Photodissociation of H_2 near Threshold Energies

F. J. Comes and U. Wenning

Institut für Physikalische Chemie der Universität Bonn, Germany

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Measurements of the atomic hydrogen fluorescence (Ly_{α}) yield important information on the dissociation behavior of molecular hydrogen under photon impact. Under certain assumptions the dissociation cross section of the molecule can be deduced from such experiments. By applying an appropriate electric field in the observation region those dissociations leading to the formation of metastable hydrogen atoms can be quantitatively determined. This information opens the possibility to describe the predissociation of the excited H_2-molecules in the C-, D- and B''-states. The experiments show that the excited molecules in these particular states dissociate into H(1S) and H(2S) by configuration interaction with the B'-state.

The spectrum of the hydrogen molecule in the vicinity of its photodissociation and photoionization limit is well known because of the experiments which were carried out in recent years. A value of 118 372·6 cm^{-1} was obtained by Namioka[1] for the dissociation limit. Recent experiments at the ionization limit of the molecule yielded a new value for the ionization potential[2–4] which should replace the value of Beutler and Jünger[5] as yet accepted in the literature. The determination of the fluorescence[3, 6] as well as combined absorption and ionization measurements[6, 7] resulted in highly valuable informations on the dissociative behavior of the molecule. From these experiments predictions on the dissociation pattern given by quantum mechanical calculations can be proven[8, 9].

The observation of metastable hydrogen atoms produced by predissociating molecular states opens a way to investigate the photochemical behavior of these reactive species[10, 11]. Through this the dependence of the reaction probability on the kinetic energy of the particles could be determined.

Experimental

The determination of the fluorescence in the present experiment was done with a refined system which, in principle, is the same as described earlier[3].

The detector consists of an open photomultiplier with tungsten cathode. A LiF-window separates it from the absorption cell. This limits the sensitvity to the wavelength region between 1050 and 1500 Å. A sensitivity maximum is to be expected at 1150 – 1200 Å, for the transmittance of LiF decreases and the photoelectric yield of tungsten increases towards shorter wavelengths. The additional use of a CaF_2-window restricts still further the sensitive region, as this material absorbs completely below 1230 Å. Ly_{α}-radiation (1216 Å) is not detected with this window.

Through the use of an O_2-absorption filter that posesses a very narrow transmission region near 1216 Å the sensitivity of the detector system is practically confined to the immediate neighbourhood of the Ly_{α}-radiation.

By placing the multiplier extremely near to the absorbing region the sensitivity was improved by a factor of about ten. This made possible the observation of the fluorescence of weakly absorbing molecular states. The cross-sections of absorption and fluorescence were determined at weak absorption $[(I_0-I)/I_0 \leqq 0.05,\ p_{H_2} \cong 1 \times 10^{-2}$ Torr] and compared. The fluorescence of the atomic dissociation products was examined with respect to its behaviour in an electric field.

For several reasons the maximum fluorescence intensity to be expected is in the order of 100 counts/sec. The intensity of the exciting radiation is about 1×10^7 quanta/sec. The photoelectric yield of tungsten at 1216 Å is only 3%, the solid angle seen by the multiplier is roughly $5/100 \cdot 4\pi$. The necessity to work at weak absorption further diminishes the intensity. It is only the electronic stabilization of the lightsource and the extremely low dark current of the multiplier (1/2 count/min) that made the measurement possible.

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Procedure and Data

The bands of H_2 examined in the region between the dissociation and the ionization limits belong to electronic states of the molecule which are members of Rydberg series. Two such series converge at the ground state of $H_2^+ (^2\Sigma_g^+)$, whose configurations are described by $^1\Pi_u$ and $^1\Sigma_u^+$. The first members of the $^1\Pi_u$-series are denoted by C, D, D′, D″, while the symbols B, B′, B″ are used for the lowest terms of the $^1\Sigma_u^+$-series. Monfils[12] and Namioka[1, 13, 14] concentrated their work on these states. Recent measurements[4, 15] yielded informations on the higher Rydberg-terms.

The metastable H(2S)-atoms produced by photodissociation are quenched in sufficiently large fields, and by emission of Ly_α-radiation they give information regarding their production mechanism. Quantitative aspects of the dissociation process are obtained from the determination of the total Ly_α-intensity.

As the metastable atoms are an important part of the primary products, the photochemical behaviour of H_2 at low pressure, near its dissociation limit, is above all determined by the reactions of H(2S)-atoms.

The result to be reported here concern the dissociative behaviour of H_2 in the $D(^1\Pi_u)$, $B''(^1\Sigma_u^+)$ and $C(^1\Pi_u)$-states at the vibrational levels $v' = 3$, 4 and 5 of the D-State, $v' = 1$ of the B″- and $v' = 13$ of the C-state. Fluorescence below as well as immediately above the dissociation limit is discussed and its connection with H_3^+-formation by chemi-ionization is shown.

Absorption measurements at the D ($v' = 3$) band show strong diffuseness of the R- and P-terms while the members of the Q-branch remain sharp[1]. This effect was explained by the radiationless transition

$$H_2(D, v'=3) \rightarrow H_2(B') \rightarrow H(1S) + H(2S, 2P) + E_{\text{kin}} . \quad (1)$$

The kinetic energy results from the fact that the absorbed energy is larger than the dissociation energy. We have proved[10] the excited atom in reaction (1) to be produced only in its metastable state 2S.

Monfils[12] examined the B″ state above the dissociation limit and found rather sharp bands but remarked that this state predissociates weakly. The rotational terms of the B″ – X(1.0)-band are, according to the most recent measurements of Takezawa[4], clearly diffuse but not as much as e. g. the terms of the D – X(3.0)-band. Upon measuring the chemi-ionization of hydrogen according to Eq. (2)

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

we were able to state[11] that the B″ state plays an important role in the formation of H_3^+. The production of H_3^+ in collisions with excited molecules must be excluded. We conclude, therefore, that the B″ state dissociates in that band to form also metastable H atoms. If this is correct the fluorescence of that state should be quenchable in an electric field.

For that reason the fluorescence intensity of the B″ – X(1.0)-band was measured as a function of a homogeneous electric field. The result is shown in Fig. 1. The ordinate is the ratio of the fluorescence intensity with field over the intensity without field. For comparison the quenching curve of the D – X (3.0)-band is given, too. The distance of the two band heads is only about 1.7 Å, thus, the excited atoms formed have nearly the same kinetic energy. If we only have dissociation into H(2S)-atoms we should expect about the same quenching behaviour. Fig. 1 shows a slight difference in the field dependence for the two bands. This difference is outside the experimental error limits.

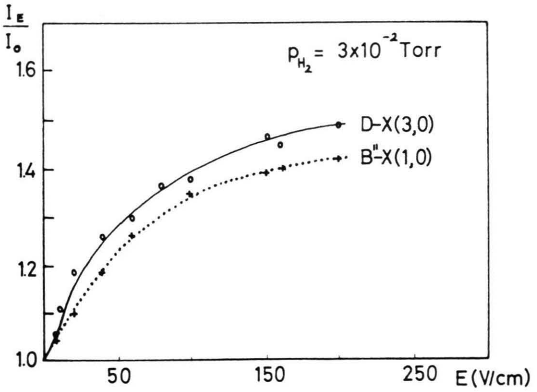

Fig. 1. Field dependence of measured Ly_α-fluorescence from the D – X (3.0) and the B″ – X (1.0) bands (I_E: Intensity at field strength E).

The determination of the photodissociation cross section of H_2 in an earlier experiment[3] was based

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upon the assumption of complete dissociation of the $D-X$, $v'=3$ state in its R- and P-branches. This assumption is supported by spectroscopic measurements at high resolution[1]. The coincidence of absorption and dissociation gross sections at some prominent parts of the H_2-spectrum between dissociation and ionization limit gave a first proof of that assumption. With the improved detector system we were able to show quantitative agreement of fluorescence (with electric field applied) and absorption (Fig. 2 a). The fluorescence has to be measured in an electric field of about 150 V/cm to make certain that the excited H-atoms do not loose their energy in radiationless collisions. In the field-free case this process is very probable at pressures of 1 to 3×10^{-2} torr used in the experiment. The electric field shortens the lifetime so much that all H(2S)-atoms radiate before undergoing collisions.

Fig. 2 a shows four different curves. The solid line gives the absorption cross section. Curve 2 (LiF) describes the fluorescence in the LiF-region with a 200 V/cm field. The intensity, originally registered in arbitrary units, was normalized versus the R(1)-term of the $D-X(3.0)$-band. The justification of this method will be carefully discussed later. The broken line shows the intensity as measured with the additional application of an O_2-filter (760 torr, 1 mm path length). This curve represents the measured Ly_α-intensity and therefore the dissociation cross section. Above the dissociation limit

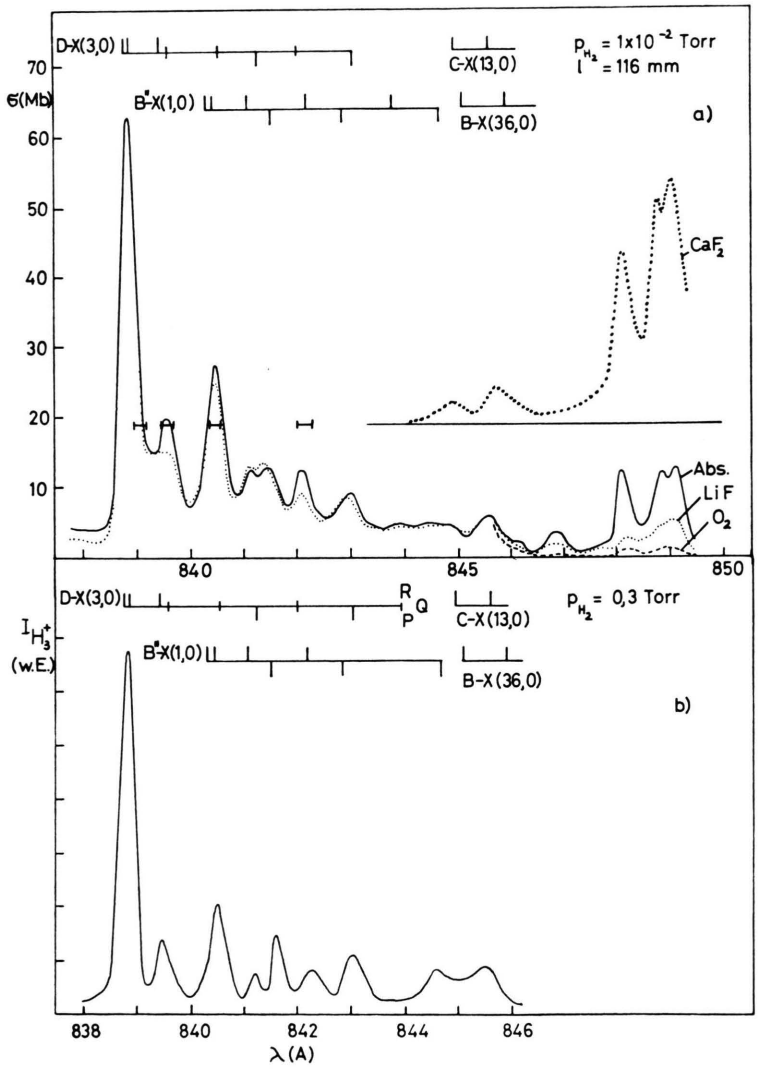

Fig. 2. a) (Abs.) Absorption cross section of H_2 (length of the cell: 116 mm). (LiF) Fluorescence intensity in the LiF-region, normalized to σ_{abs} at the $D-X$ (3.0) band head. (O_2) Fluorescence intensity of Ly_α, normalized as curve (LiF). Above 845.5 Å both curves (LiF) and (O_2) are identical within the error limits. (|—| indicate small fluorescence intensity in the CaF_2-region.) Bandwidth of primary radiation 0.25 Å. (CaF_2) Fluorescence intensity in the CaF_2-region (curve not normalized). b) H_3^+-intensity as measured with a mass spectrometer. Bandwidth of primary radiation 0.20 Å (w.E. = arbitrary units).

the two curves (LiF and O_2) are coincident showing thereby that the measured radiation is the Ly_α-emission of the atoms.

Part b of Fig. 2 pictures the H_3^+ ion intensity as published in an earlier paper[11]. The peaks coincide with those absorption maxima giving rise to the emission of Ly_α. Differences are mainly due to two reasons. In the first place the resolving power in the H_3^+ experiment is about 20% larger and shows, therefore, a more pronounced structure of this curve. Furthermore, the optical density at the ion determination is a little larger, such that rotational terms with higher quantum numbers are favoured in absorption. Taking into acount the differences due to the experimental array there remain only minor discrepancies between the Ly_α fluorescence and the ion curve. These discrepancies can be easily explained by the spectroscopic behaviour of the molecules.

As is mentioned earlier the absorption and fluorescence cross sections coincide almost completely. The remaining discrepancies are produced by non dissociative molecular states. The coincidence can be critically examined at the intense R(1) terms of the D bands. Table 1 shows the cross sections at the heads of the D bands (3.0), (4.0), and (5.0) if the dissociation cross section is normalized to the arithmetic mean of the absorption at these positions.

With enlarged scale, curve 4 (CaF_2) of Fig. 2 a represents the molecular fluorescence as determined by use of the CaF_2-window ($\lambda > 1230$ Å). Within this region of sensitivity of the uv-detector the fluorescence is only pronounced below the dissociation limit. If an O_2-absorption cell is used in combination with a LiF-window the fluorescence is lower than without the O_2-cell, corresponding to an absorption coefficient of about 20 cm^{-1}. This is a much higher value than would be expected for Ly_α only (0.5 cm^{-1}). If we measure the radiation for wavelengths shorter than 844 Å with a CaF_2-window we find the signal to be less than 1% of the maximum intensity as measured for larger wavelengths.

In an earlier work[3] the molecular fluorescence as measured with a CaF_2-window was shown to be independent of an electric field. The increased intensity enabled us to reexamine this question. In the present experiment we found a weak effect (at 849 Å) which led to a small increase of about 10% at a field strength of 200 V/cm.

The molecular states, as far as they belong to the bands $D - X(3.0)$ or $B'' - X(1.0)$ yield increments between 40 and 50% compared to the intensity without field. Immediately at the dissociation limit, the absorption shows still other molecular states with increments of about 25%. The excitation of these states also leads to chemi-ionization.

Discussion

An important point in the interpretation of the results is the question concerning the cross sections of fluorescence and dissociation, respectively. To what extent does absorption of uv-radiation lead to dissociation? This question has been already discussed in earlier works[3, 6]. But the present experiment gives exact proof for Ly_α-radiation and adds a much higher precision to the data. As before we have to accept the assumption of complete dissociation of the R(1)-term of the $D - X(3.0)$-band; this means, the fluorescence intensity identified as Ly_α-radiation at that term equals the absorption. The result of this assumption is then represented in Table 1 and Fig. 2. Under that condition there is an exact agreement between the absorption and the dissociation cross section at the band heads of the D-bands, the extent of this coincidence being the result of the new measurements. Furthermore, the two cross sections are identical over the whole spectral region shown in Fig. 2 for those states that are supposed to predissociate. Moreover, below the dissociation limit no Ly_α-radiation was found. Molecular radiation, both of shorter (LiF-region) and longer (CaF_2-region) wavelengths occurs in accordance with the absorption spectrum.

$D-X$ v'	σ_α (Mb)	I_{Ly_α} (a. u.)	cal. ratio Ly_α/abs.
3	63	235	98.2
4	46	177	101.2
5	29	110	100.6
6	36	101	74
7	39	118	80

Table 1. Absorption cross section and measured Ly_α-fluorescence at the positions of the head of the D-bands. $v' = 6$ and 7 are above the ionization limit, where part of the absorbed primary radiation is transferred to ionization. A ratio of 100 is equivalent to total dissociation.

The measurements in the region up to the ionization limit (~ 804 Å) likewise show a pronounced coincidence between absorption and dissociation. Similar indications follow from the region above the ionization limit ($\lambda < 804$ Å). As one cannot assume the ratio of dissociation over absorption to have an identical value smaller than unity for the great number of different excited states formed, one has to accept complete dissociation in the D-terms and the resulting normalization of the cross section (Fig. 2 a) as the only possibility. It then follows that the sum of the measured ionization cross section and the dissociation cross section adds up to the total absorption cross section for certain positions in the ionization region.

Another interesting result is the fact that the Q-terms of the D-bands do not predissociate according to Fig. 2 a. At all positions of the Q-terms there is an excess of absorption over dissociation. This is in accordance with earlier spectroscopic data, where the ${}^1\Pi_u{}^-$-terms are shown to have sharp absorption lines[1]. From this Namioka concluded the Σ-continuum to be responsible for the predissociation in the D-band.

According to the selection rules of radiationless transitions the dissociation of the Q-terms is forbidden for symmetry reasons. The determination of the diffuseness of spectral lines is not a sensitive standard for predissociation, as with the existing resolving power the true linewidth cannot be determined. An exact proof is the identification of the dissociation products themselves or, as in the present experiment, the proof that the dissociation products do not appear. For the first time it is shown directly that the Q-terms do not participate in the predissociation. Therefore the configuration of the interacting continuum is ${}^1\Sigma_u{}^+$. Calculations[8, 9] for the B- and B′-states show that the former dissociates into H(2P) and the latter into H(2S). Thus, the B′ continuum is responsible for the radiationless transition as the fluorescence was found to be completely due to H(2S).

On the other hand there is strong evidence from highly resolved absorption measurements that the predissociation in the D-bands is caused by the B′-continuum, proving, therefore, that the dissociation of molecules in the B′-state proceeds according to reaction (3)

$$H_2(B') \rightarrow H(1S) + H(2S). \qquad (3)$$

A similar analysis of the B″-state is made possible with the aid of the results in Fig. 1. The fluorescence of the B″-state is quenchable in an electric field which proves the production of metastable hydrogen atoms H(2S). The saturation value of the quenching curve in Fig. 1 is about 10% lower than that for the corresponding D-term although the energy of the H-atoms produced is almost equal for the two states. In analogy to calculations carried out for the D-terms this deficit means a certain amount (10 – 15%) of non quenchable Ly_α-radiation from H(2P) atoms. This small portion, with great probability, is due to absorption into the continuum of the B-state which decays according to calculations of KOLOS and WOLNIEWICZ[8] and of MULLIKEN[9] into H(1S) and H(2P). The present data disagree with the assumption by Monfils and show that the B″-state finally completely dissociates into the B′-continuum according to Eq. (4).

$$H_2(B'') \rightarrow H_2(B') \rightarrow H(1S) + H(2S). \qquad (4)$$

Additional information concerning this decay scheme is obtained from observations on the $H_3{}^+$-formation (Fig. 2 b). At the pressures used only metastable H-atoms are able to form $H_3{}^+$ by collisions with H_2. From these measurements it follows that only around 80% of the observed total absorption leads to $H_3{}^+$-formation [Eq. (2)] as compared to the ion formation which is found to occur from the D – X(3.0)-absorption. This also confirms the data from the quenching experiment where part of the Ly_α-radiation (~10%) is proven to originate from short lived H(2P) atoms. The remaining difference between the dissociation and the absorption cross section (~10%) originates from the absorption into a non dissociative state. Within the band width of the primary excitation the Q(2)-term of D – X(3.0) coincides with R(1) of B″ – X(1.0) giving rise to the observed difference in cross section.

The curves in Fig. 2 a (3) and 2 b are identical except for the amount of H(2P) fluorescence if we take into account the different resolutions used in the determination of the curves. This means that the H_2 molecules both in the D- and the B″-state completely decay and form exclusively H(2S). An additional confirmation is given by the fact that all rotationally excited states of the two bands exhibit an increase in Ly_α-radiation of 40 to 50% in an electric field which they should if only H(2S) atoms are formed.

The dissociative behaviour in the immediate neighbourhood of the dissociation limit is different. There a field dependent increase in the fluorescence of only 25% is measured. At this position in the spectrum we have the (13.0) band of the C-state, which is the first excited state of the $^1\Pi_u$-series. The C-state possesses a potential hump whose maximum was calculated by KOLOS and WOLNIEWICZ to be $105\ \mathrm{cm}^{-1}$ at an internuclear distance of 4.762 Å. NAMIOKA[2] discussed the dissociative behaviour of this band in detail. He stated that the $J=2(+)$ and $2(-)$ level do not predissociate or only to an unobservable amount by tunneling through the potential hump although energetically this would be possible. An observable predissociation was assumed for $J=3$.

The present results contradict these assumptions both by the observed Ly_α-radiation and by the H_3^+ ion intensity. As the observed increase in the electric field is only about half of that caused by the D-band, only part of the Ly_α-radiation can be due to H(2S) atoms. The remainder which comprises about 50% of the absorption is caused by the absorption in the continuum and not by the C-band. H_3^+-formation by collisions of excited molecules in the C-band is to be excluded on account of the short lifetime of that state. We conclude, therefore, that the dissociation of the C-state has to be described by Eq. (5)

$$H_2(C, v'=13, J \geqq 2) \to H_2(B') \to H(1S) + H(2S). \tag{5}$$

The predissociation of the R(1)-term of this band is also indicated by the broadened absorption line in the results of TAKEZAWA[4].

If we compare the intensities of the lower rotational levels with these of the higher ones in the $D-X(3.0)$- and the $B''-X(1.0)$-bands both in the Ly_α-emission and H_3^+ production, we can observe the influence of the kinetic energy of the metastable H atoms on the ion formation probability. The ion production is lower for atoms formed by predissociation of the higher rotational states because their kinetic energy is higher than the energy of those from the lower rotational states. The bands are red shaded. This means that at longer wavelengths within a certain band, the ion production decreases. On the other hand the ion production from the absorption due to the $C-X(13.0)$-band is enhanced because H(2S) atoms formed at the dissociation limit receive no extra kinetic energy. These atoms have, therefore, the largest reaction cross section.

According to Fig. 2 a radiation is measured below the dissociation limit both in the LiF- and the CaF_2-region. This emission is a fluorescence of excited molecules in the B-, B'- and C-states. The potential curves of these states differ in such a way that a distinctly different fluorescence is to be expected. A coupling of these states in the electric field may cause a change of the resulting secondary spectrum. As the measurements with the two windows lead to integral radiation intesities in the respective regions of sensitivity of the detector, slight variations of the indicated intensity on the application of the field are possible. The weak field effect is thus adequately explained.

Finally it can be stated that the absorption of H_2 above its dissociation limit leads mainly to the formation of quasibound states. From these states the molecule dissociates by a radiationless decay. On the other hand the absorption into the dissociation continuum is of relatively low probability.

The radiationless decay of the D-, B''- and C-states by interaction with the B'-continuum leads to metastable H atoms. These manifest themselves both by their field dependent fluorescence and by the H_3^+-production. Except for the Q-terms of the D-state absorption of uv-radiation will result in dissociation of the molecule. This provides the possibility for a highly efficient production of H atoms with a precise kinetic energy.

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