Non–Franck-Condon Distributions of Final States in Photoionization of $H_2(C\,^1\Pi_u)$

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A striking feature of recent measurements of the photoionization of $H_2(C\,^1\Pi_u)$ is that the distribution of final vibrational states of H_2^+ differs significantly from the predictions of the Franck-Condon approximation. A theory is presented that accounts for these measurements. The essential physical mechanism is photoexcitation of the dissociating, autoionizing $^1\Pi_g$ electronic state of H_2, followed by competition between dissociation of the nuclei (leading to H^*+H) and electronic autoionization (leading to $H_2^+ + e$).

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The hydrogen molecule can be probed by analysis of its behavior following absorption of light. Several recent experiments[1-4] have determined the distribution of final vibrational states of H_2^+ following photoionization of electronically excited H_2. The surprising result is that the distributions differ from the predictions of the Franck-Condon approximation. This Letter presents a theoretical model and quantitative calculations that clarify these results.

The essential mechanism considered is the photoexcitation of a dissociating, autoionizing state. The theory can be developed by invocation of the analogy to the dissociative recombination of electrons with H_2^+.[5,6] The parallel is illustrated in Fig. 1. In both cases, a neutral molecule is formed at small values of the internuclear distance R by absorption of an electron or a photon. This molecule then begins to dissociate on a potential curve along which autoionization (electron emission, shown by a dashed arrow) may occur. Autoionization yields $H_2^+ + e$. If the molecule "survives" autoionization, the dissociated products are H^*+H. A crucial feature of the process is that autoionization is spread out over a time interval long enough for the nuclei to move substantially. Hence, the distribution of final vibrational states of H_2^+ need not be Franck-Condon. Alternatively, one may say that the motion of the nuclei on the dissociating potential curve converts electronic to translational energy. This energy ultimately appears as excess vibrational energy of the molecular ion.

Another distinguishing feature of this process is that the state initially created by photoexcitation immediately begins to dissociate, in competition with electronic autoionization. Other processes, particularly in the photoionization of NO, have been treated[7] that involve photoexcitation of quasibound, molecular Rydberg states. These states may decay by predissociation and vibrational autoionization.

To summarize the results of the formal theory, let us write the wave function Ψ_i for the initial state (of H_2) as a product of a vibrational part $\chi_v(R)$ and an electronic part $\Phi_i(R,q)$. The internuclear distance is R, and q denotes collectively the electron coordinates. The final-state wave function describes the nuclear motion on the dissociating, discrete state whose electronic wave function is $\Phi_d(R,q)$. This state can autoionize to continuum states $\chi_{v^+}^+\Phi_\epsilon^+$, where $\chi_{v^+}^+$ is the vibrational state of the molecular ion, and Φ_ϵ^+ is an electronic continuum wave function. We write the final wave function as

$$\Psi_f = \psi(R)\Phi_d(R,q) + \sum\nolimits_{v^+} \int b_{v^+}(\epsilon)\chi_{v^+}^+(R)\Phi_\epsilon^+(R,q)\,d\epsilon. \tag{1}$$

We obtain a modified Schrödinger's equation for $\psi(R)$, the nuclear wave function on the dissociating potential, by invoking several approximations[5,8] to eliminate the expansion coefficients $b_{v^+}(\epsilon)$. The final equation is

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2} + V^*(R) - E\right]\psi(R) = -\frac{\hbar^2}{mea_0^3}\mu(R)\chi_v(R) + i\pi V_{\rm el}(R)\sum\nolimits_{v^+}\chi_{v^+}^+(R)\int \chi_{v^+}^+(R')V_{\rm el}(R')\psi(R')\,dR'. \tag{2}$$

Equation (2) is identical to the one used to treat dissociative recombination,[5,6] except that now the first term on the right-hand side corresponds to photoabsorption instead of electron capture. An essential feature is the description of autoionization by a nonlocal complex potential, the second term on the right-hand side. In some related problems[9] this term can be approximated by a simpler, local form $(i/2)\Gamma(R)\psi(R)$, where Γ is defined below. The other terms are defined as follows: M is the reduced nuclear mass and m is the electron mass. $V^*(R) = \langle\Phi_d|H_{\rm el}|\Phi_d\rangle$ is the potential curve describing the dissociating state, which is coupled to the electronic continuum by $V_{\rm el}(R) = \langle\Phi_d|H_{\rm el}|\Phi_\epsilon{}^+\rangle$. $H_{\rm el}$ is the electronic Hamiltonian. $\mu(R)$ is the transition dipole matrix element for photoexcitation of the autoionizing state. The coupling potential $V_{\rm el}(R)$ is related to the fixed-nuclei electronic autoionization rate $\Gamma(R)/\hbar$ of the elec-

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tronic state by $\Gamma(R)=2\pi|V_{\mathrm{el}}(R)|^2$. The sum is over open channels; χ_v, χ_v^+, and ψ have units of $(\text{length})^{-1/2}$, and the boundary conditions are $\psi(0)=0$ and $\psi(R)\rightarrow A \times\exp(ikR)$ as $R\rightarrow\infty$.

The asymptotic magnitude $|A|$ of the outgoing wave ψ is related to the strength of the photoexcitation source term and to the losses due to autoionization. Multiplying Eq. (2) by ψ^*, integrating, subtracting the complex conjugate, and using the boundary conditions yield a flux conservation equation:

$$\frac{\hbar^2 k}{2M}\lim_{R\rightarrow\infty}|\psi(R)|^2=\operatorname{Im}\frac{\hbar^2}{mea_0^3}\int\psi(R)\mu(R)\chi_v(R)dR-\pi\sum\nolimits_{v^+}\left|\int\chi_{v^+}^+(R)V_{\mathrm{el}}(R)\psi(R)dR\right|^2. \tag{3}$$

The cross sections for photodissociation $[\sigma_{\mathrm{pd}}]$ and photoionization to a particular final state $v^+[\sigma_{\mathrm{pi}}(v^+)]$ can be constructed from the outgoing flux:

$$\sigma_{\mathrm{pd}}=\frac{8\pi^2\nu}{3c}\frac{ka_0}{2}\frac{m}{M}a_0^4\lim_{R\rightarrow\infty}|\psi(R)|^2, \tag{4}$$

$$\sigma_{\mathrm{pi}}(v^+)=(8\pi^2\nu/3c)a_0^3(\pi/2\mathcal{R})\left|\int\chi_{v^+}^+(R)V_{\mathrm{el}}(R)\psi(R)dR\right|^2, \tag{5}$$

where $\mathcal{R}$ is the Rydberg. In the limit of no autoionization ($V_{\mathrm{el}}=0$), Eq. (4) for σ_{pd} is equivalent to the standard formula[9] for photodissociation.

Several approximations have been made in the preceding analysis. I have ignored the rotational degrees of freedom. I have also neglected the direct photoionization process, which does not involve the autoionizing state. The direct process can be treated independently, although a definitive calculation would include the interference with the indirect mechanism considered here. Nevertheless, Eqs. (4) and (5) quantify the competition between dissociation and electronic autoionization, and permit evaluation of the distribution of final vibrational states.

I illustrate the theory by considering photoionization of H_2 in the $C\,^1\Pi_u$ state. This system is one of several of current interest[10] that involve competition between dissociation and ionization. Experiments performed in this laboratory[4] and elsewhere[2,3] use resonant three-photon excitation ($h\nu=4.1-4.4$ eV) of the ground state of H_2 to produce specific vibrational ($v\leq 4$) and rotational levels of the $H_2(C\,^1\Pi_u)$ electronic state. These states are then photoionized by a fourth photon of the same wavelength. For comparison with theory, I focus on the photoionization step:

$$H_2(C,v)+h\nu\rightarrow H_2{}^+(v^+)+e. \tag{6}$$

The distribution of final vibrational levels v^+ of $H_2{}^+$ is determined by measuring the energy distribution of the photoelectrons. On the basis of Franck-Condon factors, one expects $v^+=v$ transitions to dominate. This is because the C state is very nearly parallel to the $H_2{}^+$ potential, as shown in Fig. 1. Deviations from the Franck-Condon approximation are therefore directly related to the production of $H_2{}^+$ with $v^+\neq v$. The experimental observation is that the deviation from the Franck-Condon approximation becomes progressively greater for increasing v. A few electrons are also detected with energies corresponding to photoionization (by the same laser pulse) of excited atoms H^* with $n=3$ and 4. These H^* are produced by photodissociation of $H_2(C,v)$, and provide a measure of the probability to survive autoionization.

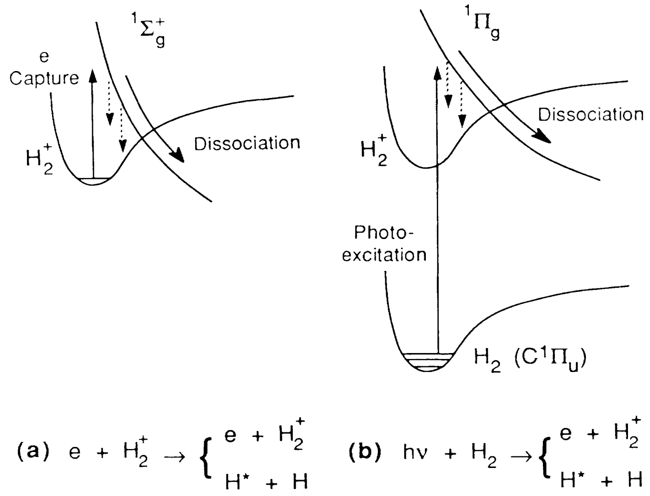

FIG. 1. Schematic illustration of the analogy between the indirect photoionization mechanism considered here and dissociative recombination of electrons with $H_2{}^+$.

These experiments stimulated theoretical activity. Dixit, Lynch, and McCoy[11] reported detailed calculations of the direct photoionization process, including higher-order terms in the transition dipole matrix element depending on internuclear separation R and photoelectron energy. They demonstrated that these additional terms cause small non-Franck-Condon transitions for $v=0$ or 1 that are comparable to the experimental observations. However, it seems clear from their work that refinements based only on direct photoionization cannot account for the larger deviations observed for $v=3$ and 4.

The present author[12] and Chupka[13] have considered an indirect mechanism for photoionization of $H_2(C\,^1\Pi_u)$ involving the $1\sigma_u 1\pi_u\,^1\Pi_g$ autoionizing state. This dissociating state is the most likely to consider, because it differs from the initial C state $[1\sigma_g 1\pi_u\,{}^1\Pi_u]$ by a single orbital, and the transition $1\sigma_g \rightarrow 1\sigma_u$ is optically allowed. I therefore solved Eq. (2) numerically for coupling terms corresponding to this autoionizing state: The transition dipole $\mu(R)$ for the $1\sigma_g \rightarrow 1\sigma_u$ transition is[14] approximately $-R/2$; $V^*(R)$ for the ${}^1\Pi_g$ autoionizing state has been calculated by Guberman,[15] and the width $\Gamma(R)$ for this state has been calculated by Tennyson and Noble[16] and Schneider, Lynch, and Collins.[17] I assumed $V_{el}(R) = [\Gamma(R)/(2\pi)]^{1/2}$ and neglected the energy dependence of the coupling matrix element.

Results for the total photoionization through the autoionizing ${}^1\Pi_g$ state are presented in Table I. The absolute magnitude for this indirect photoionization increases very rapidly with v. This behavior is due to an improving overlap between the initial vibrational wave function of $H_2(C,v)$ and the wave function ψ on the dissociative potential V^*. The translational energy (of H^*+H) used to calculate ψ is the four-photon excitation energy above the ground vibrational state of $H_2(X)$, because the same laser pulse produces the three-photon excitation of $H_2(C,v)$ and the ionization. The magnitude of the direct photoionization was estimated from the calculations of Cohn[18] to be about 3×10^{-18} cm^2. (Dixit, Lynch, and McCoy[11] did not report absolute cross sections.) This number is roughly the same for $v=0$–4. Comparing this value to the magnitude of the indirect photoionization, I conclude that the contribution of indirect photoionization to the total photoionization is negligible for $v=0$ and 1, and increasingly more important for larger values of v. This behavior explains why the results of Dixit, Lynch, and McCoy[11] for $v^+ \neq v$ based on the direct mechanism are comparable to experiment for $v=0$ and 1, but increasingly smaller than experiment for larger v.

I compare the present calculations of the final vibrational state distributions with experiment in Fig. 2. I have normalized all the $v^+=v$ transitions to unity, because the experiments reported relative cross sections. The experiments show a clear trend of increasing non-Franck-Condon transitions for increasing v. The indirect photoionization shows a similar trend. Results are not shown for $v=0$ and 1. For these v, the absolute magnitude of the indirect photoionization is much smaller than the direct process, which already accounts reasonably well for the experiments. For larger values of v, the magnitude of the indirect mechanism is large enough to account for a broad distribution of final states.

TABLE I. Photoionization cross sections σ_{pi} (summed over v^+) of $H_2(C\,{}^1\Pi_u,v)$ via photoexcitation of the ${}^1\Pi_g$ autoionization state.

v	σ_{pi} (cm^2)
0	4.64×10^{-20}
1	1.43×10^{-19}
2	5.42×10^{-19}
3	2.45×10^{-18}
4	6.60×10^{-18}

The dissociative fraction $\sigma_{pd}/(\sigma_{pd}+\sigma_{pi})$ (the "survival factor") was also calculated. For $v=2$, 3, and 4 this fraction is 0.1%, 1.3%, and 5.2%, respectively. For $v=3$, the present result may be compared with the experimental lower bounds of 2.0% (Ref. 4) and 3% (Ref. 3), which were obtained by consideration of the area under the appropriate peaks in the measured spectrum. (The experimental peak area is a lower bound because the dissociated H^* may not be ionized with unit efficiency).

In summary, this Letter has analyzed molecular photoionization occurring through dissociating, electronically autoionizing states. Quantitative calculations have provided an explanation of recently observed, anomalous distributions of final states. Additional effects that need to be probed by further study include the interference of different photoionization mechanisms, possible structure in the total photoionization cross section, and the state

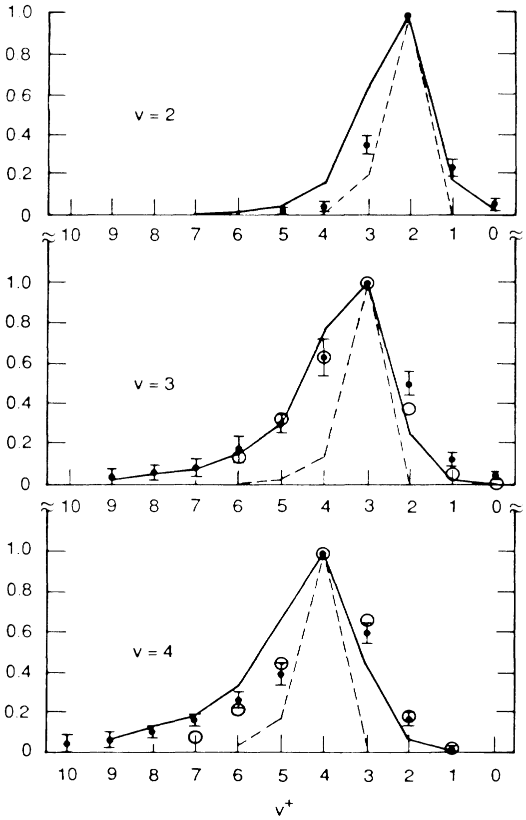

FIG. 2. Distribution of final vibrational states v^+ of $H_2{}^+$. Solid line: present calculation of indirect photoionization through the ${}^1\Pi_g$ autoionization state. Dashed line: direct photoionization calculated by Dixit, Lynch, and McCoy. Experimental points: filled circles with error bars, O'Halloran *et al.*; open circles (± 10% error limits), Xu *et al.*

distribution of these dissociated molecules surviving the autoionization.

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