Observation of selectively excited continuous vacuum ultraviolet emission in molecular hydrogen

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Vacuum ultraviolet continuous emission from selectively excited vibrational levels of the $B\,^1\Sigma_u^+$ state of molecular hydrogen into the dissociation continuum of the electronic ground state has been observed. The intensity distribution in the continuous spectra measured quantitatively proves the theory of Dalgarno, Herzberg, and Stephens. The new radiative dissociation process makes tunable vacuum ultraviolet laser action in molecular hydrogen appear feasible.

The discrete emission spectrum of molecular hydrogen in the vacuum-ultraviolet (vuv) region has been analyzed at high resolution in great detail by many authors.[1,2] In the last decade the analysis has been extended down to about 75 nm, where line emission originates from rovibronic levels above the limits for predissociation and autoionization.[3,4] Emission line transition probabilities have been measured and the dependence of the electronic transition moment on internuclear distance has been derived from these experiments for several electronic transitions to the ground state.[4-6]

Continuous vuv emission underlying the discrete spectrum of the Lyman ($B\,2p\,^1\Sigma_u^+ - X\,1s\,^1\Sigma_g^+$) and Werner ($C\,2p\,^1\Pi_u - X\,1s\,^1\Sigma_g^+$) band systems has been observed when the molecules were excited in various hydrogen discharges[7] as well as by monoenergetic fast-electron impact.[6] From the latter experiment it can be concluded, within the framework of the Bethe theory (see, e.g., Ref. 8), that the observed continuum must stem from states optically connected to the $^1\Sigma_g^+$ ground state, i.e., $^1\Sigma_u^+$ or $^1\Pi_u$ states. A quantitative theoretical prediction of the new continuous emission has been made by Dalgarno, Herzberg, and Stephens,[7] who calculated the transition moment squared $|R|^2$ of an optical transition from an initial discrete vibrational state with quantum number v' to a final continuum vibrational state with momentum $\hbar k''$ (cf. Fig. 1),

$$|R_{v'\to k''}|^2 = |\langle \psi_{v'}|D(r)|\psi_{k''}\rangle|^2. \quad (1)$$

Besides the bound and continuous vibrational wave functions $\psi_{v'}$ and $\psi_{k''}$ the electronic transition moment $D(r)$, depending on internuclear distance r, has been included in the computation of the matrix elements too. From this basic quantity the spectral distribution of the bound-free emission continuum of a specific v' level as well as the total probability for radiative decay of a v' level into the continuum was predicted by these authors.

The theoretical transition moments as function of the continuum transition energy $\Delta E = E_{v'} - E_{k''}$ were found to exhibit an oscillatory structure which was related to Condon's "diffraction bands."[9] It should be noted that the bound-free transitions dealt with here take place into the continuum of the bound electronic ground state and clearly contrast with the hydrogen continuum well known for 50 years[10,11] which arises from

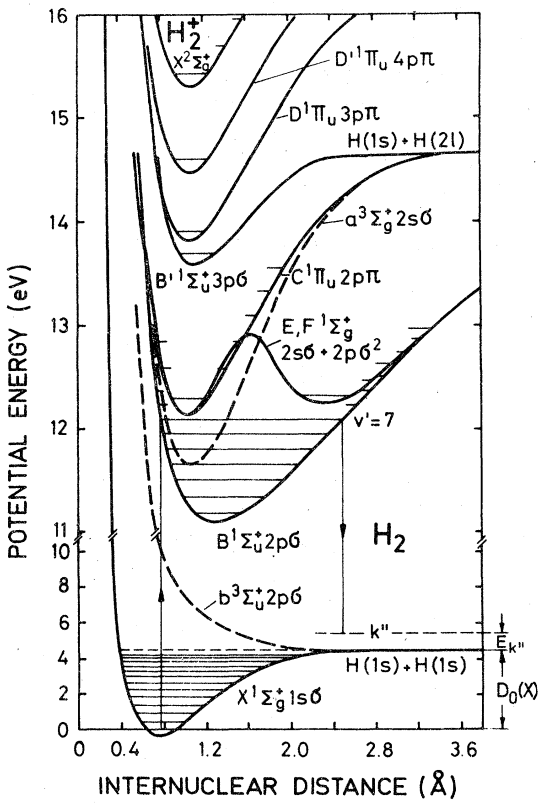

FIG. 1. Potential curves and energy-level diagram of H_2 (excerpt based on Ref. 16). Note the change of vertical scale between 10 and 11 eV.

transition from the bound $a\ 2s\,^3\Sigma_g^+$ state into the $b\ 2p\,^3\Sigma_u^+$ state, which is repulsive. Dalgarno, Herzberg, and Stephens[7] also published microphotometer traces taken from discharge spectra of different densities, which had been subjected to a procedure eliminating the effect of the discrete lines originally superposing the broad maxima and of which, as the authors pointed out, the ordinates do not represent "true intensities but a rough idea of them." These plots were compared with detailed numerical predictions of the continuum emission based on the assumption of a uniform radiation field exciting all vibrational levels v' according to the oscillator strengths of the v' progression starting out at $v''=0$. While the flat continuum assumed appears to be a reasonable choice for a first approximative description of the excitation conditions in the various types of gas discharges used in Herzberg's measurements, it is well known from the Bethe theory of inelastic collisions of fast charged particles,[8] that the optical limit of the generalized oscillator strength is closely approached for forward scattering at high collision energies only. In view of these limitations the comparison between the microphotometer traces of the superimposed emission continuum observed for the first time and the elaborate numerical results cannot be considered as a quantitative test of the theoretical predictions. However, the authors were able to conclude from the quoted "semiquantitative agreement," consistent for the isotopes H_2 and D_2, that the broad maxima observed represent the new emission continuum associated with the B-X transition.

In view of future applications of the new effect, a quantitative test of the elaborate theory, which includes the dependence of the electronic transition moment on internuclear distance, particularly of the predictions of separated continua arising from individual v', by means of a new experiment using selective excitation and true emission intensity detection appeared worthwhile.

In the present study we have succeeded in selectively exciting individual vibrational levels $v'=0,\ldots,9$ of the $B\ 2p\,^1\Sigma_u^+$ state and in recording the discrete v''-band progression as well as the adjoining (and not underlying) continuum by means of the experimental setup shown in Fig. 2 using single photon counting techniques. The intensive synchrotron radiation of the storage ring DORIS at DESY, Hamburg, was passed through a 1-m normal-incidence primary monochromator in modified Wadsworth mount.[12] The monochromatic radiation of 0.2 nm bandwidth is focused onto the open entrance aperture of the gas cell by means of a toroidal mirror. Differential pumping enables to maintain 10^{-2} mbar of H_2 in the gas cell whereas 10^{-9} mbar is required in the primary monochromator and the storage ring. The incident photon rate is detected by the reference multiplier with sodium salicylate sensitization and used for normalization of the fluorescence signal.

The secondary monochromator was specially designed for high efficiency in the vuv above 120 nm wavelength at the resolution of 1.5 nm of the present measurements. The special mount[13]

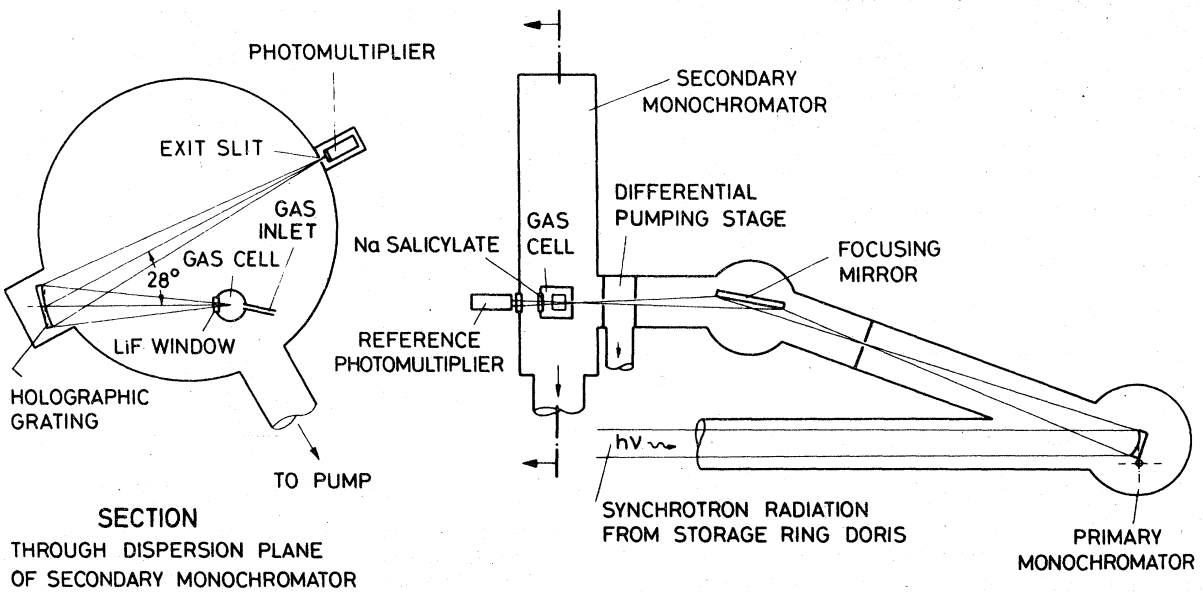

FIG. 2. Experimental arrangement for selectively excited vuv-fluorescence spectroscopy.

employs the fluorescing gas column of 1 mm width instead of an entrance slit and a holographically produced large grating of 108 by 108 mm^2 active area, corrected for the wavelength range from 110 to 200 nm (radius of curvature 0.5 m, 1200 lines mm^{-1}, $Al+MgF_2$ coated). The fluorescence radiation perpendicular to the incident beam enters the monochromator through a LiF window and is detected by a vuv-sensitive photomultiplier (EMR 541 G-08).

Fluorescence spectra have been recorded at a selected primary wavelength by stepwise scanning the secondary wavelength and storing digitally the number of fluorescence photons detected and the wavelength in a PDP 11 computer. The primary wavelength was tuned to yield maximum secondary intensity so that, within the primary bandwidth mentioned, the absorption lines $R(1)$ and $R(0)$ and, partially, $P(1)$ and $R(2)$ were used for populating $J'=0,\ldots,3$ of the B, v' states out of the rotational levels J'' of the X, $v''=0$ state thermally populated at 300 K. The population of excited levels and the intensity weighted superposition of the emission lines were calculated as described previously[6] and convoluted with the secondary resolution function in order to obtain theoretical peak positions of the $v'\rightarrow v''$ bands in the fluorescence spectrum.

The experimental fluorescence spectrum of the selectively excited vibrational level $v'=9$ of the B state is represented in Fig. 3. The members of the discrete v'' progression with $v''=10,\ldots 14$ agree with the calculated position and with theoretical emission transition probabilities[14] also shown in the graph. The limiting wavelength λ_D also drawn in is given by

$$\lambda_D(B,v',J')=\frac{hc}{E'(B,v',J')-D_0(X)}\ , \qquad (2)$$

where $E'(B,v',J')$ is the energy of the excited rovibronic level and $D_0(X)$ is the dissociation energy of the electronic ground state. Thus discrete bound-bound emission is possible for wavelengths $\lambda<\lambda_D$ only, whereas wavelengths $\lambda>\lambda_D$ must lead to dissociation of the molecule into H(1s) atoms. The spectrum clearly exhibits a structured continuum above the limiting wavelength which can be explained neither by direct transitions from the bound v' level to any bound v'' level nor by wings of unresolved rotational lines. The observed continuum is in striking quantitative agreement with the theoretical intensity distribution of Ref. 7 and proves the theory of radiative bound-free transitions between the bound B state and the dissociation continuum of the X state in much detail. Note that the experimental spectra have been corrected for the spectral sensitivity of the entire system, including window, grating, and photomultiplier, and thus represent true photon rates within the constant secondary bandwidth of 1.5 nm shown in the graph. The spectrum was slightly smoothed by the computer because of the low signal rate of less than 10 s^{-1} $(1.5\ nm)^{-1}$. No correction was made for the background rate of about 10^{-1} s^{-1} $(1.5\ nm)^{-1}$.

An optical cascade $B\rightarrow E$, $F\ ^1\Sigma_g^+\rightarrow B\rightarrow X$ is energetically possible which could in principle yield radiation for $\lambda>\lambda_D$. The branching ratios involved, however, favor the direct transitions to the ground state by several orders of magnitude because of the frequency factor ν^3 so that the indirect decay would not be detectable here. A unique experimental proof can be obtained from the fluorescence spectrum of B, $v'=7$, for which case a lower level for a radiative cascade does not exist (cf. Fig. 1). Figure 4 shows again a discrete progression and an adjoining continuum, separated at $\lambda=\lambda_D$, for the selectively excited $v'=7$ level of B, too. Thus the continuum observed cannot be falsified by a radiative cascade.

Similarly a continuous emission was observed from the vibrational level $v'=8$ of B, whereas $v'=0,\ldots,6$ did not produce a detectable amount of continuous radiation in agreement with the con-

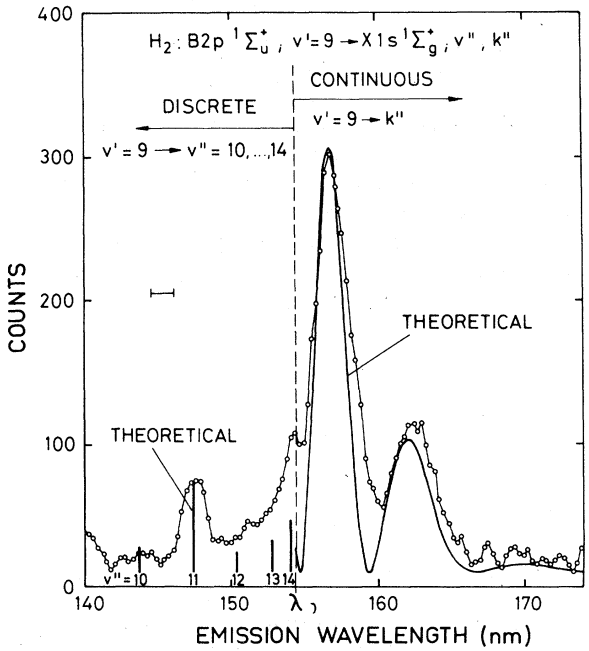

FIG. 3. Vacuum-ultraviolet-fluorescence spectrum of the selectively excited B, $v'=9$ level of H_2. Theoretical discrete emission probabilities as quoted in Ref. 14 were normalized to the experimental spectrum at $v''=11$. The theoretical continuous spectrum based on a graph in Ref. 7 was normalized to the most intensive maximum. See text for further details.

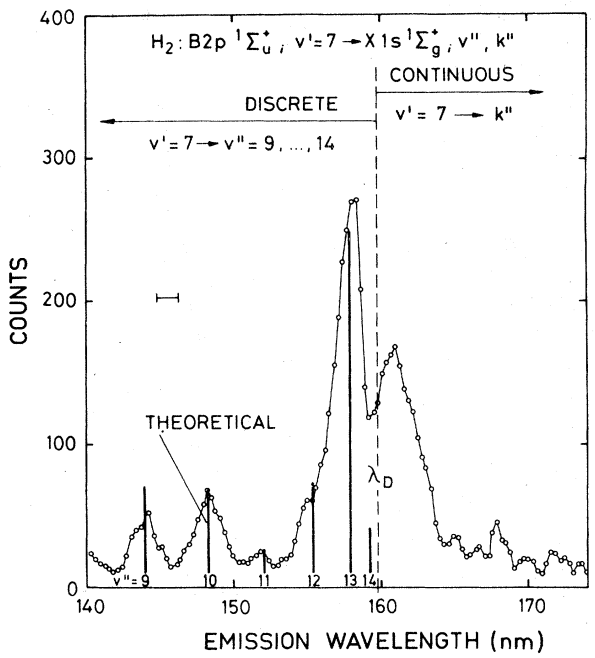

FIG. 4. Vacuum-ultraviolet-fluorescence spectrum of the selectively excited B, $v'=7$ level of H_2. Theory from Ref. 14 was normalized to the experiment at $v''=10$. See text for more details.

tinuum fractions $f_{v'}$ of the emission probabilities for the individual B, v' levels quoted in Ref. 15. For $v'=9$, e.g., a more quantitative comparison can be made: The ratio of the total number of photons detected in the observed part of the discrete spectrum ($v''=10,\ldots,14$) divided by the number of photons counted in the continuous spectrum (154.4,...,175 nm), as obtained by integrating over the corresponding parts of the spectrum investigated, amounts to 0.34 which compares well to the theoretical ratio of 0.36 derived from the data given in Ref. 15. In view of the background not subtracted in the evaluation and some continuum overlapping the discrete spectrum near the limiting wavelength the agreement can be considered quite satisfactory.

The first measurements of selectively excited H_2 B, v'-X emission continua reported which quantitatively prove the detailed theoretical predictions of the well-established radiative dissociation process[7] illustrate the unique role played by the simple quantum-mechanical system of H_2 in molecular-physics research. In addition, the type of radiative bound-free transition observed suggests itself as a potential tunable laser transition: Population inversion is readily achieved because of the unbound character of the lower state of the laser transition, a situation similar to excimer lasers. Molecular hydrogen promises a tunable vuv-laser range which can be estimated to extend from about 170 nm down to Lyman α (121.6 nm) if appropriate excitation mechanisms are applied. Selective excitation appears feasible, e.g., by means of optical pumping using higher H*I* Lyman-series-member radiation from hydrogen arcs or sufficiently energetic transitions from argon discharges. A tuned H_2 laser of the type described would in principle produce monoenergetic H(1*s*) atoms.

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