PHYSICAL REVIEW A VOLUME 34, NUMBER 5 NOVEMBER 1986

Dissociative decay of $n=3$ levels in H_2. I. Populated in charge exchange of $H_2{}^+$ with Cs

D. P. de Bruijn*, J. Neuteboom, T. R. Govers,[†] and J. Los
Stichting voor Fundamenteel Onderzoek der Materie, Institute for Atomic and Molecular Physics, Kruislaan 407,
1098 SJ Amsterdam, The Netherlands

(Received 7 April 1986)

Rotationally resolved spectra of kinetic energy releases ε in predissociations of H_2, after dissociative charge exchange of $H_2{}^+$ with Cs atoms, are obtained. The experiments are performed with natural and with pure parahydrogen. The predissociations with $\varepsilon < 1.9$ eV constitute less than 5% of the total amount of dissociations to H + H at a beam energy of 5 keV. All strong rotational peaks observed could be attributed to $n=3$ Rydberg states which predissociate to $H(1s)+H(2l)$. Vibrational-rotational series are observed of the $d\,{}^3\Pi_u^+$, $D\,{}^1\Pi_u^+$, and $J\,{}^1\Delta_g^+$ states. Predissociation by barrier tunneling is reported of $v=4$ levels of the $h\,{}^3\Sigma_g^+$ state and of $v=4$ and 5 levels of the $i\,{}^3\Pi_g$ state. Selectivity of the charge-exchange process for different $n=3$ states, or even for different parity states, is concluded.

I. INTRODUCTION

Some time ago we reported[1–4] on experimental and theoretical studies of the dissociative charge exchange of $H_2{}^+$ at keV energies. Detailed experiments on this process, producing two neutral fragments, had become feasible after the introduction of a new technique for translational spectroscopy.[5] A time- and position-sensitive detector was applied to detect both hydrogen atoms in a delayed coincidence. So far we have focused our attention on the three main channels which are open in near-resonant charge exchange (NRCE): (a) radiative dissociation via the $a\,{}^3\Sigma_g^+$ state, (b) direct dissociations by charge exchange to the repulsive $b\,{}^3\Sigma_u^+$ state, and (c) predissociation via the $c\,{}^3\Pi_u^+$ state. In all these cases the repulsive $b\,{}^3\Sigma_u^+$ state is the final state resulting in two ground-state hydrogen atoms with released kinetic energies (ε) up to 10.2 eV.

In the former experiments[1] it had been already noticed that by using alkali-metal targets not only the $n=2$ Rydberg states mentioned above but also predissociations of $n \geq 3$ united-atom states [process (d)] were observed. Rydberg $n=3$ states lie around 1.8 eV below the ground state of $H_2{}^+$ (Fig. 1). With a Cs target they can therefore be reached in the limit of NRCE (at keV energies), the asymptotic resonance energy defect ΔI amounts to 2.1 eV. From the experimental dissociation limit at 1.9 eV, observed in vibrationally selected measurements ($v \geq 3$), it was concluded that the predissociations resulted in $H(1s)+H(2l)$. This interpretation is confirmed by the detection of Lyman-α radiation $[H(n=2) \rightarrow H(n=1)]$ after charge exchange (CE) of $H_2{}^+$ with potassium by Gellene *et al.*[6] In this paper we present more detailed measurements, identifying the most important molecular states. Rotational resolution is obtained in the released kinetic energy ε by increasing the flight length of the apparatus from 455 to 750 mm.

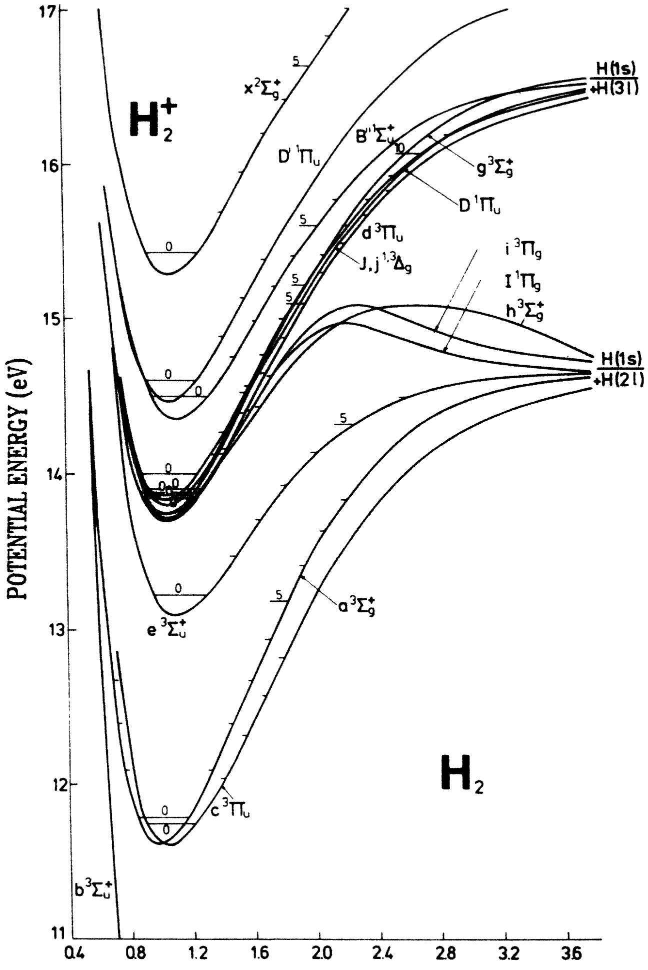

FIG. 1. Some electronic states of $H_2{}^+$ relevant to this work. The curves are taken from Sharp (Ref. 7).

II. HIGHLY EXCITED STATES OF H_2

The spectroscopy of the hydrogen molecule has been a field of continuing interest for already more than half a century. As Sharp[7] has put into words, "the simplicity of the molecule belies the complexity of its spectrum." The extensive experimental studies by Dieke[8] of the emission spectra of H_2 and its isotopes have contributed enormously to the knowledge of the structure of the most abundant molecule in the universe. Nevertheless, much is still unknown about highly excited states. Only for the lower states, converging to the $H(1s)+H(2l)$ limit ($n=2$ and some $n=3$ Rydberg states), are most potential curves accurately (better than 100 cm^{-1}) known through the *ab initio* calculations of Kolos *et al.*.[9-11] Kolos and Rychlewski have also calculated the $J\,^1\Delta_g,3d\delta$ state.[12] For the other singly excited states above the $H(1s)+H(2l)$ limit ($n\geq3$) less accurate calculations, if any at all, are available and in general only the lowest vibrational levels are experimentally determined. The interpretation of experimental data is often very difficult because the ordering of levels is very irregular in many states due to strong l uncoupling.[13,8] Very useful compilations of the available data are given by Sharp,[7] by Huber and Herzberg,[14] and by Crosswhite.[15] These authors use different notations for the molecular states. We will use here the notations of Sharp, from whom also the potential curves in Fig. 1 are taken.

Many highly excited states of H_2, also with levels far above the ionization limit, are known to be predissociative. One of the first observations was made by Dieke[16] in 1935 for the $d\,^3\Pi_u(3p)$ state through missing lines in the emission spectrum. The Π^+ part is predissociated by the $e\,^3\Sigma_u^+(3p)$ state for $v\geq3$. Other states in this energy region (see Fig. 1) which are strongly predissociated are the $D\,^1\Pi_u(3p)$, $D'\,^1\Pi_u(4p)$, and $B''\,^1\Sigma_u^+(4p)$ states.[17] Predissociations of singlet ungerade states are detected through the emission of atomic hydrogen lines (Lyman and Balmer series) after excitation of molecular states with synchrotron radiation. Triplet states can be studied by electron-impact excitation of ground-state H_2.[18,19] Bose and Linder[20] found in this way an indication of the predissociation of the $k\,^3\Pi_u(4p)$ state besides the $d\,^3\Pi_u(3p)$ state. A more accurate approach to study low vibrational levels of triplet gerade states was recently introduced by Eyler and Pipkin.[21,22] They use laser excitation starting from the metastable $c\,^3\Pi_u^-$ levels. With this method they have also observed a previously unknown electronic state, probably the $4s\,^3\Sigma_g^+$ state, which turned out to be strongly predissociative for $v=2$ (Ref. 23). If charge exchange of $H_2{}^+$ with Cs is used, then higher vibrational levels of the c state can be populated too. In a companion paper[24] we report on photodissociation of metastable H_2 produced in this way. The spectroscopic information obtained on $n=3$ triplet gerade states was very helpful in assigning the present spectra.

III. EXPERIMENTAL METHOD

The principle of the experimental method applied here is the correlated detection of both fragments formed in a dissociation event in a fast beam. Therefore a position- and time-sensitive double microchannel plate detector is used, which has been described in detail before.[3,5] The kinematics of the dissociation (see Fig. 2) is revealed by detecting the mutual translation in space and time of the two fragments in the laboratory frame. The transformation of the measured parameters R (mutal distance) and τ (flight-time difference) to the released kinetic energy ε and the c.m. recoil angle θ for equal fragment masses is given by

$$\varepsilon=\frac{E}{4l^2}[(v\tau)^2+(R^2)]\ , \tag{1}$$

$$\theta=\arctan\frac{R}{v\tau}\ . \tag{2}$$

Here v and E are, respectively, the forward velocity and the energy of the parent molecule and l is the distance from the dissociation to the detector. Besides the possibility to detect neutral fragments, this approach has the advantages of a very high efficiency (the whole solid angle in the c.m. frame is seen) and a high resolution [$<1\%$ full width at half maximum (FWHM) in ε and about 1° in θ]. As will be demonstrated for the first time in this article even rotational levels can be resolved in this way.

The experiments are carried out in a simple beam apparatus which has been described before.[1] A beam of $H_2{}^+$ ions is extracted from an electron-impact source, operated with an H_2 pressure of about 10^{-4} Torr and an 0.2—0.5-mA electron beam of 80—100 eV, and mass analyzed by a Wien filter. With only one three-element lens (einzellens) the ion beam is focused through a collision chamber into a Faraday cup, mounted on the two-particle detector. The intensity of the beam, measured in this cup, is typically 10^{-11} A. The length of the collision cell, connected to a Cs oven, is 0.5 mm and the entrance aperture has a diameter of 0.2 mm. The only modification that was made on the apparatus was a lengthening of the flight path between the collision chamber and the detector from 455 to 750 mm. Thereby the detection limit on ε is lowered and the resolution is improved considerably because the fragments fly further apart (see Fig. 2). An even longer flight length was impossible in the present apparatus. Already at this length the beam diameter exceeded 1 mm, which results in a nonoptimal R resolution.[5] Much attention was paid to careful energy calibration by measuring the exact flight length and calibrating the R and τ readouts. In this way an absolute energy scale with an accuracy of 20 meV was obtained.

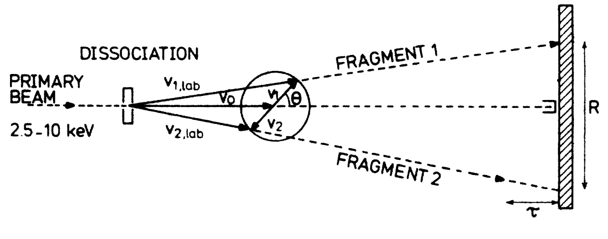

FIG. 2. Schematic representation of the experimental method.

IV. EXPERIMENTAL RESULTS AND INTERPRETATION

A. Measurements with H_2 and D_2

The first measurements were performed at a collision energy of 5 keV and with Cs as well as Rb target vapors, which showed no significant differences in the predissociation spectra. In Fig. 3 a spectrum is reproduced which was recorded directly as a function of ε with $80° < \theta < 90°$. For comparison the former spectrum,[1] obtained with a shorter flight length, is also given. On top of the continuum of process (a) (see Sec. I) seven peaks, of which some are split, are now clearly visible. The predissociation limit at $\varepsilon = 1.9$ eV that was established before[1] can just be distinguished. The positions of the peaks coincide very well (within 20 meV, see also Sec. IV C 1) with the $N=2$ levels of $v=5$–9 of the $d\,{}^3\Pi_u$ state.[7,25] A check was performed with the observation of the isotope shift through a measurement on D_2. In that case only the weak peaks of the highest vibrations ($v \geq 7$) can be observed above the detection limit of 0.3 eV.

In a second series of experiments the beam energy was lowered to 2.5 keV in order to further improve the energy resolution. A disadvantage is the lower cross section for charge exchange to $n=3$ states. The maximum of the cross section can be estimated, assuming Demkov-type coupling,[26] to lie around 25 keV. At the same time the continuum, due to the almost resonant process (a), becomes stronger. We have indeed observed an intensity ratio between the predissociation peaks and the continuum "background" which is about a factor of 2 smaller at 2.5 keV compared to 5 keV. The absolute ratio of the two processes agrees fairly well with the dependence of the cross section for NRCE on ΔI which we deduced from our earlier experiments.[1] At 5 keV the predisssociations at low ε contribute less than 5% to the total observed yield of dissociations [processes (a) + (b) + (c) + (d)].

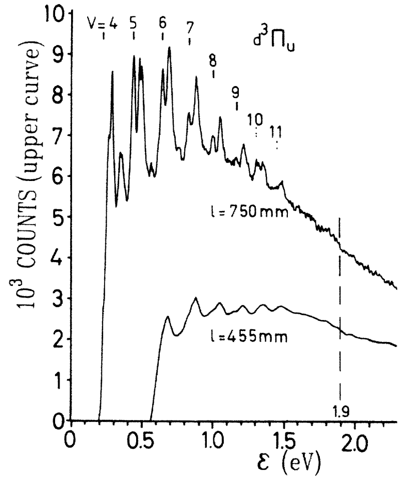

FIG. 3. Part of the spectrum of the released kinetic energy ε after dissociative charge exchange of $H_2{}^+$. The recoil angle θ (Fig. 2) has been selected as $80° < \theta \leq 90°$. The collision energy E is 5 keV and the target Cs vapor. The upper curve is recorded with a flight length l of 750 mm and the lower one with $l=455$ mm (taken from Ref. 1).

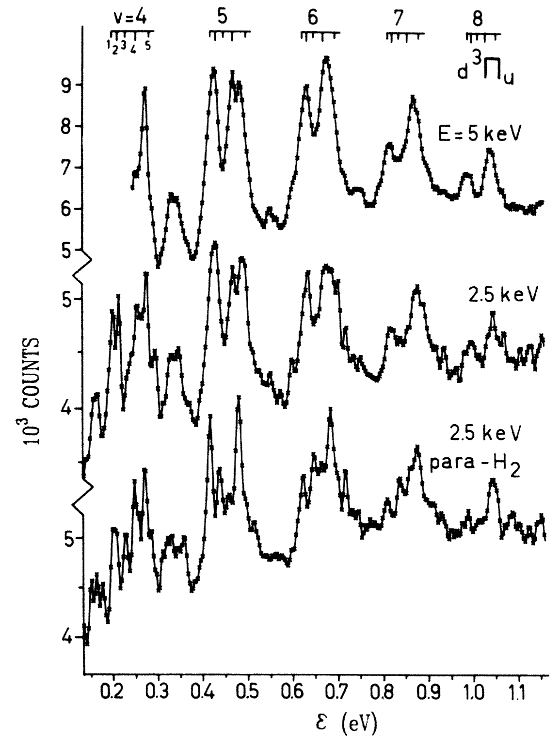

FIG. 4. Analogous to Fig. 3 with $l=750$ mm and collision energies of 5 keV (only upper spectrum) and 2.5 keV. The lowest spectrum is taken with pure parahydrogen. Indicated at top are the vibrational and rotational levels of the $d\,{}^3\Pi_u$ state of H_2.

The relatively low yield at $E=2.5$ keV made it difficult to observe the highest vibrations of the d series. On the other hand, the resolution is substantially enhanced compared to the spectrum taken at 5 keV (Fig. 4). Rotational structure is clearly observed. Since the ε limit for detection is decreased with E, new peaks can now be observed around $\varepsilon = 0.2$ eV. It is clear that the $d\,{}^3\Pi_u$ state, of which the levels are indicated in Fig. 4, is not sufficient to account for all peaks. Even within the conglomerates that are denoted $v=5$ and 6, there are peaks that do not have the correct positions to belong to the high rotational levels of this state. A comparison with the 5-keV spectrum further shows that these peaks are now relatively stronger. This indicates too that there is a second important predissociation series, due to an electronic state with (most likely) a different polarizability. In the range where structures could be resolved ($45° < \theta \leq 90°$) no significant differences were observed at different recoil angles. The anisotropy ($dN/d\theta$) was found to be almost isotropic.

B. Measurements with parahydrogen

To resolve the spectrum even further we have done measurements with pure parahydrogen. Hydrogen molecules exist, as all homonuclear diatomic molecules, in two modifications with different total nuclear spins I. A strong selection rule for all types of transitions conserves the ortho ($I=1$, weight 3) or para ($I=0$, weight 1) char-

TABLE I. Predissociation of H_2 after charge exchange of H_2^+ with Cs. Tabulated are the values of the released kinetic energy ε for the peaks measured below 1.1 eV (Fig. 5) and the most probable assignments. Also given is if the observed level belongs to ortho- or parahydrogen. The energies of the assigned levels in the last column are taken from Refs. 15 ($d\,^3\Pi_u$), 29 ($D\,^1\Pi_u$), 11 ($J\,^1\Delta_g$), and 24 (quasibound levels).

ε (meV) obs.	Para. or ortho.	$d\,^3\Pi_u$ v,N	$D\,^1\Pi_u$ v,N	$J\,^1\Delta_g$ v,N	Quasi-bound	ε (meV) assign. level
152	*p*				*i*,4,1	152.0
157	*o*		3,4		(4,1)	160.8
162	*p*				4,2	161
166	*o*				4,2	161.0
176	*p*				4,3	176.0
198	*o*				4,4	195.9
200–206	*p*	4,1				198.7
	p				4,4	196
213	*o*	4,2				211.7
227	*p*	4,3				228.0
(233)	*p*				*h*,4,0	233
238	*o*				4,1	239.3
247	*p*				4,2	250
252	*o*	4,4				251.1
269	*p*			4,2		258
274	*o*			4,3	(4.3)	276
285	*p*	4,5				280.4
293	*o*					
310–358	*p*				*i*,5,1	312
	p				5,2	320
	p		4,1			332.9
	p				5,3	333
	p				5,4	352
	p		4,3			362.8
313	*o*	(4,6)			5,1	312
327–345	*o*				5,2	320
	o				5,3	333
	o		4,2			345.0
	o				5,4	352
370	*o*					
415	*p*	5,1				417.0
427	*o*	5,2				428.1
435	*p*	5,3				444.6
456	*p*					
464	*o*	5,4				466.4
478	*p*			5,2		472
490	*o*			5,3		489
512	*p*			5,4		510
(525)	*o*	5,6				527.1
(538)	*p*		5,1			546.8
547	*o*		5,2			558.0
570	(*p*) *o*		(5,3)			577.2
596	*o*		5,4			601.6
621	*p*	6,1				621.1
631	*o*	6,2				631.6
645	*p*	6,3				647.1
659	*p*					
670	*o*	6,4				667.6
681	*p* (*o*)			6,2		672
696	*o*			6,3		688
715	*p*			6,4		708
715	*o*	(6,6)				724.7
(735)	*o*			6,5		733
744	*p*		6,1			745.9
751	*o*		6,2			756.1

TABLE I. (*Continued*).

ε (meV) obs.	Para. or ortho.	$d\,^3\Pi_u$ v,N	$D\,^1\Pi_u$ v,N	$J\,^1\Delta_g$ v,N	Quasi-bound	ε (meV) assign. level
(770)	*p*		6,3			771.2
808	*p*	7,1				811.4
815–822	*o*	7,2				821.2
836	*p*	7,3				835.7
(852)	*o*	7,4				855.1
858	*p*					
874	*p o*	(7,5)		7,2		858
889	*o*			7,3		873
910	*p*			7,4		892
917	*o*			7,5		915
928	*p*		7,1			931.3
934	*o*		7,2			940.1
(950)	*p*		7,3			953.2
961	*o*		7,4			970.7
982	*p o*					
988	*p*	8,1				987.8
996	*o*	8,2				996.8
1012	*p* (*o*)	8,3				1010.5
(1030)	*o*	8,4				1028.6
1044	*o*					
1038–1047	*p*	(8,5)		8,2		1031
1064	*o*			8,3		1044
1088	*p*			8,4		1061
1100	*p*		8,1			1099.9

acter. For Σ states the rotational levels belong alternately to one of the modifications while for states with $\Lambda \geq 1$ one of the Λ-doubled components is a para level and the other one an ortho level. From the $d\,^3\Pi_u$ state only the Π^+ levels (following the definition of Π^+ given by Herzberg[27]) are allowed to predissociate to the $e\,^3\Sigma_u^+$ state, as already observed by Dieke.[16] This means odd levels for parahydrogen and even levels for orthohydrogen.

Many rotational levels have disappeared in the para spectrum of Fig. 4 and much sharper peaks are left. To simplify the interpretation we have subtracted the para spectrum, multiplied by an appropriate normalization factor, from the full spectrum yielding an almost pure ortho spectrum (Fig. 5). In an almost alternating pattern peaks are seen to appear in the para and ortho spectra. For the vibrational levels $v=4$–8 of the $d\,^3\Pi_u$–state peaks can now be assigned to the lowest rotational levels (Sec. IV C 1).

The intensity ratio of the rotational peaks belonging to $v=5$ of the d state (Fig. 5) indicates a rotational temperature of about 400 K. Compared to a Boltzmann distribution the $N=3$ peak is, however, anomalously weak. A temperature of 400 K is also observed in the predissociation of $v=5$ of the $c\,^3\Pi_u$ state after charge exchange of H_2^+ with a Na target.[3] The rotational excitation in the charge-exchange collision [the rotational temperature in the H_2^+ beam is about 150 K for $v=5$ (Ref. 3)] is thus equal. Both cases are also very similar because the c and d states have the same symmetry ($^3\Pi_u$) and almost the same resonance energy defect ΔI in the charge exchange

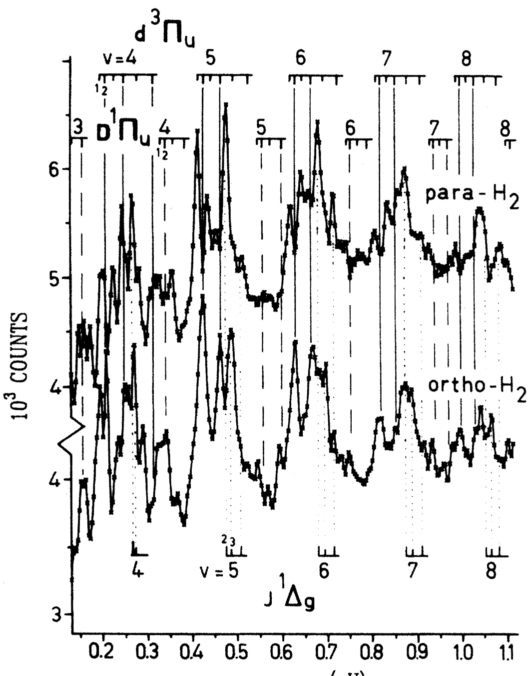

FIG. 5. Analogous to Fig. 3 with $E=2.5$ keV for both spectra. The upper spectrum is pure parahydrogen and the lower spectrum pure orthohydrogen, obtained by subtracting the paraspectrum from a "normal" spectrum. Assignments of peaks to rovibrational levels of several $n=3$ Rydberg states of H_2 are given (see Table I).

because different targets are used. For the c state it was observed that the rotational excitation increased with ΔI (for different targets) and with the vibrational level. This can be interpreted qualitatively with the argument that rotational excitation becomes more likely as the shape is better probed when the impact parameter is smaller (for larger ΔI) or when the deviation from spherical is larger (for larger v).

C. Final assignment of observed peaks

Many peaks are observed which are not due to predissociation of $d\,^3\Pi_u$ levels (Fig. 5, Table I). Due to the energy selectivity of the charge exchange these levels belong most likely to other $n=3$ united-atom states. These states converge to the H(1s) + H(3l) or the H(1s) + H(2l) dissociation limits but most of them have their lowest level around 13.9 eV. Levels of states in the first category will deliver an H(1s) + H(2l) fragment pair with ε up to 1.89 eV after predissociation. The next class, $n \geq 4$ states yielding H(1s) + H(3l) fragments, has a dissociation limit of 0.66 eV. While the 1.9-eV limit is indeed observed, no extra peaks are evident below 0.66 eV (Fig. 5). A larger density of peaks is, however, observed below about 0.35 eV. These peaks are due to quasibound levels of the h and i states which have a potential barrier (Fig. 1). The final assignments will be discussed in the Secs. IV C 1—IV C 4, separately for the different electronic states found. Most states which have been taken into consideration, except the $^3\Sigma_g^+(4s)$, the $B''\,^1\Sigma_u^+(4p)$, the $k\,^3\Pi_u(4p)$, and the $D''\,^1\Pi_u(5p)$ states, are given in Fig. 1. We have limited the tedious assignment of rotational levels to $\varepsilon \leq 1.1$ eV. Above that energy the peaks are not well resolved.

1. The $d\,^3\Pi_u(3p\pi)$ state

This state has been used in the provisional assignment discussed above. The predissociation of the Π^+ levels above the H(1s) + H(2l) dissociation limit ($v \geq 4$) to the e state was already inferred in 1935 by Dieke.[16] In our spectra also only the Π^+ levels, of the vibrational levels 4—10, appear. Above $v=6$, however, the peaks become relatively weak. This is probably due to autoionization, as already observed for the Π^- levels of $v \geq 7$ by Beutler and Junger.[14]

The energies given in Table I (last column) are Diekes values for the Π^- levels, corrected with -149.6 cm^{-1} as given by Miller and Freund,[25] and extrapolations for the higher rotational levels of $v=7$ and 8. The predicting value for the observed Π^+ levels is of course limited, according to Dieke[16] the Λ-type doubling is fairly large and irregular. Very large splittings (>1 meV) are, however, not observed for $v \leq 3$.[15] As stated before (Sec. IV A) our experimental observations for the $N=2$ levels coincided with the spectroscopic data within the experimental calibration error of 20 meV. The observed energies have been recalibrated on this data with a linear fit and these new values are given in Table I. Now all assigned Π^+ levels are found within a few meV (the accidental experimental error) from the Π^- levels. The only exception is the $N=3$ level of $v=5$, which also appears anomalously weak. Apparently this level is strongly perturbed.

2. The $J\,^1\Delta_g(3d\delta)$ state

Strong peaks are observed above $N=4$ of all vibrations of the d state. Above 0.8 eV this series even dominates the spectrum. The energies and the intensities do not fit with the higher rotational levels of the d state. The observation of only two strong peaks, the lower one in parahydrogen and the higher one in orthohydrogen, separated by about 15 meV ($v \geq 5$), leads to an assignment to one of the Δ_g states (the Δ^+ part). In a Δ state the lowest existing level is $N=2$. Further the potential curve of the state sought has to lie very close to the d state to produce vibrational levels which are systematically just above the d levels, limiting the choice to an $n=3$, Δ state. For the $J\,^1\Delta_g$ and the $j\,^3\Delta_g$ states spectroscopic data are only available for $v \leq 3$,[15] the levels below the H(1s) + H(2l) dissociation limit. These data show that the Δ states are strongly l uncoupled, the Λ-type doubling is very large (sometimes exceeding 10 meV) and irregular. On the average the singlet levels lie about 12 meV below the triplet levels. The energy levels for $v \geq 4$ of the triplet state are reported in the companion paper.[24] These energies agree within 10 meV with the levels observed here. It was, however, also observed that the $v \geq 5$ levels are broadened due to the predissociation. The widths are around 7, 15, and 22 meV for, respectively, N=2,3,4. Such an extra broadening, adding to the experimental width of 15 meV (around $\varepsilon=0.5$ eV), is not evident in our spectra. Further it was observed in the photodissociation experiments that also the $^3\Delta^-$ levels are predissociated, which are not observed here. Therefore we conclude that the predissociation of the $J\,^1\Delta_g$ state is observed in the present charge-exchange experiments. The energy levels given in Table I (last column) are calculated from the *ab initio* potential curve of Kolos and Rychlewski,[11] which was shifted down by 8 meV to reproduce the (irregular) $v \leq 3$ levels in the best possible way. Good agreement is found for $v=5$ while the theoretical level positions are somewhat too low for the higher vibrations. With reasonable confidence also two strong peaks from the multitude of peaks below $\varepsilon=0.4$ eV could be assigned to N=2 and 3 of v=4.

Due to the strong l uncoupling of the whole 3s-3d complex,[12] to which the J state belongs, we cannot apply Hund's case-b selection rules[27] (especially the convenient $\Delta\Lambda=0,\pm1$ rule). This is sustained by the observation of "forbidden" $J\,^1\Delta_g \rightarrow B\,^1\Sigma_u^+$ optical transitions by Dieke.[16] Therefore the higher vibrational levels of the J state can be predissociated by an $n=3$, Σ_g^+ state, which would explain why only the Δ^+ levels are predissociated. A selective population in the charge-exchange reaction is quite unlikely. The $G,K\,^1\Sigma_g^+(3d)$ state[28] would be the appropriate candidate to predissociate the J state.

An unassigned small parapeak which reappears just before the strong $N=2$ peak for at least v=5—7 somewhat discredits the interpretation given above. This peak cannot be due to the $N=2$ $^1\Delta^-$ level because this is an ortho level. A possibility is the $N=2$ $^3\Delta^+$ level, the $N=3$ (ortho) level could be hidden under the $v=4d$ level for v=5 and even seems to be present for v=6. The energetic mismatch with the experimentally determined triplet levels is, however, too large (20–30 meV) for this interpretation. Overuling the evidence given above for the $^1\Delta$ assignments, it could be possible that the *weak* peaks belong to $J\,^1\Delta_g^+$ and thus the strong peaks to $j\,^3\Delta_g^+$. Energetically this would be satisfying, the singlet levels are found below the triplet levels for the lower vibrations. The surprising conclusion would then follow that the $^3\Delta^+$ levels are selectively populated, the Δ^- levels are known to be predissociated but not observed here. A definite settlement of this question cannot be given on account of the present data. We believe that the chosen assignment ($J\,^1\Delta_g^+$ for the strong peaks) is the most probable one.

3. The $D\,^1\Pi_u$ state

A number of small peaks is observed which lie systematically between the conglomerates assigned to vibrational levels of the d and J states. The peaks are most clearly observed in the spectrum of orthohydrogen, but parapeaks appearing in an alternating pattern can also be distinguished (see Fig. 5). The levels of all available states (mentioned in Sec. IV C) have been compared with these observations and only the $D\,^1\Pi_u$ state yielded a satisfying agreement. The energy levels given in Table I for the D state are taken from Takezawa[29] and the experimental peaks are found within 10 meV from these values. The predissociation of the Π^+ levels by the $B'\,^1\Sigma_u^+(3p)$ state is already observed by Borrell *et al.*[17]

4. Quasibound levels of the $h\,^3\Sigma_g^+(3s)$ and $i\,^3\Pi_g(3d)$ states

After the assignment of the d, J, and D series, most peaks above 0.35 eV have been interpreted. Below this energy many peaks are still unassigned which do not belong to a long vibrational series. These peaks are attributed to the quasibound levels of the h and i states (Fig. 1, Table I). The third state with a potential barrier, the $I\,^1\Pi_g(3d)$ state, does not support quasibound levels according to our calculations using the potential curve of Kolos and Rychlewski.[10] The h state has one quasibound vibration,[30] for which level positions are obtained in our photodissociation experiments.[24] These energies are given in Table I and agree within a few meV with the present observations. The theoretical potential curve of the i state[10] supports two quasibound levels of which the upper one ($v=5$) is located very close to the top of the potential barrier. We have calculated that the rotational series breaks off at $N=6$ and all levels are considerably broadened due to the fast barrier tunneling ($\Gamma=10$ meV for $N=5$). Experimental values for the $v=4$ levels are obtained in the companion paper. These numbers, 4–10 meV above the theoretical values, are given in Table I and agree with the present observation within a few meV. All levels, Π^+ and Π^-, are predissociated as can be expected for barrier tunneling. The predissociation of $v=5$ levels, and thus their existence, is also observed. The rotational levels are not well resolved in this case but it is obvious that the $v=4$ levels of the D state are not sufficient to explain the broad structure between $\varepsilon=310$ and 360 meV. The energies of the $i,v=5$ levels given in Table I are the theoretical values which seem to agree reasonably with the experiment.

V. CONCLUSIONS

The predissociation of highly excited states of H_2, populated after charge exchange of H_2^+ with Cs, has been studied by measuring the kinetic energy releases with an ε resolution of about 15 meV FWHM. Rotational levels of the predissociative states could be resolved. All important peaks could be attributed to $n=3$ united-atom states of H_2 predissociating to $H(1s)+H(2l)$, yielding a dissociation limit of 1.9 eV. Three vibrational series are observed. The Π^+ part of the $d\,^3\Pi_u^+$ state was already presumed before to be predissociated strongly by the $e\,^3\Sigma_u^+$ state.[16] We now observe that for $v\geq 6$ autoionization becomes a competitive decay mechanism. Further a confirmation of the rotational excitation by charge exchange, reported before,[1] was found. The second, important, vibrational series observed is (most probably) the $J\,^1\Delta_g^+$ state which means the first observation of the levels $v\geq 4$ and their dissociative decay. Because the Δ^- levels are not observed, predissociation to the $G,K\,^1\Sigma_g^+$ state is proposed. The third series, which produces relatively weak peaks, is the $D\,^1\Pi_u^+$ state. The predissociation of these levels to the $B'\,^1\Sigma_u^+$ state was observed before.[17] Further we have observed the quasibound $v=4$ levels of the $h\,^3\Sigma_u^+$ state and $v=4$ and 5 levels of the $i\,^3\Pi_g$ state which predissociate by barrier tunneling.

The observed predissociations of $n=3$ Rydberg states constitute roughly 5% ($E=5$ keV) of the total amount of dissociations observed. Predissociations of $n\geq 4$ states are not observed. As discussed in the Introduction and Sec. IV C this is in agreement with the mechanism of near-resonant charge exchange (NRCE). The resonance energy defect ΔI needed to populate $n=3$ Rydberg states of H_2 is about 2 eV. Since the energetic position is the main factor in the cross section for NRCE,[2,26] one could expect a roughly equal population of all states with $\Delta I\simeq 2$ eV. This leads to the conclusion that those states among them which are not observed (i.e., the $g\,^3\Sigma_g^+$ and $j\,^3\Delta_g$ states and the Λ^- parts of the d, D, and J states) do not predissociate. Only for the j state this gives a contradiction with other experiments.[24] Thus the charge-exchange process selects the singlet J state above the triplet j state, while both have the same symmetry $[\Delta_g(3d)]$ and energetic position. In this respect the alternative interpretation of the present data, discussed in Sec. IV C 3, would not be more favorable. In that case a selective population of the $^3\Delta^+$ levels above the $^3\Delta^-$ levels has to be explained.

These experiments have shown that charge exchange is a convenient way to populate highly excited states in all vibrational levels. With the experimental technique applied here predissociations of these states can be studied in detail. The resolution can be improved even further as is already demonstrated in the photodissociation experiments on H_2^* which are carried out on a new instrument.[24] The combination of these two types of experiments is a powerful new method to study the spectroscopy and dissociative decay of highly excited states. General conclusions about the decay of $n=3$ states of H_2 are given in the conclusions of the companion article.

ACKNOWLEDGMENTS

We thank Dr. J. Korving of the University of Leiden for providing the parahydrogen. Further technical support by H. Pape is acknowledged. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research).

---

[*] Present address: Koninklijke/Shell-Laboratorium, Amsterdam Postbus 3003, 1003 AA Amsterdam, The Netherlands.

[†] Also at Laboratoire de Photo—Physique Moleculaire, Bâtiment 213, Universite Paris—Sud, Orsay, Present address: L'Air Liquide, Jouy en Josas, France.

[1] D. P. de Bruijn, J. Neuteboom, V. Sidis, and J. Los, Chem. Phys. **85**, 215 (1984).
[2] V. Sidis and D. P. de Bruijn, Chem. Phys. **85**, 201 (1984).
[3] D. P. de Bruijn, J. Neuteboom, and J. Los, Chem. Phys. **85**, 233 (1984).
[4] G. Comtet and D. P. de Bruijn, Chem. Phys. **94**, 365 (1985).
[5] D. P. de Bruijn and J. Los, Rev. Sci. Instrum. **53**, 1020 (1982).
[6] G. I. Gellene, D. A. Cleary, R. F. Porter, C. E. Burkhardt, and J. J. Leventhal, J. Chem. Phys. **77**, 1354 (1982).
[7] T. E. Sharp, At. Data **2**, 119 (1971).
[8] G. H. Dieke, J. Mol. Spectrosc. **2**, 494 (1958).
[9] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965); J. Mol. Spectrosc. **54**, 303 (1975); **86**, 420 (1981).
[10] W. Kolos, J. Mol. Spectrosc. **62**, 429 (1976); Chem. Phys. Lett. **31**, 43 (1975).
[11] W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **62**, 109 (1976); **66**, 428 (1977).
[12] W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **91**, 128 (1982).
[13] M. L. Ginter, J. Chem. Phys. **46**, 3687 (1967).
[14] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (van Nostrand, New York, 1979), Vol. IV.
[15] H. M. Crosswhite, *The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke* (Wiley, New York, 1972).
[16] G. H. Dieke, Phys. Rev. **48**, 610 (1935).
[17] P. Borrell, P. M. Guyon, and M. Glass-Maujean, J. Chem. Phys. **66**, 818 (1977).
[18] M. Misakian and J. C. Zorn, Phys. Rev. A **6**, 2180 (1972).
[19] J. A. Schiavone, K. C. Smyth, and R. S. Freund, J. Chem. Phys. **63**, 1043 (1975).
[20] N. Bose and F. Linder, J. Phys. B **12**, 3805 (1979).
[21] E. E. Eyler and F. M. Pipkin, Phys. Rev. Lett. **47**, 1270 (1981).
[22] E. E. Eyler and F. M. Pipkin, Phys. Rev. A **27**, 2462 (1983).
[23] E. E. Eyler and F. M. Pipkin, J. Chem. Phys. **77**, 5315 (1982).
[24] D. P. de Bruijn and H. Helm, following paper, Phys. Rev. A **34**, 3855 (1986).
[25] T. A. Miller and R. S. Freund, J. Chem. Phys. **61**, 2160 (1974).
[26] R. E. Olson, Phys. Rev. A **6**, 1822 (1972).
[27] G. Herzberg, *Molecular Spectra and Molecular Structure* (van Nostrand, New York, 1950), Vol. I.
[28] L. Wolniewicz and K. Dressler, J. Mol. Spectrosc. **67**, 416 (1977).
[29] S. Takezawa, J. Chem. Phys. **52**, 2575 (1970).
[30] C. B. Wakefield and E. R. Davidson, J. Chem. Phys. **43**, 834 (1965).