Rydberg Spectroscopy of H_2 via Stepwise Resonant Two-Photon Ion-Pair ($H^+ + H^-$) Production

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High-resolution spectra of new Rydberg states of H_2 in the extreme-uv region were obtained by two-step doubly resonant excitation followed by H^--ion detection. Resolved Fano-line profiles showing a sign reversal of the profile index along the Rydberg series were observed for the first time in H_2. Dynamical information such as lifetimes and relative transition strengths was also derived.

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Recently, extensive spectroscopic work on H_2, especially in the range of photon energy below 17 eV, has led to a good understanding of the autoionization process through Rydberg transitions that converge to $H_2{}^+(X\,{}^2\Sigma_g^+)$ and up to $v^+=7$.[1-5] Extension of the same level of understanding to series that converge to higher vibrational states ($v^+ > 7$) and to other important processes such as ion-pair formation and dissociative ionization is, however, inhibited by the limited amount of data available above 17 eV. Spectroscopic study of these highly excited states is made difficult by weak transition probability and the lack of intense light sources at these frequencies. With the recent advances in the development of tunable coherent extreme-uv sources,[6,7] it is now possible to apply nonlinear optical spectroscopy to the investigation of these highly excited states. By use of resonant two-photon excitation,[8] the weak transition probabilities due to small Franck-Condon factors for single-photon excitation can be greatly improved. New excited states whose transitions cannot be reached from the ground state can be studied. The spectrum can also be simplified by selective labeling of the rotational states. In this paper, we report the first application of two-step doubly resonant excitation followed by negative (H^-) ion detection to study the Rydberg states of H_2 above 17 eV. High-resolution spectra of new Rydberg states with high convergence limits (to $H_2{}^+X\,{}^2\Sigma_g$, $v^+=9$, $N^+=1,3$) were obtained and analyzed. The Fano-line profiles were resolved and reversal of the profile index along the series was observed, the latter for the first time in H_2. Dynamical information such as lifetimes and relative transition strengths from low electronic states to Rydberg states and the ion-pair dissociation continuum was deduced. Use of H^- detection was essential in this study because the alternative method of probing these Rydberg states via autoionization and detecting $H_2{}^+$ results in a two orders of magnitude larger ion signal but yields a very poor spectrum dominated by an intense ionization continuum. The H^- continuum arising from direct ion-pair formation, on the other hand, is relatively weak, rendering the observation of the Rydberg structure comparatively easy. Ion-pair formation via single-photon excitation was previously used by Chupka, Dehmer, and Jivery to study Rydberg states of H_2.[9] In this study we extended this detection technique to Rydberg states that have *gerade* symmetry. The combination of this detection with the use of coherent laser sources provided both good signal strength and improved frequency resolution, making possible the extraction of dynamical information on these new states. It should be pointed out that the use of H^- detection confines the study to a subset of molecular states that are coupled to the ion-pair continuum. Nevertheless, knowledge of this subset is essential to the understanding of the H_2 ionization and predissociation processes.

Described below are the two-photon excitation scheme and the subsequent ionization or dissociation of H_2 applicable to this experiment (see Fig. 1). Excitation:

$$H_2 + h\nu_1 \rightarrow H_2{}^*(B\,{}^1\Sigma_u^+ \text{ or } C\,{}^1\Pi_u), \tag{1a}$$

$$H_2{}^* + h\nu_2 \rightarrow H_2{}^{**}. \tag{1b}$$

Autoionization:

$$H_2{}^{**} \rightarrow H_2{}^+ + e. \tag{2}$$

Ion-pair formation:

$$H_2{}^{**} \rightarrow H^+ + H^-. \tag{3}$$

The dominant channel in the region of interest is the formation of $H_2{}^+$ by direct ionization. The thresh-

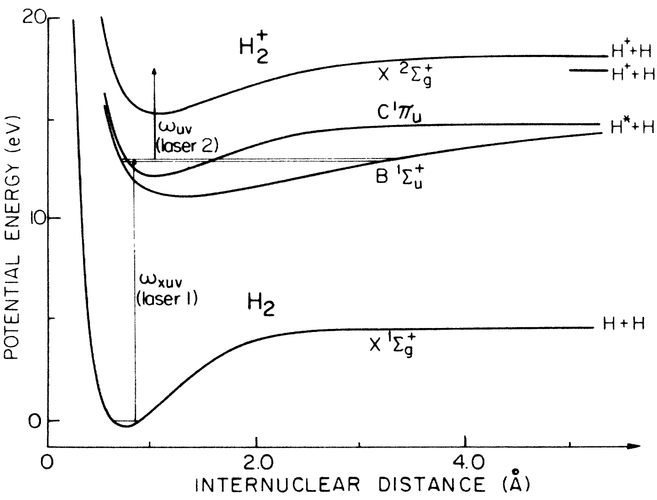

FIG. 1. Potential energy diagram for H_2 showing the levels of interest, from Sharp (Ref. 10).

old for this process is 15.43 eV. In the range of a few electronvolts above this threshold, the spectrum obtained by detecting H_2^+ consists of autoionizing lines superimposed on a continuum; the latter generally dominates as the excitation energy increases.[2] Ion-pair formation has a threshold at 17.34 eV. The intensity of the ion-pair channel immediately above its threshold is low. The interference of Rydberg states with this ion-pair continuum allows us to probe the Rydberg line spectrum in this region with high accuracy by measuring the excitation-frequency dependence of the H^--ion signal.[9]

In the experiment, the frequency-tripled output of a frequency-doubled Nd-doped yttrium aluminum garnet laser–pumped dye laser (laser 1) was tuned to selectively excite either the $v' = 2$, $J' = 1$ level of the $C\ ^1\Pi_u$ state of a pulsed beam of H_2 at 103 509.24 cm^{-1} or the $v' = 12$, $J' = 0$ level of the $B\ ^1\Sigma_u^+$ state at 103 700.91 cm^{-1}.[11] From these levels, the molecules were further excited by a second laser (laser 2). This second laser was a frequency-doubled Nd-doped yttrium aluminum garnet laser–pumped dye laser, which was tuned to have the sum of the frequencies of lasers 1 and 2 span the region from below the ion-pair formation threshold to well above that threshold. The H^- ions produced were detected by a time-of-flight mass spectrometer. The ion signals were averaged by a boxcar integrator and digitized for analysis. The signal level was as big as 100 ion counts per laser pulse. Wavelength calibration of laser 2 was performed by use of the optogalvanic effect with an argon-discharge lamp.

Figure 2(a) presents a portion of the spectrum obtained by tuning laser 2 with $C\ ^1\Pi_u(v' = 2, J' = 1)$ as the intermediate state. Its exhibits many sharp dips superimposed on a structured continuum. Analysis shows that the dips can be assigned to transitions to the high-n states of two distinct Rydberg series converging to the ion-core levels specified by the rotational quantum numbers $N^+ = 1$ and $N^+ = 3$ and the vibrational quantum number $v^+ = 9$. The effective principal quantum numbers n^* of the observed states can be determined; a portion of them is listed in Table I. Here, n^* is defined by the Rydberg series formula $\nu = S - R/n^{*2}$, where ν is the measured frequency in inverse centimeters, S is the theoretical series limit given by Wind,[12] and R = 109 707.42 cm^{-1} is the Rydberg constant for H_2. Our present signal-to-noise ratio limits the determination of n^* to ~36. Figure 2(b) gives the spectrum in the same region with $B\ ^1\Sigma_u^+(v' = 12, J' = 0)$ as the intermediate state. The lines in this spectrum can be identified as arising from transition to the same Rydberg series displayed in Fig. 2(a). Their positions relative to the ionization level of the series ($v^+ = 9$, $N^+ = 1, 3$) agree with those deduced from Fig. 2(a) to within 1 cm^{-1}, which is well within our experimental resolution of 1.5 cm^{-1}.

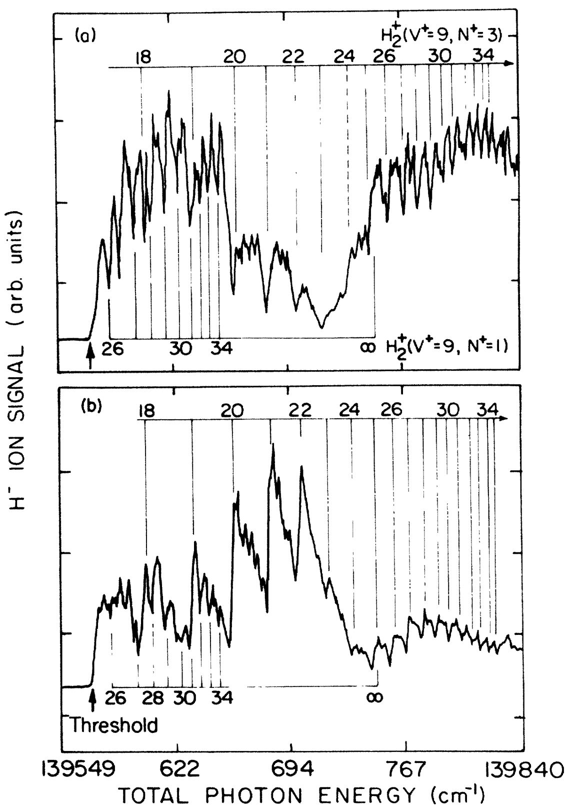

FIG. 2. Resonant two-photon ion-pair spectra of H_2 from the onset of H^- production threshold, indicating transitions assigned to series that converge to $H_2^+(X\ ^2\Sigma_g^+, v^+ = 9, N^+ = 1, 3)$. (a) Intermediate state: $C\ ^1\Pi_u(v' = 2, J' = 1)$. (b) Intermediate state: $B\ ^1\Sigma_u^+(v' = 12, J' = 0)$. Spectrum (a) is obtained with 20 times higher gain than (b).

From the values of n^*, the quantum defect for the $N^+ = 1$ series is thus determined to be 0.1 ± 0.1,

TABLE I. Fano-profile parameters for Rydberg series converging to $H_2^+(v^+=9, N^+=3)$.

Principal quantum number	Line center (± 0.5) (cm^{-1})	n^*	Linewidth (cm^{-1})	Lifetime (psec)	$q(\pm 0.05)$ $C\,^1\Pi_u)$[a]	$q(\pm 0.05)$ $(B\,^1\Sigma_u^+)$[a]
25	139 746.5	25.84	3.0 ± 0.5	1.7	[b]	0.40
26	139 757.6	26.76	1.5 ± 0.3	3.5	0.00	0.2
27	139 768.2	27.74	1.2 ± 0.2	4.3	0.00	0.60
28	139 777.5	28.69	0.8 ± 0.1	6.5	−0.10	0.55
29	139 786.0	29.65	0.6 ± 0.1	8.7	0.10	0.10
30	139 794.0	30.65	2.0 ± 0.3	2.6	0.00	0.00
31	139 801.8	31.73	1.4 ± 0.2	3.7	0.10	−0.30
32	139 808.6	32.77	3.0 ± 0.5	1.7	−0.10	−0.30
33	139 814.1	33.69	0.4 ± 0.1	13.1	0.00	−0.80
34	139 819.0	34.58	0.3 ± 0.1	17.5	[b]	−0.80
35	139 824.2	35.60	1.1 ± 0.2	4.7	[b]	−0.15

[a] Intermediate state.

[b] Not measured.

whereas that for the $N^+=3$ series is 0.7 ± 0.15. The perturbations among adjacent Rydberg states in H_2, the limited signal-to-noise ratio for the higher-n states, and the limited frequency resolution have prevented us from determining the orbital quantum number (s or d) of these series and from obtaining finer limits for the quantum defects. However, these measurements are an important first step in providing data for spectroscopists to use to improve our understanding of these high-lying states of H_2. Some additional lines which do not belong to these series also appear in the spectra. These, along with the broad structures in the spectra, are not yet assigned. The broad structures are likely to arise from transitions to low-n states of Rydberg series with v^+ higher than 9.

While the Rydberg line positions in the two cases with different intermediate states agree, the line shapes observed are very different. Those in Fig. 2(a) are sharp dips but those in Fig. 2(b) have asymmetric Fano profiles with changing profile indices. We have used Fano's line-shape formula,[13,14] which takes into account the interaction of discrete autoionizing states with a continuum, to fit individually the observed lines with $n \geqslant 25$ in Fig. 2 (those lying above the $v^+=9$, $N^+=1$ series limit of 139 746.58 cm^{-1}). The results for Fig. 2(b) are shown in Fig. 3. Values of the profile index q and linewidths deduced are given in Table I. Here $q = A^* |\langle i|z|n\rangle| / |\langle i|z|a\rangle|$, where $\langle i|z|n\rangle$ is the dipole matrix element from the intermediate state $\langle i\rangle$ to the discrete autoionizing state $\langle n\rangle$, $\langle i|z|a\rangle$ the matrix element from $\langle i\rangle$ to the continuum state $\langle a\rangle$, and A is independent of state $\langle i\rangle$ and is inversely proportional to the strength of the interaction between states $\langle n\rangle$ and $\langle a\rangle$. The laser linewidth has been deconvolved to obtain the transition widths. We did not try to fit the lines with $n < 25$ because their profiles are distorted by strong perturbation between the $N^+=1$ and $N^+=3$ series. The lifetimes obtained from the inverse linewidths are also listed in Table I.

An interesting result from the line-shape analysis is the revelation of a change of the sign of the profile index q (q reversal) at $n \geqslant 31$ (see Fig. 3). This sign reversal arises from a relative phase shift in the two transition-matrix elements that determine q. The phenomenon has been analyzed theoretically by several authors.[15-17] In this experiment, the reversal is the result of the interaction of the $N^+=3$ series with a broad state of finite bandwidth which appears to be centered around the $n=30$ transition. Unfortunately,

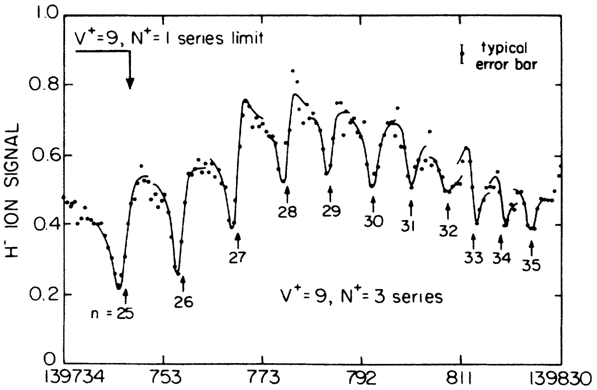

FIG. 3. Expanded ion-pair-production spectrum of H_2 between the $N^+=1$ and $N^+=3$ series limits showing the fitted Fano line profiles: Solid curves, calculated profile; circles, experimental points; and arrows, fitted line center positions.

the origin of this broad state is not yet clear. Connerade has previously reported evidence of similar q reversal in the Rydberg spectra of Tl[15] and of CH_3Br.[18] This is, however, the first time that q reversal has been observed in a diatomic molecule.

A more advanced and complete analysis of these spectra involves the use of multichannel quantum-defect theory initially applied by Fano[19] and more recently refined and extended by Jungen and his colleagues[3,4] to calculate successfully the H_2 ionization spectra. Because of the scope of this work, multichannel quantum-defect theory treatment has not been attempted.

Our results also reveal important information about the relative transition probabilities between high-lying electronic states of H_2. It is known that $C\,^1\Pi_u$ is a "Rydberg-type" state ($n=2$) whereas $B\,^1\Sigma_u^+$ is an "ion-pair-like" state.[20] This suggests that transitions from $B\,^1\Sigma_u^+$ to the ion-pair continuum should be stronger than those from $C\,^1\Pi_u$ to the ion-pair continuum. This was indeed observed in our experiment: The H^- continuum signal was ten times stronger when we excited via the B level than via the C level. On the other hand, one would also expect electronic transitions from $C\,^1\Pi_u$ to the high-lying Rydberg states to be stronger than those from $B\,^1\Sigma_u^+$ to the Rydberg states. Experimentally, however, we found that the reverse was true. A comparison of the magnitudes of q in columns 6 and 7 in Table I shows that the transitions from $C\,^1\Pi_u$ to the Rydberg states are even weaker by about an order of magnitude than the transitions from $B\,^1\Sigma_u^+$ to the ion-pair continuum. This can be easily understood by realizing that in our case, transitions from $C\,^1\Pi_u$ to the Rydberg states should have small Franck-Condon factors because of the larger change in the vibrational quantum number ($v=2 \rightarrow v=9$). If it were not for the interaction between the Rydberg states and the ion-pair continuum that leads to preionization and intensity borrowing, these transitions would not have been observed. For the transitions from B to the Rydberg states, Δv is only 3 in our case. This is consistent with the observation of Pratt, Dehmer, and Dehmer who, using multiphoton photoelectron spectroscopy, have shown a near-unity Franck-Condon factor for transitions from $C\,^1\Pi_u$ to high-lying Rydberg states with $\Delta v = 0$.[21]

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