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RADIATIVE LIFETIMES AND COLLISIONAL QUUENCHING CROSS SECTIONS OF SELECTIVELY EXCITED VIBRATIONAL STATES OF THE B $2p\ ^1\Sigma_u^+$ STATE OF H_2

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Radiative lifetimes and collisional quenching cross sections of selectively excited vibrational states of the B 2p $^1\Sigma_u^+$ state of H_2

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Abstract

Radiative lifetimes between 0.54 ns and 0.69 ns have been measured for the vibrational levels v'=0...4 of the B 2p $^1\Sigma_u^+$ state of H_2 after selective excitation by synchrotron radiation. Quenching by collisions with H_2 ground state molecules has been observed with cross sections of $5 \cdot 10^{-15}$ cm^2.

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Introduction

In a previous study[1] of the vacuum ultraviolet emission of the lowest excited singlet state B 2p $^1\Sigma_u^+$ of molecular hydrogen after vibrationally selective excitation the bound-free emission from individual B, v' states into the dissociation continuum of the bound electronic ground state X 1s $^1\Sigma_g^+$ was recorded and found to quantitatively prove quantal predictions[2]. Furthermore it was speculated on the suitability of the B, v' - X continua for tunable vuv laser action, similarly to rare gas excimer lasers[3]. The radiative lifetimes of the B, v' levels have been calculated[4] elaborately by including the variation of the electronic transition moment[5,6] with internuclear distance. An accurate experimental test of these lifetimes, besides the early non-selective phase-shift data[7] of (0.8 ± 0.2) ns for the group of levels B, v' = 3...7, has been started recently[8,9]. No indication of quenching of electronically excited H_2^* (B) molecules by collisions with H_2 ground state molecules which may be of crucial importance in laser applications has been found previously[7]. On the other hand an analogous quenching has been reported for the B, v' = 3 level of the isotopic molecule HD [10].

Experimental

Using the synchrotron radiation of the storage ring DORIS II at HASYLAB, DESY, Hamburg, the lowest five vibrational levels of the B state of H_2 were excited selectively at a bandwidth of 0.1 nm out of the ground state populated thermally at 300 K. Using the time structure of DORIS radiative lifetimes in the subnanosecond regime and collisional quenching cross sections have been determined experimentally for these levels.

The synchrotron radiation of DORIS at 20 mA beam current and 5 GeV energy was monochromatized as described earlier[1]. The bandwidth attained of 0.1 nm is sufficient to restrict rotational excitation to the rotational levels J' = 1 and 2 only through the R(0) and R(1) absorption lines. The time resolved measurements were performed mainly in the single bunch mode of storage ring operation,

i.e. at pulse repetition rates of 1.04 MHz. Operation modes at 60 or 120 bunches, however, could also be used since the lifetimes to be measured are small in comparison with the pulse distances of 16 or 8 ns, respectively.

The monochromatized synchrotron radiation was focused into a gas cell (see Fig. 1) containing hydrogen of high purity (99.999 % of H_2). The gas cell was vacuum sealed by LiF windows on the entrance side of synchrotron radiation and on the exit side of fluorescence radiation. The fluorescence radiation was detected by a double microchannel plate (VARIAN VUW 8916, test grade) within a spectral range extending from 104 nm (LiF cut-off) to about 170 nm (upper wavelength limit of detector). The detector pulses were amplified and discriminated (constant-fraction) and fed into the "start" input of a time-to-amplitude converter (TAC). The time differences between the arrival of the fluorescence photon pulses and the periodic trigger pulses of DORIS fed into the "stop" input of the TAC were accumulated as pulse heights in a multichannel analyzer and stored and processed by a minicomputer. The full width at half maximum of the response function was typically 330 ns at a bunch pulse width of 130 ns [11].

Results and discussion

The decay curves were recorded for various H_2 pressures between 10^{-2} mbar and 200 mbar, a typical time needed for recording one decay curve was one hour. All decay curves measured exhibit a strong dependence of the decay constant on pressure as shown e.g. in Fig. 2 for v' = 0 (J' = 1 and 2) of B $2p\ ^1\Sigma_u^+$ where the effective lifetime was found to decrease to one half of the radiative lifetime at a hydrogen pressure of 60 mbar. In the pressure range investigated the total decay rate R as a function of H_2 pressure p is practically linear (see Fig. 3) as expected for two-body collision quenching according to the Stern-Volmer relation (Eq. 1):

$$R = \frac{1}{\tau} + n \bar{v} \sigma \qquad (1)$$

where R denotes the total decay rate, τ the radiative lifetime, $n = p/kT$ the number density of ground state molecules, $\bar{v} = \sqrt{16\ kT/\pi m}$ the mean thermal relative velocity and σ represents the velocity averaged cross section for collisional quenching. A linear least squares fit is used to obtain the radiative lifetime by extrapolating to zero pressure and to determine the quenching cross section of the level under investigation.

Table 1 shows first results for the lifetimes of the vibrational levels v' = 0...4 of the B state (column 2 of table) and the cross sections (column 5) for quenching of these states by thermal collisions with ground state molecules. The experimental uncertainties quoted in the table result from three standard deviations of the linear fit and the uncertainty of the deconvolution of decay curves at present. The statistical error is largest for v' = 4 because of the spectral transmission curve of LiF. Within the experimental uncertainties agreement is found between the theoretical lifetimes[4] (column 3) calculated by disregarding rotational distortion and the present measurements. Earlier experimental results[7] for an unresolved group of 5 vibrational levels are also listed (column 4) for comparison. Investigations are under way in order to narrow down the experimental uncertainties by improving the counting statistics and the deconvolution procedure. Further measurements at improved primary resolution are expected to achieve complete rotational selectivity too and will be published separately.

The quenching cross sections (column 5 of table 1) are as large as $5 \cdot 10^{-15}$ cm^2. Within the experimental uncertainty they are independent on vibrational quantum number. It should be noted that for the vibrational states investigated here, discrete Lyman band emission is the only radiative decay channel known. Continuous B - X emission, as observed previously[1], becomes important for higher vibrational levels only. The potential curves [12] of H_2 do not indicate resonant energy transfer processes which may be responsible for the quenching of the lowest v' levels of the

B 2p $^1\Sigma_u^+$ state. On the other hand the electronic excitation energy of any of the vibrational states under investigation is sufficient to supply twice the dissociation energy of the electronic ground state. From energy considerations alone the quenching process (Eq. 2)

$$H_2^* (B,v') + H_2(X, v''=0) \rightarrow 4\ H\ (1s) + E_{kin} \quad (2)$$

resulting in production of four hot hydrogen atoms is suggested.

Acknowledgement

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Table 1

Radiative lifetimes τ and mean cross sections σ for H_2^* - H_2 collisional quenching for individual vibrational levels v' of the B $2p\ ^1\Sigma_u^+$ state of H_2

v'	τ(ns) this work	τ(ps) theor.Ref.4	τ(ns) exp.Ref.7	$\sigma(10^{-15}cm^2)$ this work
0	0.54 ± 0.05	535		5.1 ± 1.5
1	0.59 ± 0.09	574		5.0 ± 1.2
2	0.62 ± 0.11	613		5.1 ± 1.2
3	0.67 ± 0.09	651	0.8 ± 0.2	5.2 ± 2.1
4	0.69 ± 0.15	690		5.4 ± 1.2

Figure captions:

Fig. 1 Schematic diagram of experimental arrangement for subnanosecond lifetime measurements

Fig. 2 Vuv decay curves of the H_2 B, v'=0 state (J' = 1 and 2) at different pressures

Fig. 3 Decay rate versus pressure for H_2 B, v' = 0 (J' = 1 and 2) with least-squares-fit

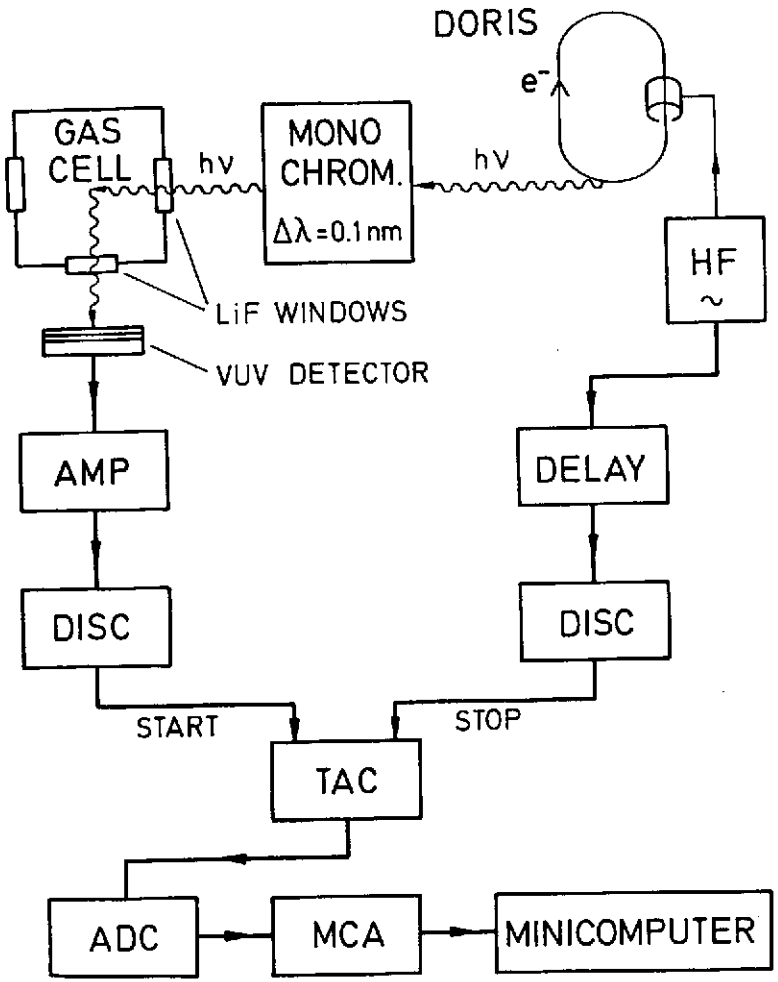
DORIS
e⁻
GAS CELL
hν
MONO CHROM.
Δλ=0.1nm
hν
HF
LiF WINDOWS
VUV DETECTOR
AMP
DELAY
DISC
DISC
START
STOP
TAC
ADC
MCA
MINICOMPUTER

Fig. 1

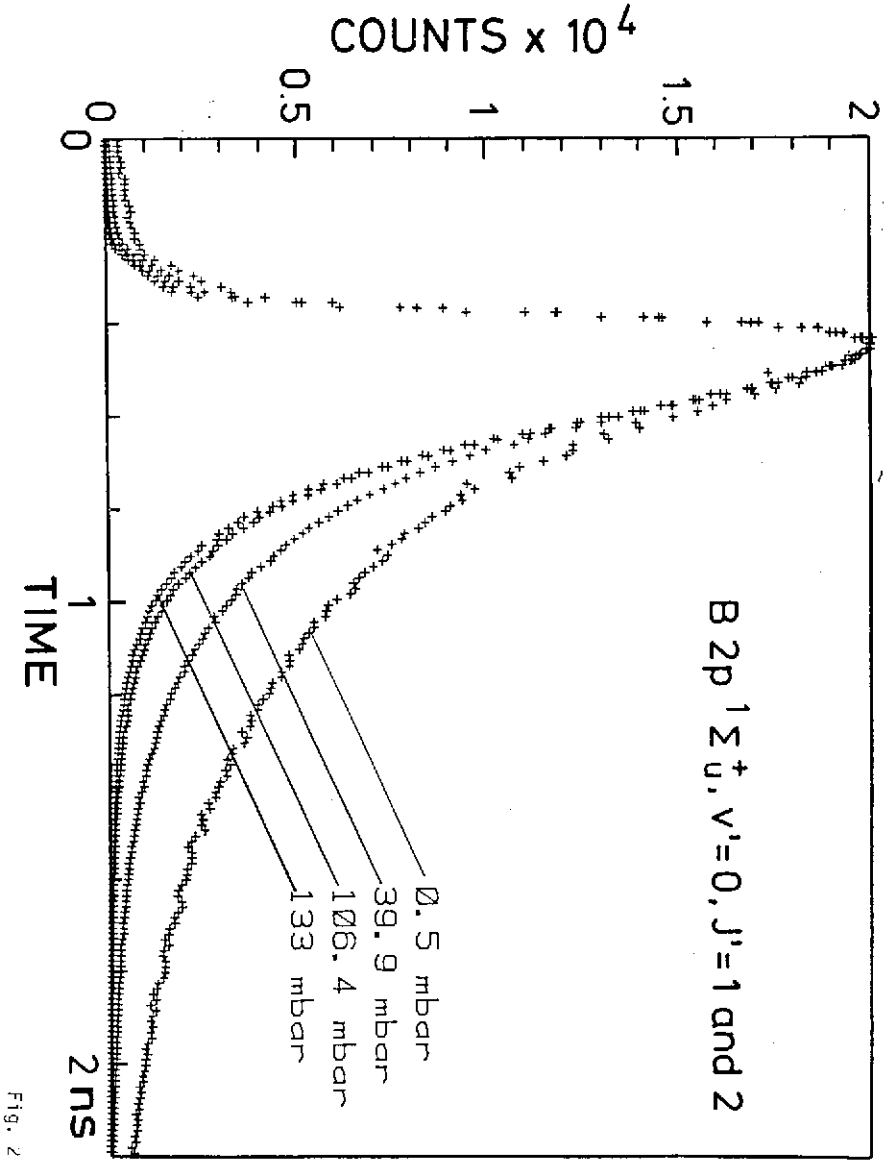
COUNTS x 10⁴
0
0.5
1
1.5
2
TIME
1
2 ns
B 2p ¹Σ⁺u, v'=0, J'=1 and 2
0.5 mbar
39.9 mbar
106.4 mbar
133 mbar

Fig. 2

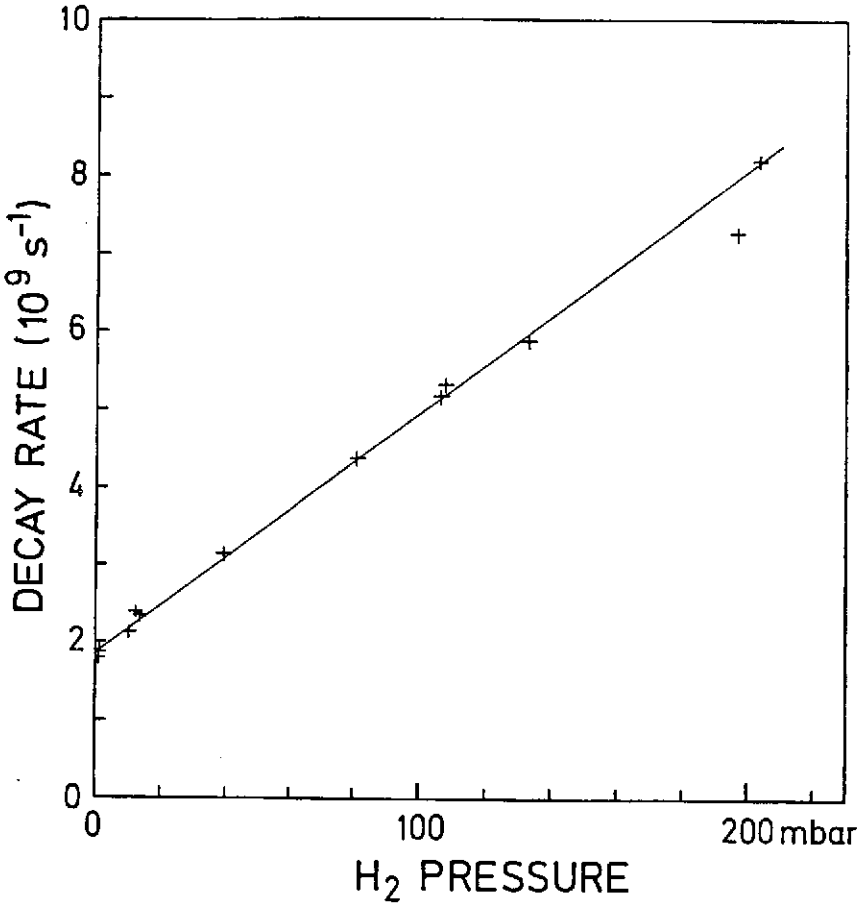

Fig. 3