

(2+1) resonant enhanced multiphoton ionization of H₂ via the $E,F^1\Sigma_g^+$ state

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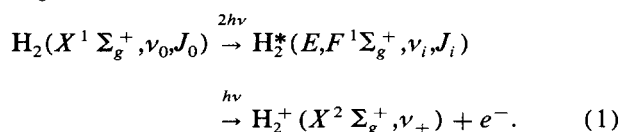
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In this paper, we report the results of *ab initio* calculations of photoelectron angular distributions and vibrational branching ratios for the (2 + 1) REMPI of H₂ via the $E,F^1\Sigma_g^+$ state, and compare these with the experimental data of Anderson *et al.* [Chem. Phys. Lett. **105**, 22 (1984)]. These results show that the observed non-Franck–Condon behavior is predominantly due to the R dependence of the transition matrix elements, and to a lesser degree to the energy dependence. This work presents the first molecular REMPI study employing a correlated wave function to describe the Rydberg–valence mixing in the resonant intermediate state.

INTRODUCTION

Resonant enhanced multiphoton ionization (REMPI) techniques provide a useful tool for the study of highly excited states and of the dynamics of the photoionization of these rovibrationally selected states. Furthermore, for systems with inversion symmetry, REMPI studies can be effectively used to access dipole-forbidden bound and continuum states. Several groups have experimentally exploited these advantages to demonstrate interesting aspects of REMPI dynamics.^{1–9} In a previous paper,¹⁰ we have discussed the development of our theoretical framework for analyzing REMPI processes in diatomic molecules. In this theory, an $(n + m)$ REMPI is viewed as a two-step process with n -photon absorption to the resonant intermediate state followed by an m -photon ionization out of it. Coupling the formalism with *ab initio* calculations of molecular properties, we have analyzed several recent REMPI experiments with encouraging results.^{11–14}

Recently Zare and co-workers¹⁵ have measured the photoelectron angular distributions and vibrational branching ratios in a one-color (2 + 1) REMPI of H₂ via the $E,F^1\Sigma_g^+$ state:



The low resolution (150 meV) photoelectron spectra display highly non-Franck–Condon behavior as seen by the departure of the vibrational branching ratios from Franck–Condon values and by a strong vibrational state dependence of the photoelectron angular distributions. The potential energy curve of the $E,F^1\Sigma_g^+$ state has the well-known double-well structure^{16,17} with the nature of the electronic wave

function changing from Rydberg-like in the inner well (E state) to valence-like in the outer well (F state). This presents an interesting situation for theoretical investigation as the electronic wave function for the E,F state has to be described in a multiconfigurational scheme to incorporate the continuous change of its character with internuclear distance (R). We have, therefore, carried out *ab initio* calculations of photoelectron angular distributions and vibrational branching ratios for the REMPI process of Eq. (1). Our results are in general agreement with the measured values¹⁵ and indicate that the observed non-Franck–Condon behavior results primarily from the R dependence of the electronic transition moments. In contrast to our earlier REMPI studies in which the resonant state was described by a single electronic configuration, i.e., the improved virtual orbital (IVO) approximation,¹⁸ we have used a correlated wave function to describe the Rydberg–valence mixing in the E,F state. Rydberg–valence mixing is a common feature in the spectrally congested region and must influence REMPI processes through the highly excited states.^{5–9} As such, the present study, due to the isolated and “clean” nature of the E,F state, forms a prelude to forthcoming investigations of such effects in heavier diatomic molecules. An additional motivation for investigation of the REMPI process of Eq. (1) is the proposed use of this REMPI scheme for detecting product H₂ molecules in reactions.¹⁹

In the following we briefly review our theoretical approach and present the relevant details of the calculations. In the last section we discuss the calculated vibrational branching ratios and photoelectron angular distributions and compare them to the experimental results of Anderson *et al.*¹⁵

THEORY

The general theory for REMPI molecular processes is given in Ref. 10, and here we briefly describe only those details which are necessary for the specific scheme given in Eq. (1). As in the experiments, we assume that the molecules are excited from an isotropic ground state by linearly polarized light of weak intensity. Under these conditions the

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population ρ_{ii} of each $|J_i M_i\rangle$ level of the resonant intermediate state is proportional to¹⁰

$$\rho_{ii} \propto \sum_{M_0} \left| \frac{\langle J_i M_i | \mu \cdot \epsilon | J_i M_i \rangle \langle J_i M_i | \mu \cdot \epsilon | J_0 M_0 \rangle}{E_1 - E_0 - h\nu} \right|^2, \quad (2)$$

where $|J_0 M_0\rangle$ is the ground $X^1\Sigma_g^+$ state with angular momentum J_0 and its z projection M_0 , $|J_i M_i\rangle$ is a virtual state connected to the ground state by a one-photon transition and $h\nu$ is the photon energy. In the absence of M -mixing interaction, e.g., collisions, each $|J_i M_i\rangle$ level will form an independent ionization channel, and the probability $P(\theta, \phi)$ of ejecting an electron in the direction (θ, ϕ) with respect to the polarization vector (ϵ) of the light is given by¹⁰

$$\frac{dP(\theta, \phi)}{dt} = \sum_{M_i} \Gamma_{M_i, M_i}(\theta, \phi) \rho_{ii}, \quad (3)$$

where $\Gamma_{M_i, M_i}(\theta, \phi)$ is the ionization width defined by Eq. (29) of Ref. 10. $P(\theta, \phi)$ itself can be expanded in Legendre polynomials $P_L(\cos \theta)$ as

$$P(\theta) = \sum_{L=0}^{L_{\max}} \beta_L P_L(\cos \theta). \quad (4)$$

For these weak field studies L_{\max} is determined by the rotational quantum state of the intermediate level and is, for the $(2+1)$ REMPI process of Eq. (1), the smaller of $2J_i + 2$ or 6. The infinite summation in Eq. (2) goes over the complete set of rovibrational electronic states $|J_i M_i\rangle$ of H₂. We have included in this summation only the lowest states of ungerade symmetry ($B^1\Sigma_u^+$, $C^1\Pi_u$) and kept up to $\nu = 9$ in the vibrational manifolds at the one-photon level. The relative vibrational branching ratios for $Q(0)$ excitation are unaffected by this truncation. For the $Q(1)$ excitation, based on the study of Huo and Jaffe,²⁰ we estimate the truncation error to be about 10% in the relative populations of the $M_J = 0$ and $M_J = 1$ levels. The summation over rotational states was performed implicitly using closure relations.²¹ The bound-bound transition moments were taken from previous calculations by Wolniewicz²² and Wolniewicz and Dressler,²³ and the vibrational wave functions were obtained numerically using the potential curves compiled by Sharp.¹⁷ The electronic wave function for the $E, F^1\Sigma_g^+$ state was determined from a configuration interaction (CI) calculation using a $(6s5p1d)$ uncontracted Gaussian basis set. This calculation produces 240 configurations of the proper overall $^1\Sigma_g^+$ symmetry. The wave function was determined at the internuclear distances $R(\text{a.u.}) = 1.00, 1.401, 1.911, 2.50, 3.12, 3.70, 4.39, 5.00$ which cover the relevant range of the potential. The resulting energies are within 0.6% of the accurate calculated values.¹⁷ The photoelectron continuum wave functions for the $k\sigma_u$ and $k\pi_u$ channels were calculated in the frozen-core Hartree-Fock approximation using the iterative Schwinger variational method.²⁴ Finally, the bound-free electronic transition moments $\langle X^2\Sigma_g^+; k\sigma_u, k\pi_u | \mu \cdot \epsilon | E, F^1\Sigma_g^+ \rangle$ were calculated for each R and for a range of photoelectron kinetic energies, $k^2/2$, between 1.22 and 4.12 eV. Interpolation was performed in both R and k to obtain the necessary matrix elements for integration over the numerical vibrational wave functions and for specific kinetic energies.

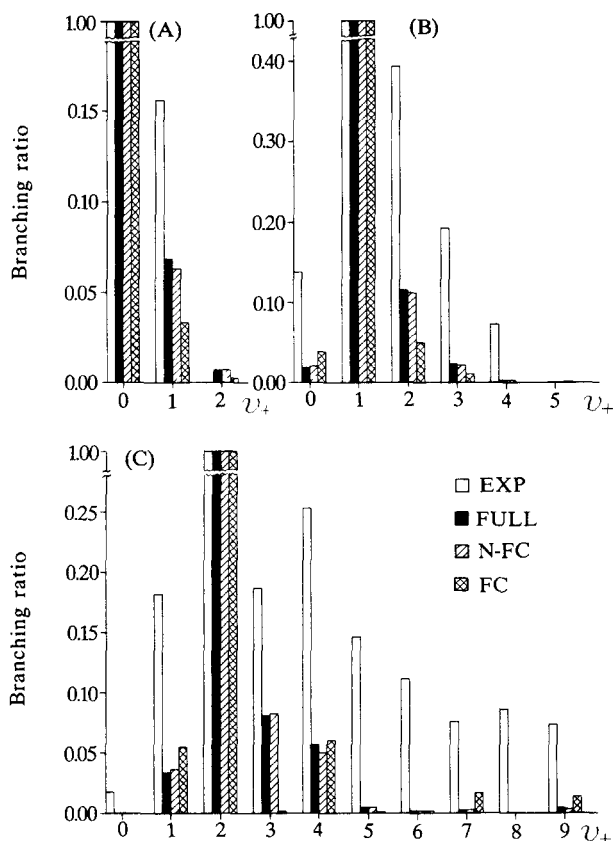


FIG. 1. Vibrational branching ratios for $(2+1)$ REMPI via (A) $\nu_{E,F} = 0$, $Q(0)$ level; (B) $\nu_{E,F} = 3$, $Q(1)$ level; (C) $\nu_{E,F} = 6$, $Q(1)$ level.

RESULTS

Figure 1 shows our calculated vibrational branching ratios for the $\nu_i = \nu_{E,F} = 0, 3, 6$ levels of the E, F state. For convenience the plotted data are reproduced in tabular form in Table I. The vibrational wave functions for $\nu_i = 0, 3$ states

TABLE I. Comparison of the experimental and the theoretical vibrational branching ratios in three different approximations, as explained in the text. Entries less than 10^{-3} are not listed.

ν_i	ν_+	Exp ^a	Full	N-FC	FC
0	0	1.000	1.000	1.000	1.000
0	1	0.156	0.068	0.064	0.033
0	2	...	0.007	0.007	0.003
3	0	0.126	0.018	0.020	0.038
3	1	1.000	1.000	1.000	1.000
3	2	0.359	0.116	0.112	0.049
3	3	0.176	0.023	0.021	0.010
3	4	0.066	0.003	0.003	...
3	5	0.001	0.001
6	0	0.018
6	1	0.182	0.034	0.036	0.055
6	2	1.000	1.000	1.000	1.000
6	3	0.187	0.081	0.083	0.002
6	4	0.253	0.057	0.050	0.060
6	5	0.146	0.005	0.005	0.001
6	6	0.111	0.002	0.002	0.002
6	7	0.076	0.002	0.003	0.017
6	8	0.086
6	9	0.073	0.005	0.004	0.014

^a From Ref. 15.

are primarily located in the E well and look like $\nu_E = 0, 1$ wave functions for a Rydberg state. The wave function for $\nu_i = 6$ has considerable spread over the F well but still looks somewhat like a $\nu_E = 2$ wave function.^{15,20} The plotted values are proportional to the probability of photoelectron ejection along the direction of the polarization of the light, $P(\theta = 0, \phi = 0)$. For each vibrational level of the ion four bars are shown. The experimental data is taken from Ref. 15. The three bars labeled Franck–Condon, non-Franck–Condon, and full correspond to our calculated results using different levels of approximation,¹¹ i.e., (1) neglecting the energy and internuclear distance dependence of the bound–free matrix elements, (2) neglecting the energy dependence but retaining the internuclear distance dependence, and (3) including both the internuclear distance and energy dependence, respectively. The plots are normalized to the most intense peak determined experimentally,¹⁵ which, as expected from the Rydberg character of the E state, is $\Delta\nu \equiv \nu_+ - \nu_E = 0$, where ν_E is the vibrational quantum number defined for the inner-well levels. The similarity between the non-Franck–Condon and full branching ratios indicates the weak dependence of the results on the kinetic energy of the photoelectron. However, the larger difference between the Franck–Condon and non-Franck–Condon results indicate a greater sensitivity to the internuclear distance dependence of the photoionization matrix elements. This points to the inadequacy of the Franck–Condon approximation.¹⁵ The disagreement between the calculated and measured vibrational branching ratios are substantial, although it is difficult to be very specific at this time, the disagreement could arise, on the theoretical side, from our neglect of autoionization and saturation effects. On the other hand they may also be due to inherent difficulties in the experimental determination of such branching ratios.

We compare the calculated and experimental photoelectron angular distributions for the $Q(0)$, and $Q(1)$ branches via the $\nu_{E,F} = 3$ vibrational levels in Figs. 2 and 3, respectively. In these figures the vertical direction corresponds to $\theta = 0^\circ$. The non-Franck–Condon behavior for

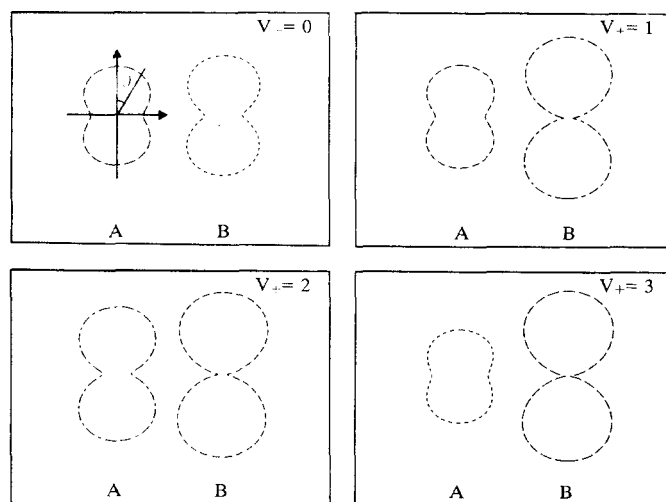


FIG. 2. Photoelectron angular distributions for the $Q(0)$ branch via the $\nu_{E,F} = 3$ level. (A) Experimental results of Ref. 15, and (B) present full results. $\theta = 0^\circ$ is vertical.

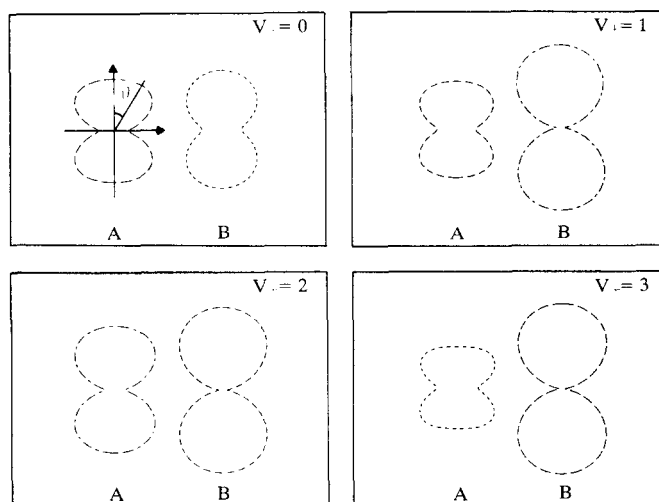


FIG. 3. Same as Fig. 4 but via the $Q(1)$ branch.

these transitions is seen by the dependence of the angular distributions on the final vibronic levels particularly for $\nu_+ = 0$ to $\nu_+ = 1$. Recent $(3 + 1)$ REMPI studies in H₂ via the $C^1\Pi_u$ state have also demonstrated such non-Franck–Condon effects on the photoelectron angular distribution.²⁶ The calculated distributions reported are the “full” results where both the internuclear and photoelectron kinetic energy dependence are retained in the evaluation of the transition moments. A quantitative comparison between the calculated and measured angular distributions is difficult for reasons discussed in Ref. 15; however, the general trends are reproduced. The lack of “sharpness” around 90° for some of the experimental distributions may be attributed to the finite angular resolution ($\approx 3^\circ$) of the photoelectron detector.

It is clear from the Figs. 2 and 3 that the angular distributions for the $Q(0)$ and $Q(1)$ excitations are almost identical. The β_4 of Eq. (4) in the latter case is about 5%–10% of the β_2 coefficient. This implies that either the alignment in the $Q(1)$ excitation is small or, that the partial waves larger than the p wave are contributing weakly to the photoionization. Indeed, our calculations confirm that both these effects contribute significantly to the REMPI, resulting in a suppression of β_4 .

CONCLUSION

We have presented results for the photoelectron angular distributions and vibrational branching ratios resulting from a $(2 + 1)$ one-color REMPI of H₂ via the $\nu_E = 0, 3, 6$ vibrational levels of the $E, F^1\Sigma_g^+$ state. A correlated electronic wave function has been used to consistently describe the Rydberg–valence mixing in the $E, F^1\Sigma_g^+$ state. The calculated vibrational branching ratios are in general agreement with the experimental results of Anderson *et al.*¹⁵ indicating that the pronounced non-Franck–Condon behavior observed is primarily due to the internuclear distance dependence of the electronic transition moments. General agreement between the theoretical and experimental angular distributions is obtained. We have, in the present work, neglected the effects of saturation and the possible presence of autoionization features in the continuum. In a previous pa-

per¹⁴ we have shown the sensitivity of the calculated results to the inclusion of saturation effects. The effects of the Rydberg–valence mixing on the photoelectron angular distributions and vibrational branching ratios are expected to be even more dramatic if the outer-well vibrational states $\nu_F = 0, 1, 2, 3$, i.e., $\nu_{E,F} = \nu_i = 1, 2, 4, 5$ were accessed. Further theoretical and experimental studies for ionization through the outer well would therefore be very useful in unraveling the dynamics of these molecular photoionization processes.

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