Three-photon resonant four-photon ionization of H_2 via the $C\,^1\Pi_u$ state

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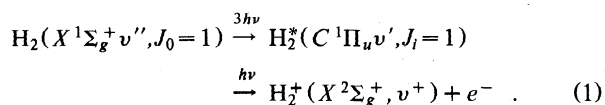Pasadena, California 91125*

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Ab initio calculations are presented for the vibrational branching ratios in three-photon resonant four-photon ionization of H_2 via the $C\,^1\Pi_u$ state. Energy and internuclear distance dependences of the bound-free electronic transition matrix element are explicitly included to estimate deviations from the Franck-Condon approximation. While our calculated branching ratios confirm certain important trends seen experimentally, some differences remain.

I. INTRODUCTION

Resonant enhanced multiphoton ionization (REMPI) is a powerful probe of electronically excited states. The high-power lasers used in such studies not only provide high selectivity in energy (of the order of the laser bandwidth), but also make accessible, via multiphoton absorption, states that are single-photon forbidden by dipole selection rules. When combined with photoelectron energy analysis, REMPI allows us to focus very directly on the photoionization of the excited states and on the dynamics of multiphoton ionization. Recent experiments[1-12] on REMPI processes in diatomic molecules such as H_2, CO, NO, and N_2 have begun to reveal several interesting features. A theoretical understanding of these features is obviously needed.

Recently, Pratt, Dehmer, and Dehmer[12] analyzed the photoelectron energy spectrum resulting from a three-photon resonant four-photon ionization of H_2 via the $C\,^1\Pi_u$ state. This resonant state, Rydberg in character, overlaps in energy with the valence $B\,^1\Sigma_u^+$ state. The Π^+ component of this $C\,^1\Pi_u$ state interacts with the $B\,^1\Sigma_u^+$ state via the Rydberg-valence mixing, while the Π^- component is unaffected. Pratt, Dehmer, and Dehmer[12] were able to select only the Π^- component of the $C\,^1\Pi_u$ state as the resonant intermediate state by tuning the laser frequency in resonance with the three-photon $Q(1)$ transition line. This illustrates the tremendous selectivity achievable in REMPI processes. The kinetic energy of the photoelectrons ejected from this resonant intermediate state was analyzed. These data provide the branching ratios for ionization out of a specific vibrational level v' of the $C\,^1\Pi_u$ state into different vibrational level v^+ of the $X\,^2\Sigma_g^+$ state of H_2^+. These vibrational branching ratios deviated significantly from the appropriate Franck-Condon factors. Possible reasons for this behavior are the energy and the internuclear distance dependence of the electronic transition moment, autoionization, and perturbations with overlapping, allowed transitions. Autoionization and perturbations are less probable due to other considerations.[12] In this Rapid Communication, we quantitatively assess the role of energy and R dependence of the electronic transition moment on the vibrational branching ratios in these $(3+1)$ REMPI experiments of Pratt, Dehmer, and Dehmer,[12] i.e.,

$$H_2(X\,^1\Sigma_g^+\,v'',J_0=1) \xrightarrow{3h\nu} H_2^*(C\,^1\Pi_u v',J_i=1)$$

$$\xrightarrow{h\nu} H_2^+(X\,^2\Sigma_g^+,v^+)+e^- \quad . \tag{1}$$

Comparison with the measured branching ratios shows good agreement for vibrational branching ratios for $v'=0$ and 1 excitations although differences exist between theory and experiment for $v'=2$, 3, and 4 excitations.

II. THEORY

An analysis of REMPI cross sections and the related angular distributions requires molecular parameters such as the transition moments and transition frequencies and their incorporation into the dynamics equations. These steps are nontrivial even for the simplest of diatomic molecules H_2 and, hence, it is not surprising that very few theoretical calculations have been carried out for molecular REMPI processes.[13,14] Our framework for analyzing the dynamics has been presented elsewhere.[15] For the process in Eq. (1), the probability for ejection of an electron in the direction (θ,ϕ) with respect to the light polarization vector (linearly polarized light was used in the experiment of Ref. 12 and is assumed here) obeys

$$\frac{dP(\theta,\phi)}{dt} = \sum_{M_iM_i'} \Gamma_{M_iM_i'}(\theta,\phi)\rho_{i'i} \quad . \tag{2}$$

In this equation, $\rho_{i'i}$ is the density matrix element $\langle J_iM_i'|\rho|J_iM_i\rangle$ (all indices other than J_i and M_i needed to describe a molecular state have been suppressed for clarity) and $\Gamma_{M_iM_i'}$ a generalized differential ionization rate. Detailed expressions for $\Gamma_{M_iM_i'}$ are given in Ref. 15, where it is also shown that in the absence of M_i mixing, ionization through each $|J_iM_i\rangle$ forms an independent channel. Thus, $\rho_{i'i}$ is proportional to $\delta_{M_iM_i'}$, and, therefore, for photoionization of the $C\,^1\Pi_u$ state excited from the ground state via a three-photon $Q(1)$ transition $(J_i=1)$, Eq. (2) reduces to

$$\frac{dP(\theta,\phi)}{dt} = \Gamma_{11}\rho_{11} + \Gamma_{00}\rho_{00} + \Gamma_{-1-1}\rho_{-1-1} \quad . \tag{3}$$

$\Gamma_{M_iM_i'}$ can in turn be expanded in spherical harmonics[15] as

$$\Gamma_{M_iM_i'} = \sum_{L,M}^{L_{max}^{(\Gamma)}} \gamma_{LM;M_iM_i'} Y_{LM}(\theta,\phi) \quad , \tag{4}$$

where the coefficients $\gamma_{LM;M_iM_i'}$ depend on the bound-free radial matrix elements and scattering phase shifts. $M=0$

for $M_i = M_i'$ and $\Gamma_{M_i M_i}$ and $P(\theta, \phi)$ in Eqs. (3) and (4), are independent of ϕ and consist of only Legendre polynomials. Furthermore, as the accessible partial waves (σ_g, π_g, and δ_g) are all of the same g symmetry only even order Legendre polynomials up to $L_{\max}^{(\Gamma)} = 4$ [see Eq. (40) of Ref. 15] survive in Eq. (4). Thus,

$$\Gamma_{M_i M_i} = \sum_{L=0,2,4} \gamma_{L0;M_i M_i} Y_{L0}(\theta,\phi) \ . \tag{5}$$

Equation (3) shows that, in addition to $\Gamma_{M_i M_i}$, $\rho_{ii}(i=0, \pm1)$ are needed to calculate the actual REMPI angular distributions. For the weak-field excitation conditions of Ref. 12, ρ_{ii} is given by

$$\rho_{ii} \propto \sum_{M_0} \left| \sum_{\substack{|J_1 M_1\rangle \\ |J_2 M_2\rangle}} \frac{\langle J_i M_i | \vec{\mu} \cdot \vec{\epsilon} | J_2 M_2 \rangle \langle J_2 M_2 | \vec{\mu} \cdot \vec{\epsilon} | J_1 M_1 \rangle \langle J_1 M_1 | \vec{\mu} \cdot \vec{\epsilon} | J_0 M_0 \rangle}{(E_{J_1} - E_{J_0} - h\nu)(E_{J_2} - E_{J_0} - 2h\nu)} \right|^2 \ . \tag{6}$$

From the $X\,{}^1\Sigma_g^+$ initial state, the dipole allowed intermediate states, at the one-photon level, are of Σ_u^+ and Π_u symmetry, while those at the two-photon level are of Σ_g^+, Π_g, and Δ_g symmetry. For an overall three-photon $Q(1)$ transition, $J_0 = J_i = 1$, which restricts J_2 to be 1 or 2. Note that the two-photon transition from the $J_0 = 1$ level of the $X\,{}^1\Sigma_g^+$ state to the $J_2 = 0$ level of a Σ_g^+-type state is forbidden by parity selection rules. Moreover, the $J_2 = 0$ level does not exist in Π_g- and Δ_g-type states. Of these allowed states, the $J_2 = 2$ state contributes only if the electronic state is of Π_g or Δ_g type. In H_2, the lowest states of Π_g and Δ_g symmetry are, respectively, the $I\,{}^1\Pi_g$ and $J\,{}^1\Delta_g$, which lie at about 14–15 eV above the ground state.[16] The $E, F\,{}^1\Sigma_g^+$ state, on the other hand, is about 12 eV from the ground state. For photon energies $h\nu \sim 4$ eV, the detuning $(E_{J_2} - E_{J_0} - 2h\nu)$ for these Π_g and Δ_g states is about 6 eV while that from the $E, F\,{}^1\Sigma_g^+$ state is about 4 eV. Hence, in the preliminary results presented here, we neglect the contribution to ρ_{ii} from states other than those of Σ_g^+ symmetry. Such contributions will be included in later studies. Neglecting this contribution eliminates the need to calculate any ρ_{ii}, if one is interested only in the relative branching ratios. This comes about as $\rho_{00} = 0$ for Σ_g^+ states with $J_2 = 1$. Furthermore, $\rho_{11} = \rho_{-1-1}$, and $\Gamma_{11} = \Gamma_{-1-1}$ which, combined with Eq. (3) imply

$$\frac{dP(\theta)}{dt} \propto \Gamma_{11}(\theta) \ . \tag{7}$$

In the absence of saturation as assumed here, the solution of the above equation is

$$P(\theta) = \mathrm{const} \times \Gamma_{11}(\theta) \ . \tag{8}$$

Since we are only interested in relative contributions, we shall set the constant in the above equation to unity and use, hereafter,

$$P(\theta) = \Gamma_{11}(\theta) \ . \tag{9}$$

In the same spirit, we also ignore factors such as the laser intensity in the expression for $\Gamma_{11}(\theta)$ [see Eq. (29) of Ref. 15].

Thus, to investigate relative branching ratios, all we need to calculate is the differential cross section for ionization out of the $|J_i = 1, M_i = 1\rangle$ state. From the analysis in Ref. 15, $\Gamma_{11}(\theta)$ depends on the bound-free electronic transition matrix elements of the type

$$\bar{r}_{fi}^{(\mu)} = \int \chi_{v^+}^*(R) \chi_{v'}(R) r_{fi}^{(\mu)}(k;R) \, dR \ , \tag{10}$$

where

$$r_{fi}^{(\mu)}(k;R) = \langle \psi_{\gamma f}^{(e)}(\{\vec{r}_i'\};R) | \sum_S r_S Y_{1\mu}(\hat{r}_S') $$
$$\times |\psi_{\gamma i}^{(e)}(\{\vec{r}_i'\};R)\rangle \tag{11}$$

denotes the transition moment for the $i \to f$ transition at a given internuclear separation R and electron momentum k. In our studies of the non-Franck-Condon effects on vibrational branching ratios, we adopt the following notation. (a) Franck-Condon (FC): $r_{fi}^{(\mu)}(k,R)$ inside the integral in Eq. (10) is replaced by its value at some $k^2 = k_0^2$ and $R = R_e$. $r_{fi}^{(\mu)}$ then simplifies to a product of $r_{fi}^{(\mu)}(k_0;R_e)$ and the Franck-Condon overlap between the v^+ vibrational level of the ion and v' vibrational level of the $C\,{}^1\Pi_u$ state. (b) Non-Franck-Condon (non-FC): $r_{fi}^{(\mu)}(k;R)$ in Eq. (10) is replaced by $r_{fi}^{(\mu)}(k_0;R)$ and is retained inside the R integral. These calculations assess the effect of the R dependence of the transition matrix element on the branching ratios. (c) Full: here both the k and R dependences of $r_{fi}^{(\mu)}(k;R)$ are retained. For a fixed photon energy $h\nu$, selecting v' and v^+ fixes k^2 by the energy conservation equation (in atomic units):

$$E_{v'} + h\nu = E_{v^+} + \frac{k^2}{2} \ . \tag{12}$$

These results include both the energy dependence as well as the R dependence of the cross sections and should, therefore, be most complete.

In our calculations, the $C\,{}^1\Pi_u$ wave function was obtained using the improved-virtual-orbital (IVO) technique.[17] The energies of the $C\,{}^1\Pi_u$ state obtained this way as a function of R are within 5% of the correct values.[16] The continuum wave functions for the photoelectron in σ_g, π_g, and δ_g channels were calculated by solving the Hartree-Fock equations using the iterative Schwinger variational techniques.[18] $r_{fi}^{(\mu)}(k;R)$ was then calculated at $R = 1$, 1.4, 2, 3, and 5 a.u. and for a range of k (0.05–0.45 a.u.). Interpolation was performed in R and in k to obtain required $r_{fi}^{(\mu)}(k;R)$. For part (a), $R_e = 1.4$ a.u. The value of k_0^2 for parts (a) and (b) was determined from Eq. (12) with $v' = v^+$ and $h\nu$ taken from Ref. 12 for excitation to the $Q(1)$ branch of $C\,{}^1\Pi_u(v')$ state. For part (c), the correct value of k is determined from Eq. (12) for each v^+. Finally, the vibrational wave functions $\chi_{v'}$ and χ_{v^+} were calculated using the finite element method of Malik, Eccles, and Secrest[19] with the potential curves of Sharp.[16]

III. RESULTS

In Fig. 1 we compare the branching ratios calculated at the various levels of approximation (a), (b), and (c) with the experimental results of Pratt *et al.*[12] As in the experimental data, we plot $P(\theta=0)$. The results are normalized such that the $v'=v^+$ peak in all three approximations and in the experiment is of unit height. (Note the break in the graph for the $v'=v^+$ peak.) As expected, the $v'=v^+$ peak is dominant. This is due to the Rydberg character of the $C\,^1\Pi_u$ state which makes the potential surface for the $C\,^1\Pi_u$ state nearly identical to (but shifted in energy from) that of the $X\,^2\Sigma_g^+$ state of H_2^+. The theoretical branching ratios decrease rapidly for $v^+\neq v'$. The results of approximations (a), (b), and (c) reveal an interesting feature: the branching ratios decrease for $v^+<v'$ as the R and k dependences of $r_{fi}^{(\mu)}$ are included and increase for $v^+>v'$ with these dependences included. The difference between "non-Franck-Condon" and "full" results is simply a reflection of

the increasing of the cross section for decreasing energy which skews the branching ratios towards higher v^+ values. [Note that, since v^+ is increasing to the left, k increases to the right as indicated by Eq. (12).] The difference between Franck-Condon and non-Franck-Condon results arises from the particular R dependence of the photoionization cross section for the $C\,^1\Pi_u$ state. This difference is probably specific for the photoionization process under study and may be different for other states and molecules.

We now compare the results of our studies with the data of Pratt *et al.*[12] For $v'=0$ and $v'=1$ excitations, the agreement between theory and experiment seems quite good. For $v'=2-4$, the experimental branching ratios for $v^+\neq v'$ are much larger than the theoretical predictions. In particular, for $v'=4$, the $v^+=3$, 5, and 6, experimental peaks are all of about equal height, while theory predicts the $v^+=3$ and 6 peaks to have 0.11 and 0.2 times the height of $v^+=5$ peak (which is $\sim$18% of $v^+=4$ peak). A similar discrepancy exists in the $v'=3$ and $v'=2$ excitation data as
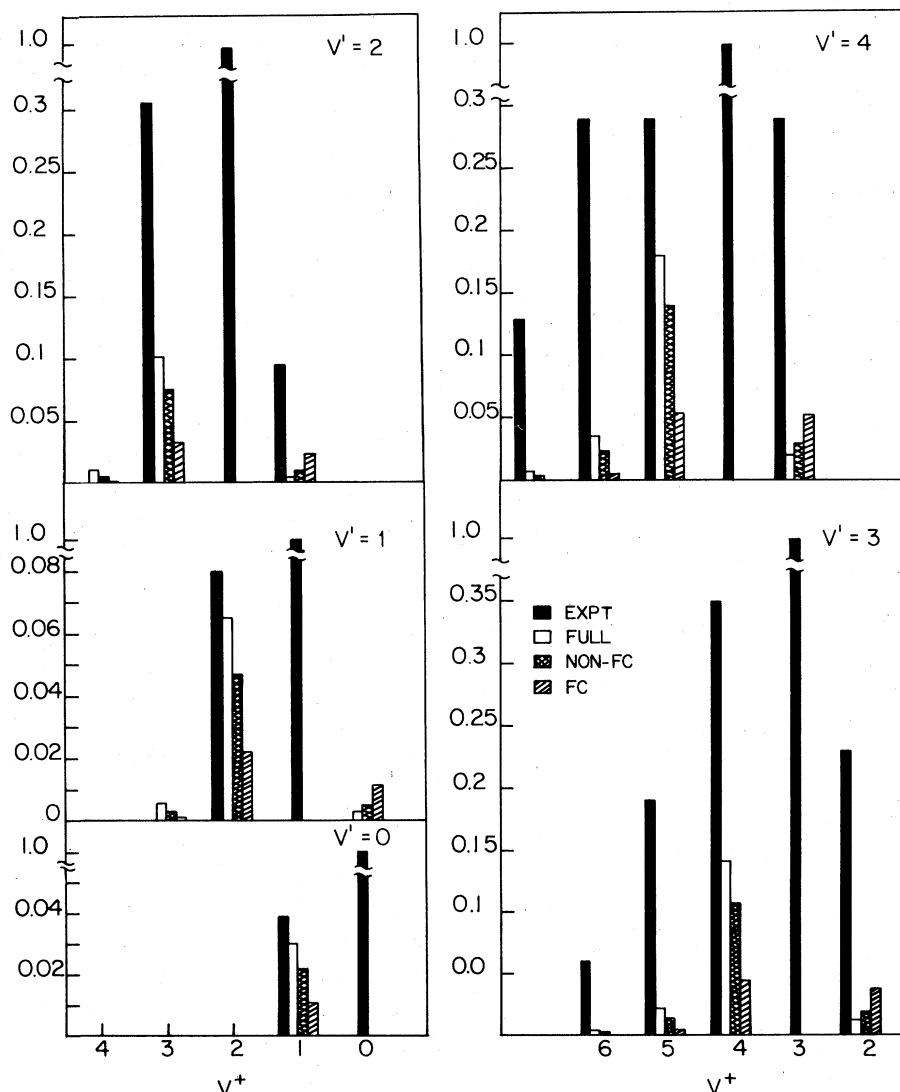

FIG. 1. Vibrational branching ratios in $(3+1)$ REMPI of H_2 via the $C\,^1\Pi_u$ state. v' denotes the vibrational state of $C\,^1\Pi_u$ state and v^+ that of the $X\,^2\Sigma_g^+$ state of the ion.

well. These differences may be due to autoionization, accidental resonances at the three-photon excitation level, and the contribution of the Π_g and Δ_g states to the three-photon excitation amplitude, which are neglected in our present studies. Of these, autoionization seems to play no role as the results of Ref. 12 are insensitive to changes in photon frequency. To analyze the contribution of Π_g and Δ_g states to the excitation, we have calculated Γ_{00} in Eq. (3) and observe that the branching ratios in $\Gamma_{00}(\theta = 0)$ are very similar to those quoted here. Thus, the inclusion of the $\Gamma_{00}\rho_{00}$ term in Eq. (3) will not significantly alter the relative branching ratios. The existence of accidental resonances with the P branch of some high vibrational level of the $B\,^1\Sigma_u^+$ state can also be ruled out for all v' states except $v' = 3$ (Ref. 12). Another improvement in our calculations would be the inclusion of correlation effects. Such studies are currently underway.

In summary, we have presented *ab initio* calculations for vibrational branching ratios in $(3+1)$ REMPI of H_2 via the $C\,^1\Pi_u$ state. Calculated ratios are in good agreement with recent experimental results[12] for excitation through lower vibrational level of the $C\,^1\Pi_u$ state. Differences do exist for excitation through higher vibrational levels. Further studies are needed to understand these differences.

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