dotted line) state light, at 600 nm and 100 TW/cm. Data are given for initial vibrational states v = 2, 3, 6. The left panel shows the low kinetic energy distribution, and the right panel shows higher energies. The arrows indicate the "ideal" quantized kinetic energies as determined by eq 45. For the v = 6 results we included the calculated photodissociation spectra of ref 17 (dashed line).

the asymptotic wave packet. We use the wavepacket itself as follows. At a any asymptotic point $R > R_a$, the potentials are assumed flat and decoupled. At this point then the wavepacket obeying the Schrodinger equation is a sum of plane waves with well-defined momentum and energy:

$$\psi_{nj}(R,t) = \int_{-\infty}^{\infty} A_{nj}(k)\mathrm{e}^{\mathrm{i}kR}\mathrm{e}^{-\mathrm{i}[(\hbar^2k^2/2M)+u_j-n\hbar\omega]t/\hbar}\,\mathrm{d}k \qquad R > R_a \tag{42}$$

The absolute square of the amplitude $|A_{nj}(k)|^2$ is proportional to the momentum distribution. From these considerations we determine the kinetic energy distribution as

$$K_{nj}(E_k|v_i,nj) = \sqrt{\frac{2E_k}{h^2M}} \times \left| \int_0^{\infty} \psi_{nj}(R_a,t'|v_i)\mathrm{e}^{\mathrm{i}(E_k-n\hbar\omega)t'/\hbar}\,\mathrm{d}t' \right|^2 \tag{43}$$

where the prefactor is the normalization constant, ensuring that the integral of K_{nj} over all values of the kinetic energy is equal to the total photodissociation probability:

$$P_{nj}(t\to\infty|v_i) = \int_0^{\infty} K_{nj}(E_k|v_i,nj)\,\mathrm{d}E_k \tag{44}$$

IV. Results for Photodissociation of H_2^+

In the specific calculation made here we used $R_a = 6$ Å and then repeated the calculation with $R_a = 12$ Å. The kinetic energy distribution up to 3 eV was almost unaffected by the two choices. For higher kinetic energies we found significant discrepancies. A component with kinetic energy E_k arrives at the asymptote R_a within time $R_a(2E_k/M)^{-1/2}$. The kinetic energy measurement at R_a (i.e., eq 43) is only valid if the coupling between the surfaces is already zero by then. Thus, we estimate $R_a > \tau_p(2E_k/M)^{1/2}$ for the kinetic energy distribution at E_k to be valid. In practice we notice that this happens even sooner (probably even if R_a is smaller by a factor 2 this still holds) and we conclude that measuring kinetic energy distributions up to 5 eV with $R_a = 12$ Å gives reasonably converged results.

In Table 1 we show the calculated photodissociation probabilities for the Fock and coherent states from initial vibrational states of the molecule. For the low vibrational states the Fock state is twice as efficient in dissociating the molecule whereas for the $v = 6$ eigenstate the two field states give similar probabilities.

More information can be obtained by looking at the kinetic energy distributions given in Figure 3. The initial state is an eigenstate of the unperturbed Hamiltonian so the kinetic energy distribution is expected to reflect energy conservation rules:

$$E_{\mathrm{kin}}(n,v) = \hbar\omega n + [u_0(R_0) + E_v] - u_0(\infty) \tag{45}$$

where the quantum number n indicates the number of photons absorbed and E_v is the vibrational energy of the initial vibrational state. Equation 45 holds for an infinite pulse. In our calculations the pulse is turned on and off within 40 fs. This switching leads to deviations from eq 45: the kinetic energy distribution is smeared and may shift. We denote by arrows in Figure 3 the kinetic energies derived from eq 45. Rather large deviations are observed. In all cases but one (the low kinetic energy arrow for $v = 3$) the peaks are shifted to lower kinetic energies by a few tenths of an electronvolt. For the $v = 6$ case we also show results published in reference 17. We do not expect full agreement to our results (coherent or Fock) because we measure the kinetic energy distribution when the H atom is in its ground electronic state whereas in ref 17 the dissociated H atom is in any bound electronic state. Despite this, the yields at the energy range shown are not much different. For kinetic energies above 3 eV the yield of photoproducts in our calculation drops sharply. This happened even though we included in our treatment 6 photon states; i.e., we allowed the system to absorb up to 6 photons. The results in ref 17 do not decrease at higher energies.

V. Summary and Discussion

The purpose of this Article is to investigate the sensitivity of light-induced photodissociation of H_2^+ to the particular quantum nature of the light field. This issue is of practical interest in view of the rapid developments of new advanced light sources with precise quantum-state control. Our results can also be useful as a stability analysis: how much can Fock perturbations of the coherent state[13] affect the photodissociation dynamics? We have developed a computational framework that can be used to answer such questions in a controlled and accurate manner. Although our equations bare resemblance to a Floquet approach to the coherent state, the main difference is in the way these equations are applied, i.e., using an initial state at time $t = 0$ and a time-dependent envelop. Floquet analysis is strictly true for stationary-periodic applications. To apply it for finite pulses, specialized techniques are required.[9] These are not needed in the present application, because we are not trying to solve the coherent-state-induced dynamics but a different problem: the Fock-state-induced dynamics.

Our results show that photodissociation probabilities especially of the low vibrational states of H_2^+ change significantly (by a factor of 2 or more) whereas the kinetic energy peaks shift and line shapes are different. These findings are significant for attempting to produce quantitative benchmark quality description of the most basic photodissociation, that of H_2^+.

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