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Collisional Quenching of H(2*S*) Atoms by Molecular Hydrogen: Two Competitive Reactions

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From an H_2 photodissociation experiment the destruction of the H(2*S*) metastable fragments, colliding with an H_2 molecule, is shown to proceed through two competitive processes: the 2*S*-2*P* mixing induced by the H_2 quadrupole moment and a nonradiative process. This nonradiative process has a cross section of about 50 Å^2 for thermal velocities. Its identification as H_3^+ production is discussed.

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Quenching of metastable hydrogen atoms by low-energy collisions with hydrogen molecules was studied more than ten years ago by the attenuation of a metastable-atom beam passing through molecular hydrogen gas.[1-4] In one such experiment,[2] the Lyman-α radiation emitted from the collision was monitored. The Ly$_\alpha$ emission cross section and the metastable destruction cross section were observed to exhibit identical velocity dependences within experimental errors.[2] Since then, the collisional destruction of metastable hydrogen at low energy was commonly interpreted as proceeding "solely through 2*S*-2*P* mixing with subsequent emission of Ly$_\alpha$ radiation."[3-5] This was in disagreement with two other experiments, using completely different techniques,[6,7] where a radiationless quenching process was reported with its relative importance being a quarter[7] or a half[6] of the total metastable destruction. Besides, the theoretical calculations of the collisional quenching of the H atoms in the 2^2S state by Stark mixing with the 2^2P state[5,8,9] lead to values that are roughly two thirds of the experimental destruction cross-sectional values.[4,5] We have now performed a new experiment, improving the technique used in Ref. 7, which gives new evidence of the competition of a radiationless quenching process with the 2*S*-2*P* mixing.

Monochromatized synchrotron radiation was used to photodissociate the molecules of hydrogen contained in a cell, and the Ly$_\alpha$ fluorescence of the atomic fragments was detected by an EMR solar-blind photomultiplier. At low pressure the H(2*S*) fragments, being metastable and having roughly thermal velocities, leave the field of view of the detector without being detected, while the H(2*P*) fragments with a short lifetime are easily detected.

At higher pressure, collisions between H(2*S*) and $H_2(X^1\Sigma_g^+)$ quench the metastable atoms, giving rise to additional Ly$_\alpha$ fluorescence. An applied electric field can be used to induce Stark mixing between the 2*S* and 2*P* states, destroying the metastable atoms with Ly$_\alpha$ emission. The ratio of the fluorescence signal without and with an electric field was measured for pressures ranging from 0.1 to 15 mTorr. Extrapolation to zero pressure was used to determine the H(2*P*) to H(2*S*) fragment branching ratio.[10] The dependence of the fluorescence signal as a function of pressure gives information about the collisional quenching. Such dependences were recorded for six different photodissociation energies, i.e., for six fragment velocities. The calculated relative H_2-H(2*S*) velocities range from 2.9 to 6.4 km/s.

The Ly$_\alpha$ fluorescence intensity, without any electric field, is proportional to

$$I(0) \propto \alpha\sigma_p + \sigma_s(\sigma_{\mathrm{Ly}_\alpha}/\sigma_d)[1-\exp(-N\sigma_d L)]\,, \qquad (1)$$

where σ_p and σ_s denote the photodissociation cross section for H(2*P*) and H(2*S*) fragments, respectively, $\sigma_{\mathrm{Ly}_\alpha}$ denotes the collisional quenching cross section with Ly$_\alpha$ emission, σ_d denotes the collisional destruction cross section, N is the H_2 number density ($N = 3.3 \times 10^{13}$ times the pressure p in mTorr), and L is the characteristic dimension of the detection zone ($L = 13$ mm). α is a corrective factor due to the polarization of the fragment fluorescence.[10,11] It has no importance here, being constant in the pressure range used. With the electric field E on, the Ly$_\alpha$ intensity is

$$I(E) \propto \alpha\sigma_p + B\sigma_s\,, \qquad (2)$$

if the Stark quenching is much faster than the collisional quenching, which is easily achieved with an electric field of 60 V/cm in the experimental conditions. β is a polarization corrective factor. For a detection perpendicular to the electric field, its measured[12] and its theoretical[13] value is $\beta = (1 - P/3)^{-1} = 0.903$, P being the polarization of the induced Ly$_\alpha$ emission.

Let R be the signal ratio:

$$R = I(0)/I(E)\,. \qquad (3)$$

If R_0 is the extrapolated value at zero pressure, the signal ratio is equal to

$$R = R_0 + (1 - R_0)(1/\beta)\sigma_{\mathrm{Ly}_\alpha}/\sigma_d[1 - \exp(-p/\bar{p})]\,. \qquad (4)$$

R_0 depends only on the H(2*P*) to H(2*S*) branching ratio as discussed previously.[10] The pressure width $\bar{p}$ is such that $\sigma_d L\bar{p}(3.3\times10^{13})=1$ which is directly correlated to σ_d. The asymptotic R_∞ value at high pressure

$$R_\infty = R_0 + (1-R_0)(1/\beta)\sigma_{\mathrm{Ly}_\alpha}/\sigma_d \qquad (5)$$

gives the relative importance of the collisional quenching with Ly_α emission, $\sigma_{\mathrm{Ly}_\alpha}$, to the collisional destruction σ_d.

For the six values of the incident wavelength, the R dependences with pressure were fitted independently with an exponential law by a least-squares procedure. Such a fit is displayed in Fig. 1. The fitted parameters R_0, R_∞, and $\bar{p}$ are determined with quite large uncertainties, because the experimental points correspond in several cases to very-low-intensity signals (less than a count per second). Nevertheless, in no case may the ratio $\sigma_{\mathrm{Ly}_\alpha}/\sigma_d$ be taken as 1, which yields the solid-line asymptote in Fig. 1. Even if the polarization P of the Ly_α emission due to the electric quenching of the $2S$ state were in error, it could only be in error by a few percent, and in no way could β be as high as 1.5 (P would be equal to $+1$ instead of -0.343), as needed to explain the observed R_∞ values.

The σ_d values deduced from the $\bar{p}$ determinations at the six different collisional velocities are in very good agreement with all the previous measurements[2,4,5]; see Fig. 2(a). Our error bars are comparable to the dispersion of the other determinations.[2,4,5]

From these σ_d values and from the R_0 and R_∞ values it is easy to determine the $\sigma_{\mathrm{Ly}_\alpha}$ ones. They are displayed in Fig. 2(b). (All the uncertainties with independent sources were added quadratically.) In every case, $\sigma_{\mathrm{Ly}_\alpha}$ represents only 60% of σ_d, and there is no evidence for a velocity dependence of the $\sigma_{\mathrm{Ly}_\alpha}/\sigma_d$ ratio. This is in agreement with the observations of Dose and Hett for higher velocities[2] but in apparent disagreement with the Comes and Wenning conclusions,[6] although their uncertainties were not reported.

The first theoretical study of the collisional quenching of the metastable H atoms with Ly_α emission was made by Gersten[8] who calculated the Stark mixing of the $2S$ and $2P$ states due to the electric field produced by the quadrupole moment of the H_2 molecule, in a time-dependent perturbation theory. He took rotation into account in the classical approximation. Ryan, Czuchlewski, and McCusker[4] and Weissmann, Hartmann, and Burch[5] improved Gersten's treatment with a quantal approach to the H_2 molecule rotation. They obtained a quite good dependence of σ_d but not its absolute values.[4,5] The theoretical values of $\sigma_{\mathrm{Ly}_\alpha}$ are systematically 30% lower than the experimental σ_d values, only a

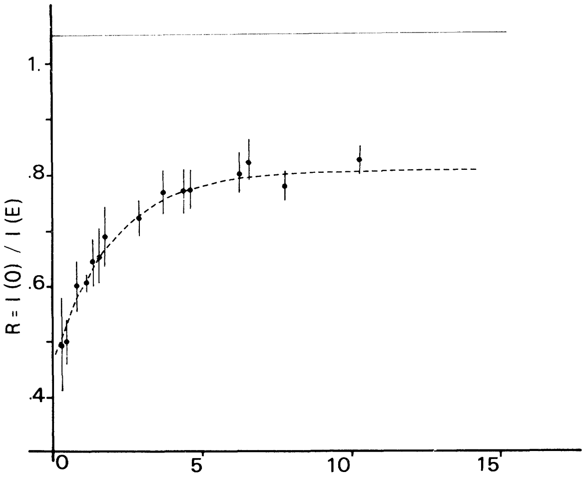

FIG. 1. Typical plot of the ratio of detected Ly_α emission without $[I(0)]$ and with $[I(E)]$ an applied electric field, as a function of pressure for an excitation wavelength of 838.9 Å and a mean relative $H(2S)$-H_2 velocity of 4.14 km/s. The horizontal line represents the expected asymptote for $\sigma_{\mathrm{Ly}_\alpha}=\sigma_d$.

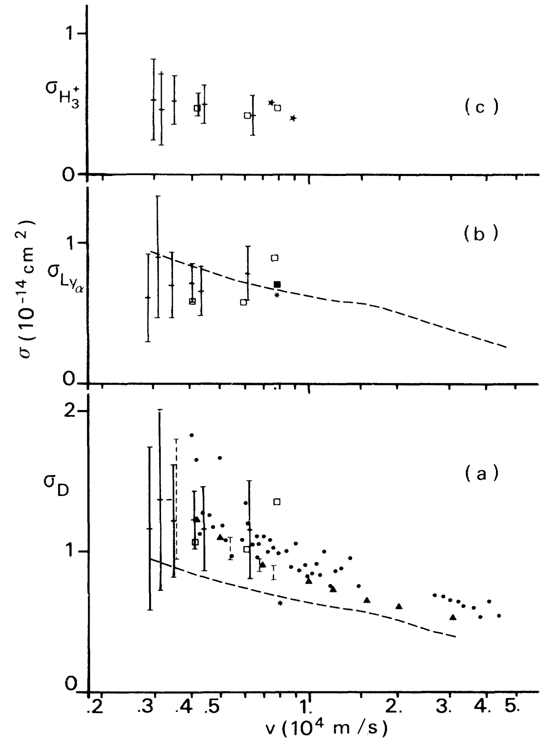

FIG. 2. Cross sections for the various $H(2S)$ quenchings in H_2. (a) The destruction cross section σ_d; (b) the quenching cross section with Ly_α emission $\sigma_{\mathrm{Ly}_\alpha}$; and (c) the cross section of the nonradiative process identified as the formation of $H_3{}^+$. The solid error bars are our results, the dashed error bars are from Ref. 5, the dots are from Ref. 4, the triangles are the mean determinations of Ref. 2, and the open squares are from Ref. 6. The dashed curves are the theoretical prediction of the $2S$-$2P$ mixing quenching (Refs. 4 and 5), and the asterisks are the calculation of Ref. 9. The solid square represents the measurement of Ref. 14. The stars note our determinations using the spectra of Ref. 15.

bit higher than our experimental $\sigma_{\mathrm{Ly}_\alpha}$ values and just within the limits of the error bars, corroborating our analysis.

Our experimental values also agree well with the only previous $\sigma_{\mathrm{Ly}_\alpha}$ determination of Fite *et al.*[14]

The remaining problem is to identify the nonradiative process involved. Twenty years ago Chupka, Russell, and Refaey[15] detected H_3^+ after photodissociation of H_2 into $H(n=2)+H(1S)$ which they attributed to the following reaction (I):

$$H(2S)+H_2 \rightarrow H_3^+ + e^- .$$

They also observed the reaction (II)

$$H_2^+ + H_2 \rightarrow H_3^+ + H .$$

From their photoionization efficiency curves for H_2^+ and H_3^+, we can estimate the cross section of reaction I relative to the cross section of reaction II. We compared the amplitudes of the H_3^+ and H_2^+ peaks at 818 Å to the corresponding absorption cross sections.[16] At 803 Å, all the created molecules are autoionized[17] while at 818 Å, they are all predissociated[18] into $H(n=2)+H(1S)$. Knowing that only 60% of the excited fragments are in the $2S$ state[10,19] and that reaction I competes with the $2S$-$2P$ mixing quenching, we can estimate that the cross-sectional value of reaction I with a relative mean velocity of 7 km/s is 50% of the cross-sectional value of reaction II with a thermal velocity (803 Å is very near the ionization threshold 804 Å). From Ref. 20, this value is around 100 Å^2, giving an estimated value for the reaction-I cross section of 50 Å^2 with an uncertainty of about 20%. We also compared the amplitudes of the H_2^+ and H_3^+ peaks observed at 804.2 Å to the photoionization and photodissociation efficiencies observed for this wavelength.[17,18] We deduced a second determination of the reaction-I cross section, for a mean relative velocity of 8.7 km/s: 40 Å^2. Both values are in excellent agreement with the cross section of the observed nonradiative process [see Fig. 2(c)].

Therefore, we believe that the observed nonradiative process of destruction of the metastable $H(2S)$ atoms when colliding with molecular hydrogen is mainly the formation of H_3^+ ion through reaction I. It would imply that the collision-induced predissociation (reaction III),

$$H(2S)+H_2 \rightarrow H(1S)+H(1S)+H(1S) ,$$

predicted in Ref. 21, is slow compared to reaction I, which has to proceed from the autoionization of a dissociative H_3 state. More theoretical and experimental work is necessary to settle that assumption unambiguously.

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