# Experimental Evidence of an Interference between Photodissociation Continua

M. Glass-Maujean
*Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France, and*
*Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris Sud, 91405 Orsay, France*

H. Frohlich
*Laboratoire de Collisions Atomiques et Moléculaires and Laboratoire pour l'Ultilisation du Rayonnement Electromagnétique, Université de Paris Sud, 91405 Orsay, France*

and

J. Alberto Beswick
*Laboratoire pour l'Utilisation du Rayonnement Electronmagnétique, Université de Paris Sud, 91405 Orsay, France*
(Received 2 May 1988)

The two states $^1\Sigma_u^+$ $B$ and $B'$ of $H_2$, dissociating adiabatically to $H(2p)+H(1s)$ and $H(2s)+H(1s)$, respectively, are simultaneously excited by vacuum-ultraviolet photon absorption, above threshold. The combination of the coherent excitation of the two continua and of a nonadiabatic transition occurring at large internuclear distance produces a quantum interference effect in the partial photodissociation cross section which strongly affects the branching ratio $\sigma_p(H_2 \rightarrow H(2p)+H(1s))/\sigma_s(H_2 \rightarrow H(2s)+H(1s))$. Comparisons with theoretical predictions are presented and discussed.

PACS numbers: 33.80.Gj

Recently,[1] it has been theoretically shown that partial photodissociation cross sections into $H(2s)+H(1s)$ and $H(2p)+H(1s)$ in the vacuum-ultraviolet photodissociation of $H_2$ are expected to present pronounced oscillations as a function of the photon energy. These oscillations are the result of a quantum interference effect between two dissociation paths leading to the same final state. The condition for this interference to occur is the existence in the Franck-Condon region of two dissociative states which can be excited coherently and which are coupled to each other, by nonadiabatic or some other electronic interactions. In $H_2$ both the $B$ and $B'$ states (symmetry $^1\Sigma_u^+$) can be simultaneously excited by photon absorption at $\lambda \leq 845$ Å. In the adiabatic approximation the $B$ state correlates to the $H(2p)+H(1s)$ limit while $B'$ correlates to $H(2s)+H(1s)$. They are coupled to each other by radial nonadiabatic terms at large internuclear distance ($R \simeq 15a_0$).[2,3] Thus the condition for the existence of two dissociative paths leading to the same final state is met for $H_2$ in this energy region. The $H(2s)+H(1s)$ final state, for instance, can be obtained by photoabsorption into the $B'$ state followed by adiabatic dissociation, or by photoabsorption into the $B$ state followed by a nonadiabatic transition to the $B'$ state. Similarly, the $H(2p)+H(1s)$ channel can be produced by photoabsorption into the $B$ state and adiabatic dissociation, or photoabsorption into the $B'$ state followed by nonadiabatic transition to the $B$ state.

We report here the first experimental observation of this effect. This is accomplished by measurement of the branching ratio

$$\sigma_p(H_2 \rightarrow H(2p)+H(1s))/\sigma_s(H_2 \rightarrow H(2s)+H(2s))$$

for different values of the excess energy in the region of direct dissociation and also on an intense predissociation peak. In brief, synchrotron radiation from the storage ring ACO at Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (Orsay) was dispersed by a 1-m normal-incidence monochromator used with a typical bandwidth of 0.2 Å, small enough to isolate the background from the predissociated lines and sufficiently broad to get a sensible counting rate. Ly-$\alpha$ fluorescence was detected perpendicularly to the incident light beam by an EMR solar-blind photomultiplier. Absorption and Ly-$\alpha$ excitation high-resolution spectra obtained with such an apparatus have been published elsewhere.[4]

The $H(2p)$ excited fragments have a short radiative lifetime and thus Ly-$\alpha$ fluorescence can be easily detected. On the other hand, $H(2s)$ fragments are metastable with thermal or higher velocities. Therefore, at low pressure they leave the field of view of the detector without being detected. An applied electric field is used to induce Stark mixing between the $2s$ and the $2p$ states, allowing the $H(2s)$ fragments to emit Ly-$\alpha$ fluorescence. At higher pressures, collisions between $H(2s)$ and $H_2(X)$ quench the metastable atoms of $H(2p)$, giving rise to additional Ly-$\alpha$ fluorescence, as well as to some other nonidentified dark channels.[5] Thus, extrapolation to

 

zero pressure with and without an applied electric field can be used to determine the branching ratio between $H(2p)$ and $H(2s)$ fragments. This technique has already been applied in the past[6] to a very intense predissociation peak.

The measured signals being extremely weak, the pressure was scanned between 0.1 and 10 mTorr in order to get a sensible counting rate (few counts per second). In this pressure range, however, the dependence of the fluorescence signal as a function of pressure is no longer linear. Let $\sigma_Q$ be the collisional quenching cross section of $H(2s)$ by $H_2$, $\sigma_{\text{Ly-}\alpha}$ the partial collisional quenching cross section giving Ly-$\alpha$ emission, $N=(3.3\times10^{13}/\text{mTorr})p$ the $H_2$ density number, and $L$ the characteristic dimension of the detection zone. The fluorescence intensity emitted in the whole space, with the electric field off, will be proportional to

$$I_e^{(0)} \propto \sigma_p + \sigma_s(\sigma_{\text{Ly-}\alpha}/\sigma_Q)[1-\exp(-N\sigma_Q L)], \quad (1)$$

where we have denoted by $\sigma_p$ and $\sigma_s$ the photodissociation cross sections $\sigma_p(H_2 \rightarrow H(2p)+H(1s))$ and $\sigma_s(H_2 \rightarrow H(2s)+H(1s))$, respectively. On the other hand, with the electric field $E$ on, we have

$$I_e^{(E)} \propto \sigma_p + \sigma_s. \quad (2)$$

If the fluorescence emissions were isotropic, the detected fluorescence intensity would be proportional to $I_e^{(0)}$ and $I_e^{(E)}$. Actually, the collisional-induced radiation is the only one that is isotropic. The emission induced by the applied electric field is known to be strongly polarized in the direction of the electric field ($\mathcal{P}=-0.323$).[7,8] Thus the observed signal has to be corrected for this anisotropy. In addition, the $H(2p)$ fragments are aligned by the photodissociation process[9] and therefore the $H(2p)$ fragment emission is also polarized. The amount of polarization has been calculated[10] for incident linearly polarized light in the range of 0 to 4000 $\text{cm}^{-1}$ of excess energy. The monochromatized synchrotron radiation is partly polarized with the electric vector parallel to the direction of detection. The degree of polarization for the conditions of our experiment has been measured to be of the order of 0.6.[11] With these data, the correction for the anisotropy of the $H(2p)$ emission can be easily determined.

If we take into account this correction, the ratio between the detected fluorescence with the electric field off, $I_d^{(0)}$, and that with it on, $I_d^{(E)}$, is

$$R = I_d^{(0)}/I_d^{(E)} = \frac{\alpha\sigma_p + \sigma_s(\sigma_{\text{Ly-}\alpha}/\sigma_Q)[1-\exp(-N\sigma_Q L)]}{\alpha\sigma_p + \beta\sigma_s}, \quad (3)$$

with $\alpha$ varying between 0.79 and 0.90 depending on the excess energy,[10] while $\beta$ is independent of energy and equal to $\beta=(1-\mathcal{P}/3)^{-1}=0.903$.

We have measured the intensity ratio $R$ as a function of pressure at six different energies in the direct-dissociation continuum and at the energy of one intense predissociation peak corresponding to the transition $3p\pi\,^1\Pi \leftarrow X\,^1\Sigma_g^+(3\text{-}0)R(1)$. In every case, we have fit the experimental points by an exponential using the same parameters $\sigma_{\text{Ly-}\alpha}$ and $\sigma_Q$. Once these parameters are fixed, the zero-pressure $R_0$ and the asymptotic $R_\infty$ values are related by

$$1-R_0=(R_\infty-R_0)\beta\sigma_Q/\sigma_{\text{Ly-}\alpha}, \quad (4)$$

which has been taken into account in our fit. Two typical plots of $R$ as a function of pressure are presented in Fig. 1. In the energy region explored here, the ratio $R_0=\alpha\sigma_p/(\alpha\sigma_p+\beta\sigma_s)$ varies from 0.43 to 0.70. Therefore, $\alpha\sigma_p/\sigma_s$ varies from 0.68 to 2.1. Such a variation cannot be accounted for by an adiabatic description of the dissociation. Adiabatically, the $H(2p)$ fragments are produced by the $B\,^1\Sigma_u^+$ and the $C\,^1\Pi_u$ states while the $H(2s)$ fragments come from dissociation through the $B'\,^1\Sigma_u^+$ state. The $B$, $C$, and $B'$ partial photodissociation cross sections are smooth functions of the excess energy in the adiabatic approximation.[12] The corresponding values for the branching ratio $\sigma_p/\sigma_s$ are 0.52 at 100 $\text{cm}^{-1}$ above threshold and 0.34 at 3000 $\text{cm}^{-1}$. The correction factor $\alpha$ lowers these values. On the predissociation peak, the measured value for $\alpha\sigma_p/\sigma_s$ is $0.71\pm0.09$. In the adiabatic limit, this value would be zero as the predissociation involves the bound $D$ state interacting through Coriolis coupling with the $B'$ state only. The measured value for the branching ratio $\sigma_p/\sigma_s$ agrees with the one obtained by Mentall and Guyon[6]

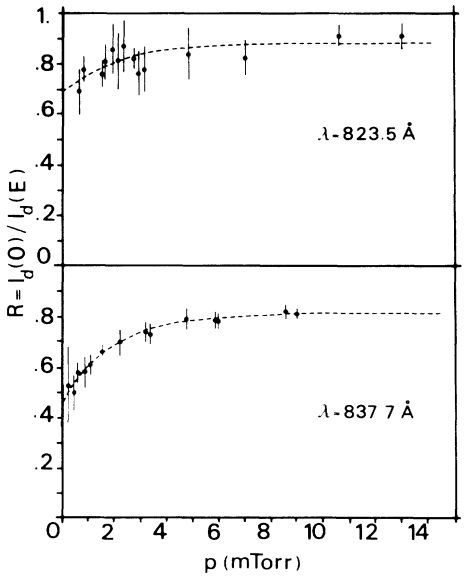


FIG. 1. Typical plots of the ratio of detected Ly-$\alpha$ emission without ($I_d^{(0)}$) and with ($I_d^{(E)}$) applied electric field, as a function of pressure for two different excitation wavelengths.

where $\alpha$ is modified to take into account their detection geometry.

We present in Fig. 2 a comparison between the experimental values for $\alpha\sigma_p/\sigma_s$ and the theoretical predictions in the adiabatic limit. Clearly the adiabatic approximation gives very poor results as compared with experiments. Also represented in Fig. 2 are the results which take into account the nonadiabatic interactions with use of the couplings calculated in Ref. 3. The calculations were performed according to the theoretical treatment presented in Refs. 1 and 10. Although the overall behavior of the experimental results are qualitatively described by these calculations, there are quantitative differences which can be the result of an underestimation of the nonadiabatic transition probability. In Ref. 1, two of us have shown that the partial photodissociation cross sections can be written as

$$\sigma_p = \sigma_C + \sigma_D(1-P) + \sigma_{B'}P - 2[\sigma_B\sigma_{B'}P(1-P)]^{1/2}\cos(\delta_B - \delta_{B'}),$$
$$\sigma_s = \sigma_B P + \sigma_{B'}(1-P) + 2[\sigma_B\sigma_{B'}P(1-P)]^{1/2}\cos(\delta_B - \delta_{B'}), \quad (5)$$

where $\sigma_C$, $\sigma_B$, and $\sigma_{B'}$ represent the adiabatic partial photodissociation cross sections into the $C$, $B$, and $B'$ states, respectively, $\delta_B$ and $\delta_{B'}$ represent the phases of the continuum vibrational wave functions associated with the $B$ and $B'$ states, respectively, and $P$ represents the nonadiabatic transition probability to jump between $B$ and $B'$ states during the half-collision after the photon absorption. The oscillatory term involving the phase difference $\delta_B - \delta_{B'}$ is due to the quantum interference effect mentioned above. The quantum-chemistry calculations of Ref. 3 give $P$ of the order of 0.2. The oscillating dashed curve represented in Fig. 2 is the result of our using this $P$ value in Eqs. (5). Clearly, $P$ is too small. If we deduce the value of $P$ from the measured branching ratio on the resonance peak, we obtain $P = 0.43 \pm 0.02$. We have recalculated the branching ratio at all other points using this empirical determination of $P$. The results are represented in Fig. 2 by triangles. All the calculated points are now in very good agreement with the experiment. The same value of $P$ was used to calculate $\alpha$ according to Ref. 1. $\alpha$ was found to vary from 0.79 at $\lambda = 844.1$ Å to 0.90 at $\lambda = 837.3$ Å.

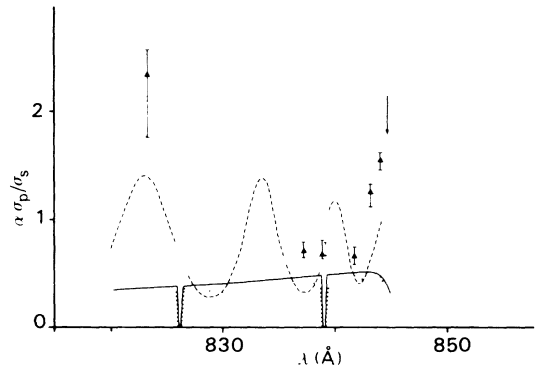


FIG. 2. Branching ratio $\sigma_p/\sigma_s$ (multiplied by the anisotropic correction factor $\alpha$) for H($2p$) to H($2s$) fragments in the photodissociation of $H_2$ as a function of the radiation excitation wavelength. The experimental values are represented by their error bars. The dotted error bar corresponds to the Mentall-Guyon results (Ref. 6) after correction for their experimental geometry. The full curve is the adiabatic isotropic ($\alpha = 1$) theoretical result. The dotted line is the $\alpha$-corrected adiabatic result. The dips are due to the strong predissociation peaks of the $D$ state. The dashed curve corresponds to the calculation taking into account nonadiabatic interactions with use of the *ab initio* couplings of Ref. 3. The triangles are the results of a quantum calculation using a modified transition probability (see text).

In conclusion, the experimental branching ratio of H($2p$) to H($2s$) in the vacuum-ultraviolet photodissociation of $H_2$ confirms the interference effect between direct-dissociation continua predicted in Ref. 1. We have shown that this effect is very sensitive to the actual value of the probability $P$ for a transition from one dissociative continuum to the other in the half-collision following the photon absorption. Use of the *ab initio* nonadiabatic coupling of Ref. 3 gives a transition probability $P$ which is too low for a quantitative description of the experimental branching ratio. On the other hand, good agreement is obtained with $P = 0.43$. It is worth noting that this value is very close to the one deduced from the adiabatic description of the interaction between ionic and valence channels.[2,13] Further theoretical work is needed in order to clarify this point. In particular, it will be interesting to determine whether the small value of $P$ obtained with the *ab initio* nonadiabatic coupling[1,3] is due to an underestimation of the coupling or to the neglect of the effect of the interaction of the $B$ and $B'$ states with the upper $B''$ state.

Laboratoire de Spectroscopie Hertzienne de l'Ecole Normale Supérieure and Laboratoire de Collisions Atomique et Moléculaires are laboratoires associés au Centre National de la Recherche Scientifique. Laboratoire pour l'Utilisation du Rayonnement Electromagnétique is a laboratoire du Centre National de la Recherche Scientifique, Commissariat à l'Energie Atomique, et Ministéra de l'Education Nationale.

[1] J. A. Beswick and M. Glass-Maujean, Phys. Rev. A **35**, 3339 (1987).

[2] I. V. Komarov and V. N. Ostrovsky, J. Phys. B **12**, 2485

(1979).
[3]F. Borondo, J. R. Eguiagaray, and A. Riera, J. Phys. B **15**, 899 (1982).
[4]M. Glass-Maujean, J. Breton, and P. M. Guyon, Z. Phys. D **5**, 189 (1987).
[5]F. J. Comes and O. Wenning, Z. Naturforsch. **24a**, 587 (1969).
[6]J. E. Mentall and P. M. Guyon, J. Chem. Phys. **67**, 3845 (1977).
[7]W. R. Ott, W. E. Kauppila, and W. L. Fite, Phys. Rev. A **1**, 1089 (1968).
[8]G. W. F. Drake, P. S. Fargo, and A. van Wijngaarden, Phys. Rev. A **11**, 1621 (1975).
[9]M. Glass-Maujean and J. A. Beswick, Phys. Rev. A **36**, 1170 (1987).
[10]M. Glass-Maujean and J. A. Beswick, to be published.
[11]P. M. Guyon, private communication.
[12]M. Glass-Maujean, Phys. Rev. A **33**, 342 (1986).
[13]D. R. Bates and J. T. Lewis, Proc. Phys. Soc. A **68**, 173 (1955).