Effect of laser intensity on (2+1)-photon ionization of the hydrogen molecule via the $E,F\,^1\Sigma_g$ state

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We have studied theoretically the effect of laser intensity on (2+1)-photon resonance-enhanced multiphoton ionization of the H_2 molecule via both the inner-well and the outer-well vibrational levels of the double-minimum $E,F\,^1\Sigma_g$ state. The branching ratios for the vibrational distribution of the H_2^+ ion, the photoelectron angular distribution, and the corresponding asymmetry parameters have been calculated as functions of laser intensity ranging from 10^7 W/cm^2 to 5×10^9 W/cm^2 (peak intensity). For ionization via the vibrational levels v_E of the inner well, it has been found that the branching ratios depend on laser intensity, the peak of the distribution being at $\Delta v=0$, i.e., $v_E=v_{\rm ion}$ transition, and our results are in good agreement with experiment. For ionization via the outer-well levels v_F we have shown that the lower the value of v_F, the more the ion yield is shifted towards higher $v_{\rm ion}$ levels. We find that the photoelectron angular distribution remains unchanged over the whole intensity range studied in this work.

INTRODUCTION

Resonance-enhanced multiphoton ionization (REMPI) has been extensively used as a probe for understanding the photoionization dynamics of selectively excited molecular states in a strong laser field.[1–8] To explain the experimentally observed features and to theoretically predict the expected behavior of atomic and molecular systems under different conditions of transition, detailed *ab initio* calculations are necessary. Since MPI occurs in strong laser fields, the laser-intensity effect on MPI or REMPI should be taken into consideration. Moreover, the effect of autoionizing Rydberg or core-excited states on REMPI is of much importance in these studies.[6] Strong-field effects on multiphoton autoionization are of considerable interest in atoms[9] as well as molecules.[10] In previous works[11] on multiphoton autoionization in the H_2 molecule, we have studied the effect of laser intensity and the bandwidth on the two-photon autoionization of H_2 via the lowest core-excited autoionizing states of $^1\Sigma_g(1\sigma_u^2)$ symmetry; the laser intensity and bandwidth were found to have significant effects on photoelectron (PE) angular distribution, line shape, and autoionization rate. In view of the recent progress in the experimental study[7] on REMPI of H_2 via different intermediate resonant states, we have embarked upon a project for a thorough theoretical investigation of multiphoton ionization dynamics in H_2. In this work we have studied (2+1)-photon REMPI of H_2 via the $E,F\,^1\Sigma_g$ state, taking into account the effect of variations in laser intensity on the branching ratios and on the PE angular distributions. There exist only a few calculations[12] on REMPI of H_2 in the weak-field limit, and our results for the v_E levels in the low-intensity regime ($\sim10^7$ W/cm^2) are in good agreement with a previous calculation.[12(c)]

It is well known that the double-minimum state $E,F\,^1\Sigma_g$ results mainly from configuration interaction between the Rydberg-like configurations $1\sigma_g2\sigma_g$, the core-excited configuration $1\sigma_u^2$, and the ground-state configuration $1\sigma_g^2$. In the inner well the Rydberg-like configuration $1\sigma_g2\sigma_g$ is the dominant configuration, but in the outer well both the configurations $1\sigma_g2\sigma_g$ and $1\sigma_u^2$ are important. Therefore, it is expected that the photoionization dynamics of the rovibrational levels of the inner and outer wells would be different. In the present work we have considered the (2+1)-photon ionization via rovibrational levels of both the inner and the outer wells. For the inner well we have compared our results with experimental data,[7(b)] but for the outer well no data for the branching ratios exist, although these vibrational levels have been detected by the REMPI technique.[7(c)] To our knowledge this is the first calculation for the REMPI via the outer-well levels, and we have predicted some interesting features in the branching ratios which can be tested experimentally. The effect of laser-intensity variation on the REMPI process has been studied in this work for a particular value of the laser bandwidth (~1.9 cm^{-1}) that had been used in experiment.[7(b)]

THEORY

In an $(m+n)$-photon REMPI transition one has to consider an infinite number of nonresonant (bound +continuum) states both in the first m-photon and in the next n-photon excitation steps. Furthermore the ionization continuum, the initial state (usually the ground state), and the resonant state are also involved in the calculations. In the resolvent-operator technique,[9,10] application of which to the present problem is discussed below in some detail, an infinite number of equations for the matrix elements of the resolvent operator can be written down which, after elimination of the intermediate non-

resonant states and the continuum states, reduce to two equations containing the m-photon matrix element for the initial resonant-state transition, the n-photon ionization width, and the ac Stark shift for the resonant state. Hence one can obtain an expression for the transition probability per unit time under the condition that the other decay channels are much faster than the Rabi oscillation between the initial and the resonant state. In very strong fields, however, when this oscillation is faster than the other decay channels, one has to consider the time development of the total ionization yield.[10]

The (2+1)—photon REMPI process considered here is shown schematically in Fig. 1. By the first photon the molecule is excited from the ground state $|g\rangle$ to an intermediate virtual state which can be represented as a complete set of actual states $|b\rangle$; thereafter by the second photon the molecule is excited to the resonant intermediate state $|i\rangle$; next the third photon raises the molecule to the ionization continuum $|c\rangle$. All the states referred to above are connected by single-photon dipole transitions.

Let $G(z)$ be the resolvent operator defined as $G(z)=(z-H)^{-1}$, where H is the total Hamiltonian given by (H_M+H_R+D), H_M and H_R being the Hamiltonians of the free molecule and the radiation field, respectively, and D the electron-radiation interaction written as $D=-e\mathbf{r}\cdot\mathbf{E}(t)$, $\mathbf{E}(t)$ being the electric field. Restricting ourselves to a single radiation mode and making the dipole approximation we have

$$E(t)=i(2\pi\hbar\omega)^{1/2}[a(t)\varepsilon-a^{\dagger}(t)\varepsilon^{*}]\ , \tag{1}$$

where ω is the field frequency, $a(t)=ae^{-i\omega t}$, $a^{\dagger}(t)=a^{\dagger}e^{i\omega t}$, where a and $a^{\dagger}$ are the annihilation and creation operators, respectively, and ε is the polarization vector. The states used for the uncoupled (molecule+field) system are written as products of molecular wave functions (i.e., eigenfunctions of H_M) and the photon-number states, viz., $|g\rangle|n\rangle$, $|b\rangle|n-1\rangle$, $|i\rangle|n-2\rangle$, and $|c\rangle|n-3\rangle$, n being he number of photons initially present in the single mode. The corresponding energies are given by $E_g=\mathcal{E}_g+n\hbar\omega$; $E_b=\mathcal{E}_b+(n-1)\hbar\omega$; $E_i=\mathcal{E}_i+(n-2)\hbar\omega$ and $E_c=\mathcal{E}_c+(n-3)\hbar\omega$, the $\mathcal{E}$'s being the molecular energies.

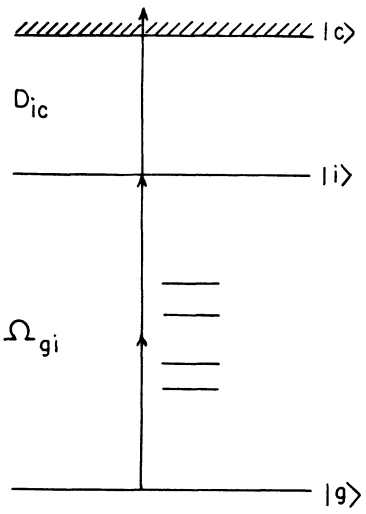

FIG. 1. (2+1)-photon REMPI. Two photons excite the molecule from the ground $X\,^1\Sigma_g$ state $|g\rangle$ to the $E,F\,^1\Sigma_g$ state $|i\rangle$, whereafter a third photon excites it to the $[H_2^+(X\,^2\Sigma_g)+e]$ continuum $|c\rangle$.

Taking the matrix elements of the resolvent operator between the states of interest, the operator equation $(z-H)G(z)=1$ yields the following algebraic equations:

$$(z-E_g)G_{gg}-\sum_b D_{gb}G_{bg}=1\ , \tag{2a}$$

$$(z-E_b)G_{bg}-D_{bi}G_{ig}-D_{bg}G_{gg}=0\ , \tag{2b}$$

$$(z-E_i)G_{ig}-\sum_b D_{ib}G_{bg}-\int D_{ic}G_{cg}dE_c=0\ , \tag{2c}$$

$$(z-E_c)G_{cg}-D_{ci}G_{ig}=0\ . \tag{2d}$$

We solve Eqs. (2b) and (2d) for G_{bg} and G_{cg} and substitute the latter in Eqs. (2a) and (2c), thereby obtaining

$$(z-E_g)G_{gg}-\Omega_{gi}G_{ig}=1\ , \tag{3a}$$

$$\left[z-E_i-\int |D_{ic}|^2(z-E_c)^{-1}dE_c\right]G_{ig}-\Omega_{ig}G_{gg}=0\ , \tag{3b}$$

where $\Omega_{gi}=\sum_b D_{gb}D_{bi}/(z-E_b)$.

To evaluate Ω_{gi} one can replace z by E_g (pole approximation) as long as the intermediate nonresonant states $|b\rangle$ are far apart from the resonant level so that near-resonance effect are not important. Similarly, to evaluate $\int |D_{ic}|^2(z-E_c)^{-1}dE_c$ we replace z in the denominator by $E+i\eta$, where $E=E_g$, and taking the limit $\eta\to 0+$, obtain

$$\int \frac{|D_{ic}|^2}{E-E_c+i\eta}dE_c=P\int\frac{|D_{ic}|^2}{E-E_c}dE_c-i\pi|D_{ic}|^2_{E_c=E}$$
$$=S_I-\tfrac{1}{2}i\gamma_I\ , \tag{4}$$

where S_I is the ac Stark shift and γ_I the ionization width.

Using relation (4) and introducing the spontaneous decay width γ_S and the laser bandwidth γ_L phenomenologically in Eq. (3b), we obtain

$$(z-E_g)G_{gg}-\Omega_{gi}G_{ig}=1\ , \tag{5a}$$

$$[z-E_i-S_I+\tfrac{1}{2}i(\gamma_I+\gamma_S+2\gamma_L)]G_{ig}-\Omega_{ig}G_{gg}=0\ , \tag{5b}$$

where the factor 2 in front of γ_L follows[13] from the phase diffusion model of laser phase fluctuations. Replacing $(z-E_g)$ by z' in Eqs. (5), we obtain

$$z'G_{gg}-\Omega_{gi}G_{ig}=1\ , \tag{6a}$$

$$[z'+\delta-S_I+\tfrac{1}{2}i(\gamma_I+\gamma_S+2\gamma_L)]G_{ig}-\Omega_{ig}G_{gg}=0\ , \tag{6b}$$

where $\delta=E_g-E_i=2\hbar\omega-(\mathcal{E}_i-\mathcal{E}_g)$ is the detuning from the resonant state $|i\rangle$.

We solve Eqs. (6) for G_{gg} and G_{ig} and, in the weak-field limit $\Omega_{ig}\ll\gamma_I$, obtain the following expression for the ionization rate:

$$\frac{dP}{dt}=\frac{\gamma_I \mid \Omega_{ig} \mid^2}{(\delta-S_I)^2+\gamma^2/4} ,$$

where $\gamma=\gamma_I+\gamma_S+2\gamma_L$.

When the weak-field limit does not hold, one has to evaluate the inverse Laplace transform of the resolvent-operator matrix elements to obtain the populations of the states $\mid g\rangle$ and $\mid i\rangle$ as $\mid U_g(t)\mid^2$ and $\mid U_i(t)\mid^2$, respectively, whereupon the total ionization yield is obtained as $P(t)=1-\mid U_g(t)\mid^2-\mid U_i(t)\mid^2$.

To obtain the photoelectron (PE) angular distribution, the ionization yield is evaluated as a function of the scattering angle (θ,ϕ) of the PE with respect to $\hat{\varepsilon}$ which is chosen as the axis of quantization. The matrix elements involving the electronic continuum, viz. γ_I and S_I are expressed as functions of (θ,ϕ); setting $\phi=0$, we obtain

$$\frac{dP(\theta)}{dt}=\frac{\gamma_I(\theta) \mid \Omega_{ig} \mid^2}{[\delta-S_I(\theta)]^2+[\frac{1}{2}\gamma(\theta)]^2} , \quad (7)$$

where $\gamma(\theta)=\gamma_S+2\gamma_L+\gamma_I(\theta)$. For a dipole transition $\gamma_I(\theta)=\sum_l \beta_l P_l(\cos\theta)$ and in the lower-intensity regime where $\gamma_I(\theta)$, $S_I(\theta)\ll\gamma_L$, the denominator is practically angle independent, and the angle dependence of the ionization rate follows that of $\gamma_I(\theta)$, the numerator. However, as the intensity is increased, $\gamma_I(\theta)$ and $S_I(\theta)$ are no longer negligible compared to γ_L, and as a result, the denominator develops an angle dependence which we can express as another Legendre polynomial series expansion. Thus the ionization rate becomes the ratio of two different Legendre polynomial series, viz. another (in general infinite) series in Legendre polynomials:

$$\frac{dP(\theta)}{dt}=N[1+\alpha P_2(\cos\theta)+\beta P_4(\cos\theta)+\cdots] , \quad (8)$$

where the coefficients are functions of Clebsch-Gordan coefficients and the dipole transition moments.

CALCULATIONS

The transitions considered in this paper are

$$H_2\ X\,^1\Sigma_g(v_g,j_g)\xrightarrow{2\hbar\omega}E,F\,^1\Sigma_g(v_E,j_E \text{ and } v_F,j_F)\xrightarrow{\hbar\omega}H_2^+\ X\,^2\Sigma_g(v_I,j_I)+e .$$

Calculations have been done in three steps: evaluation of (i) electronic and nuclear wave functions, (ii) dipole transition moments between states of interest (bound-bound and bound-continuum), and (iii) ionization rate and PE angular distribution for transition to the different vibrational levels of the H_2^+ ion.

For the E,F state we chose a molecular-orbital–configuration-interaction wavefunction with four configurations $1\sigma_g^2$, $1\sigma_u^2$, $1\sigma_g 2\sigma_g$ and $1\sigma_u 2\sigma_u$ built from a minimal Slater basis. The exponents were variationally adjusted at all values of the internuclear separation R to minimize the energy. The electronic energies agree with the values given by Kolos and Wolniewicz[14] to within 3–4%. The continuum functions were constructed as a spin-coupled Slater determinant containing the $1\sigma_g$ orbital for H_2^+ [variational linear combination of atomic orbitals (LCAO)] and the Coulomb function for the free electron. The latter was obtained by summation over partial waves $l=1$ and 3, contributions from higher l's being found to be negligibly small. Transitions to both the $^1\Sigma_u$ continuum and the $^1\Pi_u$ continuum were summed to obtain the total ionization.

The two-photon matrix element Ω_{ig} was obtained using a truncated summation approximation over the vibrational levels of two intermediate electric states, the $B\,^1\Sigma_u$ and the $C\,^1\Pi_u$, the bound-bound electronic dipole transition moments

$$X\,^1\Sigma_g\rightarrow\begin{Bmatrix}B\,^1\Sigma_u\\C\,^1\Pi_u\end{Bmatrix}\rightarrow E,F\,^1\Sigma_g$$

being taken from the literature.[15] We restricted ourselves to these two states ($B\,^1\Sigma_u$ and $C\,^1\Pi_u$) only since the higher states are energetically far above the first-photon absorption level, and hence it is expected that contribution from the higher-lying states would be small due to the larger energy denominator and the smaller values of the dipole transition moments.[10] The vibrational wave functions for the $X\,^1\Sigma_g$, $B\,^1\Sigma_u$, $C\,^1\Pi_u$ and $X\,^2\Sigma_g$ (H_2^+) were computed using Cooley's method,[16] whereas for the double-minimum $E,F\,^1\Sigma_g$ state the method as modified by Kolos and Wolniewicz[14] was used; energy values obtained from the literature[17] were spline fitted to obtain the potential curves for these computations. Integrations over nuclear coordinates were done using Simpson's one-third rule, with a step size of 0.01 bohr. We have restricted ourselves to $Q(0)$ and $Q(1)$ two-photon transitions.

To compute the ionization width γ_I, the bound-continuum electronic dipole transition moments D_{ic} were calculated for several values of R and, for each value of R, at a series of photoelectron energies E, yielding a family of $D_{ic}(E,R)$ curves. For any laser frequency ω that connects the ground state $X\,^1\Sigma_g$ to a particular continuum level $\mid c\rangle$ via a three-photon transition, there is a distribution of population of the H_2^+ photoion among the

TABLE I. Allowed rotational levels j_I of the H_2^+ ion for different rotational levels j_i of the $H_2(E,F)$ state and different partial waves l of the continuum.

j_i ($i=E$ or F)	l	j_I
0	1	0,2
	3	2,4
1	1	1,3
	3	1,3,5

TABLE II. Branching ratios for ionization from different v_E levels at different intensities. The ratios are normalized to unity at the peak.

v_E	j_E	v_I	Branching ratio Experiment[a]	Branching ratio Theory[b]	Intensity (W/cm^2)	Branching ratio (this work)
0	0	0	1	1	All	1
		1	0.156	0.068	1×10^7	0.072
					1×10^8	0.074
					1×10^9	0.094
					2×10^9	0.121
					3×10^9	0.152
					4×10^9	0.187
1	1	0	0.126	0.018	1×10^7	0.021
					1×10^8	0.023
					1×10^9	0.042
					2×10^9	0.074
					3×10^9	0.115
					4×10^9	0.166
		1	1	1	All	1
		2	0.359	0.116	1×10^7	0.124
					1×10^8	0.132
					1×10^9	0.227
					2×10^9	0.366
					3×10^9	0.531
					4×10^9	0.712
		3	0.176	0.023	1×10^7	0.025
					1×10^8	0.026
					1×10^9	0.048
					2×10^9	0.084
					3×10^9	0.131
					4×10^9	0.188
2	1	0	0.018	–	1×10^7	0.001
					1×10^8	0.001
					1×10^9	0.002
					2×10^9	0.003
					3×10^9	0.004
					4×10^9	0.005
		1	0.182	0.034	1×10^7	0.022
					1×10^8	0.023
					1×10^9	0.035
					2×10^9	0.052
					3×10^9	0.074
					4×10^9	0.099
		2	1	1	All	1
		3	0.187	0.081	1×10^7	0.048
					1×10^8	0.050
					1×10^9	0.075
					2×10^9	0.110
					3×10^9	0.153
					4×10^9	0.203
		4	0.253	0.057	1×10^7	0.089
					1×10^8	0.093
					1×10^9	0.135
					2×10^9	0.194
					3×10^9	0.265
					4×10^9	0.347

[a]Reference 7(b).

[b]Reference 12(c). Entries smaller than 10^{-3} are left blank.

vibrational levels v_I that lie below $\mathcal{E}_c$, leading to a corresponding distribution over photoelectron energies $E_e(v_I)=\mathcal{E}_c-\mathcal{E}_{v_I}$ for that $\mathcal{E}_c$. The total bound-continuum transition moment was obtained, for ionization to different vibrational levels v_I, by integrating over nuclear coordinates using Simpson's one-third rule as before; at each value of R, the electronic element $D_{ic}[E_e(v_I),R]$ was obtained by interpolation from the family of the $D_{ic}(E,R)$ curves mentioned above. The total ionization width γ_I was obtained by summing over all the allowed rotational levels j_I of the H_2^+ ion, as enumerated in Table I.

To obtain the ac Stark shift S_I we evaluated the principal-value integral by utilizing the fact the energy dependence of the bound-continuum dipole transition moment is weak,[18] and obtained $S_I=-(3/2\pi)\gamma_I$. For the spontaneous decay of the v_E levels we used the data for the spontaneous decay time, γ_s^{-1} from the literature[19]

TABLE III. Asymmetry parameters for photoelectron angular distribution at different intensities. For each $(v_E,j_E)\rightarrow v_I$ transition, the first line corresponds to an intensity 1×10^9 W/cm^2; second line, 3×10^9 W/cm^2; third line, 5×10^9 W/cm^2.

			Asymmetry parameters			
			This work		Experiment[a]	
v_E	j_E	v_I	α	β	α	β
			1.431	−0.003		
0	0	0	1.420	−0.011		
			1.412	−0.017		
			1.570	−0.0005		
0	0	1	1.569	−0.002		
			1.569	−0.002		
			0.982	0.006		
1	0	0	0.982	0.006	0.59	0
			0.981	0.005		
			1.404	−0.002		
1	0	1	1.399	−0.008	1.29	0
			1.392	−0.013		
			1.616	−0.0008		
1	0	2	1.615	−0.001	0.75	0
			1.615	−0.002		
			0.715	0.005		
1	1	0	0.715	0.005	0.71	−0.32
			0.715	0.005		
			1.173	−0.003		
1	1	1	1.151	−0.016	1.34	−0.18
			1.127	−0.029		
			1.451	−0.005		
1	1	2	1.448	−0.007	0.85	−0.23
			1.445	−0.009		
			1.352	0.007		
1	1	3	1.352	0.006	1.02	−0.28
			1.351	0.005		
			1.780	−0.005		
2	1	0	1.780	+0.004		
			1.780	0.012		
			0.390	0.008		
2	1	1	0.390	0.008		
			0.390	0.008		
			1.113	0.002		
2	1	2	1.098	0.008		
			1.084	0.013		
			1.898	−0.029		
2	1	3	1.898	−0.030		
			1.898	−0.031		
			1.009	0.014		
2	1	4	1.005	0.014		
			1.000	0.013		

[a]Reference 7(b).

ranging from 213 to 100 ns, and for the v_F levels we have chosen γ_s^{-1} to be the same (100 ns) for all levels. However, in this work $\gamma_s \ll \gamma_L$ ($=1.9$ cm^{-1}) and has no effect on the REMPI process.

We have calculated the branching ratios for the vibrational distribution of the H_2^+ ion and the PE angular distribution with the associated asymmetry parameters as functions of the laser intensity. The $Q(0)$ transitions have been considered for excitations from the ($v_g=0$) level of the ground state to the ($v_E=0$) and ($v_F=0$) levels of the E,F state, while the $Q(1)$ transitions have been considered for the excitations to the ($v_E=1,2$) and ($v_F=2,3$) levels. In a preliminary work[20] some results for the v_E levels were presented. However, that work was of a somewhat exploratory nature, and in calculating the bound-continuum matrix elements we had ignored the variation of D_{ic} with v_I and approximated $D_{ic}(E_e(v_I),R)$ by $D_{ic}(E_e(v_I=0),R)$ within the radial integral. This accounts for the discrepancy between the branching ratios in the present work (Table II) and in the earlier work.[20]

The photoelectron angular distributions have been computed for the transitions to $v_E=0,1,2$ and, for each transition, to different values of v_I; the asymmetry parameters for each $v_E \rightarrow v_I$ ionization channel were obtained by numerically fitting[11] $dP(\theta)/dt$ [Eq. (7)] to the form $N(1+\alpha P_2(\cos\theta)+\beta P_4(\cos\theta))$, which is the same as Eq. (8) truncated after the P_4 term as the coefficient β turned out to be smaller than α by two orders of magnitude or more over the range of laser intensity [10^7–(5×10^9) W/cm^2] considered in this work. Table III shows the parameters α and β as functions of the laser intensity.

RESULTS AND DISCUSSION

In Table II we present the branching ratios for the different vibrational levels of H_2^+ for the $Q(0)$ and $Q(1)$ two-photon transitions to $v_E=0$ and $v_E=1,2$, respectively, as functions of laser intensity. It is clear from this table that the vibrational distribution pattern depends on laser intensity, although it is peaked at $\Delta v=0$ for all intensities. In the low-intensity region where γ_I and S_I of the resonant level are negligible compared to $2\gamma_L$, the branching ratios are effectively proportional to the ionization widths for transitions to the different vibrational levels of the ion. In this limit our values are in good agreement with a previous calculation.[12(c)] With increase in laser intensity, S_I and γ_I become comparable to $2\gamma_L$, and the branching ratios cease to be proportional to the ionization widths and become nonlinear functions of intensity.

The experimental values of branching ratios given by Anderson, Kubiak, and Zare[7(b)] agree quite well with our calculated values in the high-intensity region ($>10^9$ W/cm^2). These authors did not report their final focused beam intensities; however, their typical vacuum-ultraviolet pulse energies were $\sim$70–80 μJ. In a previous experiment[7(c)] from the same group with pulse energies in the range $\sim$10–20 μJ, the authors verified the results obtained by Kligler *et al.*,[21] namely, that the ionization rate from the E,F state should predominate over electronic quenching by the ground state of the H_2 molecule, radiative decay, and rotational relaxation for intensity above 10^9 W/cm^2. To obtain this laser power density from pulses of energy 10–20 μJ and duration $\sim$2 ns, an estimate for the focused beam spot area turns out to be $\sim$750 μm^2. Thus with pulses of 70–80 μJ energy, power densities of order $\sim10^9$ W/cm^2 would be obtained over a focused beam spot area $\sim$1500 μm^2, assuming a pulse duration of $\sim$5 ns. It is to be mentioned here that in our calculations we have assumed a rectangular pulse of constant intensity (no fluctuations). Moreover, the effect of the autoionizing state of $^1\Sigma_u(1\sigma_u 2\sigma_g)$ symmetry on the vibrational distribution has not been considered.

Throughout this work we have used a laser bandwidth of 1.9 cm^{-1}, the same as used in experiment.[7(b)] The intensity dependence of the branching ratios are shown in Fig. 2. It is seen that for intensities $\lesssim 10^8$ W/cm^2, the branching ratios depend relatively weakly on I, whereas from $\sim5\times10^8$ W/cm^2 onwards the intensity dependence becomes quite strong.

Table IV gives the values of the branching ratios for the transitions from the outer-well levels $v_F=0,2,3$ at different laser intensities. It is clear that for ionization from the outer well, there is no propensity for the $\Delta v=0$ transition. This is due to the fact that the overlap between the v_F and v_I states depends on the geometry of the molecular potential curves. Since the equilibrium internuclear separation for the outer well (4.39 a.u.) is far away from that of the ground state of the H_2^+ ion (2.0 a.u.), it would be expected that the lower the v_F level is, the more the ionizing transitions to the higher v_I levels will dominate. It is evident from the table that from ionization from $v_F=0$, the ionic population distribution is peaked around $v_I=9$, whereas for $v_F=2$ and 3 the peak of the distribution is shifted towards the lower v_I levels.

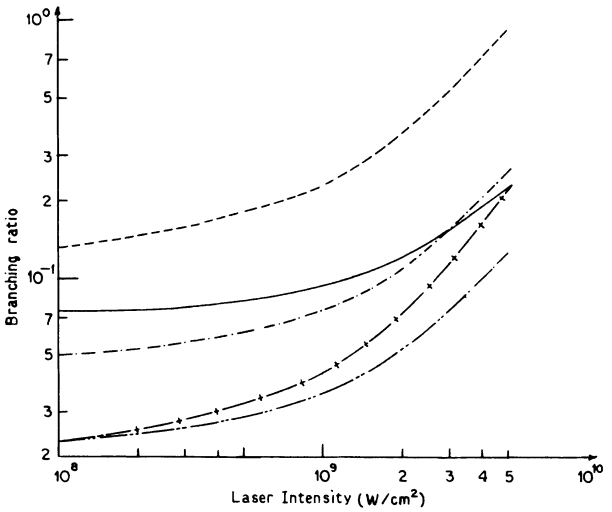

FIG. 2. Branching ratio as a function of laser intensity. ——, $(v_E=0,j_E=0)\rightarrow v_I=1$ transition; – + – + –, $(v_E=1,j_E=1)\rightarrow v_I=0$; – – –, $(v_E=1,j_E=1)\rightarrow v_I=2$; – ··· – ···, $(v_E=2,j_E=1)\rightarrow v_I=1$; – · – · –, $(v_E=2,j_E=1)\rightarrow v_I=3$.

As mentioned above, for intensities $\gtrsim 5\times10^8$ W/cm^2 the branching ratios vary significantly with I. However, the qualitative nature of the PE angular distribution does not seem to vary with intensity over the whole range considered in this work (10^7–5×10^9 W/cm^2). We have plotted the PE angular distribution at an intensity 10^9 W/cm^2. The polar plots show only the quantity $1+\alpha P_2(\cos\theta)+\beta P_4(\cos\theta)$ as a function of θ. Figure 3 shows the polar plots for ionization from the ($v_E=0$, $j_E=0$), ($v_E=1$, $j_E=1$), and ($v_E=2$, $j_E=1$) levels to different vibrational levels of the H_2^+ ion. As is seen, the angular distribution depends both on the intermediate vibrational levels as well as on the final ionic vibrational levels. The asymmetry parameters for the different transitions are given in Table III for three values of laser intensities. Three features are at once evident from the table: (i) the α's change very little, if at all, with intensity; (ii) in about half of the cases, the β's change significantly, and (iii) β is smaller than α by two to three orders of magnitude. It is due to this latter feature that the calculated PE angular distribution shows no qualitative change with variation in laser intensity. The calculated α parameters are in good agreement with the experimental values, considering the error bars, in most of the cases. However, the higher-order asymmetry parameter β in the experimentally observed angular distribution for the ionization of the ($v_E=1$, $j_E=1$) level turns out to be much stronger than the present theoretical values. As has been mentioned earlier,[12(c)] this may be due to the fact that the angular resolution is low ($\sim3°$) in the measurement. Another possible reason for this discrepancy may be the effect of core-excited or Rydberg autoionizing states on the REMPI process, an effect we have not con-

TABLE IV. Same as Table II for ionization via v_F levels.

v_F	j_F	Intensity (W/cm^2)	v_I	Branching ratio
0	0	1×10^8	4	0.006
			5	0.039
			6	0.166
			7	0.418
			8	0.595
			9	1
			10	0.246
		2×10^9	4	0.007
			5	0.046
			6	0.188
			7	0.457
			8	0.633
			9	1
			10	0.276
2	1	1×10^8	0	0.001
			1	0.058
			2	0.055
			3	0.063
			4	0.403
			5	0.934
			6	1
			7	0.083
			8	0.552
		2×10^9	0	0.001
			1	0.064
			2	0.060
			3	0.068
			4	0.426
			5	0.939
			6	1
			7	0.090
			8	0.575
3	1	1×10^8	1	0.001
			2	0.247
			3	0.205
			4	0.784
			5	1
			6	0.348
			7	0.168
			8	0.742
		2×10^9	1	0.001
			2	0.262
			3	0.218
			4	0.798
			5	1
			6	0.366
			7	0.179
			8	0.757

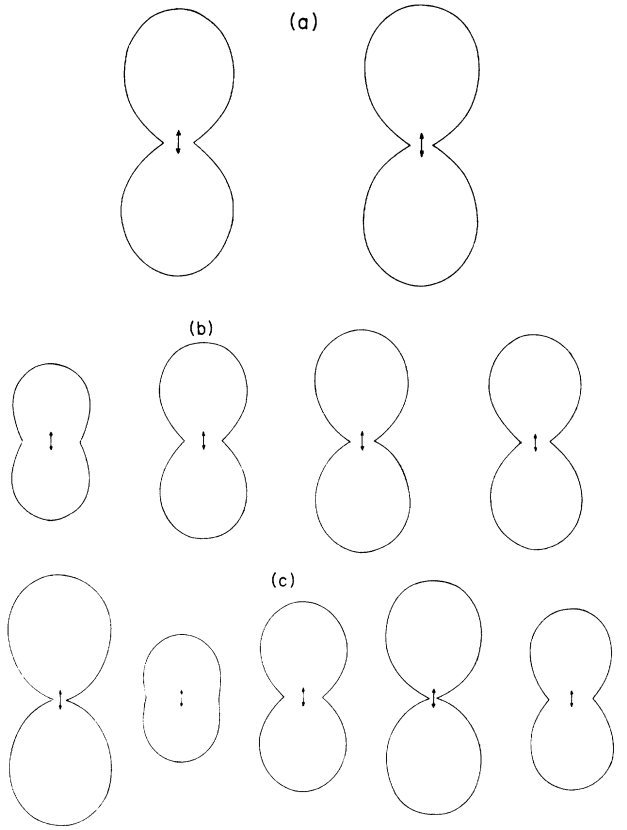

FIG. 3. Polar plots for photoelectron angular distribution. (a) $(v_E=0, j_E=0)\rightarrow v_I=0$ and 1 from left to right. (b) $(v_E=1, j_E=1)\rightarrow v_I=0$, 1, 2, and 3 from left to right. (c) $(v_E=2, j_E=1)\rightarrow v_I=0$, 1, 2, 3, and 4 from left to right.

sidered in this paper.

Summarizing, we have presented results for $(2+1)$-photon ionization of the hydrogen molecule via the double-minimum E,F state, and to our knowledge this is the first calculation for ionization of the outer-well (v_F) levels. We have obtained some interesting features in the branching ratios which are amenable to experimental verification since lasers of wavelengths corresponding to these transitions are available.[7(c)] The effect of laser intensity variation on the branching ratios can also be observed as long as the intensity is lower than the intensity required for above-threshold ionization.

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