
01 Jan 1990

Rotational Effects In The Continuous Vacuum-ultraviolet Fluorescence Spectrum Of H₂ Associated With Spontaneous Dissociation

H. Schmoranzer

T. Noll

E. Roueff

H. Abgrall

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/phys_facwork/2641

Follow this and additional works at: https://scholarsmine.mst.edu/phys_facwork

 Part of the [Physics Commons](#)

Recommended Citation

H. Schmoranzer et al., "Rotational Effects In The Continuous Vacuum-ultraviolet Fluorescence Spectrum Of H₂ Associated With Spontaneous Dissociation," *Physical Review A*, vol. 42, no. 3, pp. 1835 - 1838, American Physical Society, Jan 1990.

The definitive version is available at <https://doi.org/10.1103/PhysRevA.42.1835>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Rotational effects in the continuous vacuum-ultraviolet fluorescence spectrum of H₂ associated with spontaneous dissociation

H. Schmoranzner and T. Noll*

Fachbereich Physik, Universität Kaiserslautern, D-6750 Kaiserslautern, Federal Republic of Germany

E. Roueff and H. Abgrall

*Département Atomes et Molécules en Astrophysique,
Observatoire de Paris-Meudon, F-92195 Meudon, France*

R. J. Bieniek

Department of Physics and Laboratory for Atomic and Molecular Research, University of Missouri, Rolla, Missouri 65401

(Received 7 September 1989; revised manuscript received 6 June 1990)

The effects of rotational-vibrational interaction, and of rotational coupling between the $B\ 2p\ ^1\Sigma_u^+$ and $C\ 2p\ ^1\Pi_u$ electronic states, on the B - X fluorescence continuum of H₂ associated with spontaneous dissociation were investigated spectroscopically using monochromatized synchrotron radiation for selective excitation of rovibronic states. The rotational shifts and perturbations in the modulated continua intensities observed agree well with close-coupling and Jeffreys-Wentzel-Kramers-Brillouin calculations also performed, and are explained in terms of nonadiabatic coupling effects and rainbow-interference structures. A straightforward experimental technique is described to detect mixed electronic states.

Rovibronic singlet states of H₂ can spontaneously dissociate through transitions to the ground electronic state via vuv photon emission. Although the resulting continua spectra are rich in structure, heretofore experimental techniques have not been able to obtain the fluorescence spectra from individual states. This has hindered the detection and unambiguous theoretical analysis of rotational effects in this half-collisional process involving the most fundamental molecule. This Rapid Communication reports successful observations, from selectively excited rovibronic states, of several types of rotational shifts and perturbations in B - X continua spectra. These can now be clearly attributed to rotational distortions of vibronic wave functions and to $B\ ^1\Sigma_u^+$ - $C\ ^1\Pi_u$ rotational coupling, through excellent agreement with parallel quantal computations and Jeffreys-Wentzel-Kramers-Brillouin (JWKB) stationary-phase calculations. These collectively represent a stringent test of current experimental and theoretical techniques of investigating intermolecular interactions.

Initial studies of the dissociative fluorescence of H₂ involved only vibrationally selective preparation, using monochromatized synchrotron radiation.¹ However, spectroscopic studies of individual rotational-vibrational states of the electronic states B and C have recently been made feasible by the development of a high-luminosity vuv fluorescence spectrometer.² The first spectra measured after rotationally selective excitation³ revealed a red shift of the individual intensity maxima in the structured continuous fluorescence spectrum when the rotational quantum number of the excited state was raised. These experiments were in qualitative agreement with a prior theoretical calculation in which rotational distortions were included approximately, but rotational coupling was ignored.⁴

In a previous study on the line intensities of the H₂ Ly-

man bands,⁵ the very high sensitivity of fluorescence intensities to perturbations as compared to the relatively small level shift produced by the same perturbation was pointed out. More recently, theoretical calculations of line intensities for the Lyman and Werner bands have been performed, in which the rotational coupling between the $B\ ^1\Sigma_u^+$ and $C\ ^1\Pi_u^+$ states has been fully taken into account and which agree well with relative line intensity measurements.⁶ Studies by other investigators on different molecules have shown some coupling effects in vibrationally selective continua spectra.⁷ But we report here a level of experimental measurements and theoretical calculations that reveal the shifting and modulation of emission continua due to rovibrational interactions, and "heterogeneous" intensity perturbations due to rotational mixing of B and C electronic states. A simple, yet sensitive method to detect such mixing will also be described.

The apparatus has been described previously.² Briefly, vuv radiation from Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY) (Berlin) was monochromatized by a 3-m normal-incidence monochromator equipped with a 1200-lines/mm, Pt-coated grating blazed at 60 nm. The monochromatized radiation (chosen bandwidth 0.02 nm) was focused by a toroidal mirror into the open entrance aperture of the gas cell, which was differentially pumped in order to maintain a pressure of 0.2 mbar in the cell and 10^{-9} mbar in the primary monochromator mentioned above.

The secondary monochromator was home built and equipped with a 0.5-m, 1200-lines/mm, 110 mm diam, Al-MgF₂-coated grating for generating first-order fluorescence spectra in the vuv spectral region directly on a one-dimensionally position-sensitive microchannel-plate detector. The detector was sensitized for long-wavelength vuv by adding a specially made photocathode (Pt on LiF) in front of the first microchannel plate. The position of the

incident photon was registered by a backgammon-structured conducting anode and processed by analog pulse electronics. Very low signal rates [0.1 (counts/sec)/nm] could be recorded at reasonable signal-to-noise ratios. The wavelength resolution was limited to 1.5 nm because it was necessary for intensity reasons to use the fluorescing column of H₂ in the gas cell instead of a narrow slit.

The radiation for the undispersed fluorescence studies described later was detected directly by an open microchannel plate mounted closely outside the LiF window of the gas cell. The spectral sensitivity range in this setup (later called short-wavelength detection) extends from 104 nm (LiF cutoff) to about 130 nm. Another broad detection range for fluorescence excitation spectra (later called long-wavelength detection) was obtained by using the grating to disperse the fluorescence radiation, and then limiting the spectral range detected by placing a rectangular aperture in front of the microchannel-plate backgammon-anode detector operated without evaluating photon position. The grating was set to detect total emission in the range of 123–147 nm.

Recent theoretical works^{8,9} have shown the importance of nonadiabatic effects for specific excited rovibrational states of even parity, which can be reached from the ground state through *P* and *R* transitions only. These effects are due to the electron-rotational coupling between Σ and Π states. In the energy range of the synchrotron radiation considered, the coupling is principally between *B* and *C*. One can define the percentage of *B* character of each rovibrational state as given in Tables 1 and 2 of Ref. 8. We concentrate here on experimental studies of the two following distinct cases: (i) $v'=13, J'=4$ of the $B^1\Sigma_u^+$ state, which is an almost pure *B* state⁸ (percentage of *B* is 99.6%), and (ii) $v'=12, J'=4$ of the $B^1\Sigma_u^+$ state which has⁸ 84% *B* character and which was incorrectly labeled $C(v'=2, J'=4)$ in a previous study.¹⁰

The differential emission rate for fluorescent transitions to the continuum of the $X^1\Sigma_g^+$ state can then be calculated:^{4,8}

$$\frac{d^2N}{dt d\lambda} = \frac{64\pi^4 c}{3h} \frac{1}{2J'+1} \lambda^{-5} |M_{v',J'}^a|^2, \quad (1)$$

where M^a is the bound-free dipole transition moment between the initial bound radial wave function and the final energy-normalized continuum wave function. a refers to *P*, *Q*, and *R* transitions, and λ is the wavelength of the fluorescent photon.

By tuning the primary monochromator to the *B*-*X* ($v'=13 \leftarrow v''=0$) R_3 and P_1 absorption lines, the fluorescence spectra for the rotational state $J'=4$ (Fig. 1, upper part) and for $J'=0$ (Fig. 1, central part) were measured. Since the fluorescent *P* and *R* branches cannot be distinguished in measurements of the continuum emission, we summed and convoluted the *P* and *R* contributions for comparison with the experimental spectra. The agreement between the measured spectra and the close-coupling calculations (smooth curve) is very good since the effect of rotation-vibration interactions on the continuum intensity distribution has been fully accounted for. In the lower part of Fig. 1, the two experimental continua were plotted together in order to show more clearly the

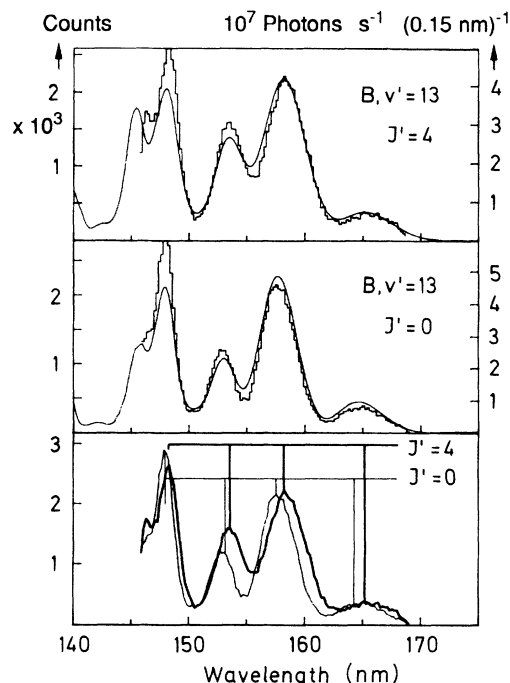


FIG. 1. Continuous fluorescence spectrum of $B, v'=13, J'=0$ and 4. Experiment: stepped curve in upper and central part; both curves in lower part. Theory: smooth curve in upper and central part; close-coupling convoluted with experimental resolution function per experimental stepwidth of 0.15 nm.

red shift of the continuum peaks with increasing J' , which amounts to between 0.5 and 1 nm. The shift here is clearly due to centrifugal effects since both of the upper states involved are pure *B* states.

The spectra's undulations are fine examples of rainbow-interference structures,¹² readily explained with JWKB stationary-phase methods. Because the *B*-*X* difference potential has a minimum, there are typically two localized transition (Condon) points associated with each wavelength. Using uniform JWKB stationary-phase methods,¹³ one can show that the fluorescence rate is proportional to the square of a *T*-matrix element which explicitly depends on the localized contributions from the two Condon points at R_1 and R_2 :

$$T = T_1 + T_2, \quad (2a)$$

where

$$T_C \propto \frac{M(R_C)}{k(R_C)} \cos(\xi_C) \text{Ai}(y_C), \quad (2b)$$

and $M(R)$ is the transition dipole moment, $k(R)$ is the local wave number, and ξ_C and y_C are functions of the phase change, and its derivatives, between initial and final heavy-particle wave functions. ξ_C is effectively the average of the two phase changes at the Condon points, while y_C is related to their difference.

Table I shows the good agreement of the JWKB predictions of the spectral structures, compared to the close-coupled results reported here. Furthermore, the predicted JWKB rotational shifts were identical to the quantal ones (e.g., 0.45 nm for the 158-nm peak). The rapid oscillations (and centrifugal shifts) in the spectra are due to a

TABLE I. Comparison of theoretical spectral peaks for the $B(v'=13, J'=0)$ level. λ_q is the peak wavelength of unconvoluted quantal computations, while λ_{SP} is the corresponding JWKB stationary-phase prediction. r is the ratio of the fluorescent rate of the given peak to the rate of peak No 2.

Peak No.	λ_q (nm)	λ_{SP} (nm)	r_q	r_{SP}
1	164.7	164.3	0.19	0.18
2	157.7	157.5	1.00	1.00
3	153.0	152.9	0.55	0.47

sensitive variation in the average of the heavy-particle wave-function phase changes at the transition points; this reflects variation in the accumulated phases from the turning points as the exit energy of the atoms is scanned. The more slowly undulating intensity envelope is a "rainbow" structure arising from the extremum in the difference potential, and is governed by the interference between the two Condon points. Classically, no radiation can be emitted beyond the minimum in the difference potential, corresponding to a wavelength of 162.4 nm. The continuum peak occurring at the longest wavelength in each spectrum, e.g., in Fig. 1 (or No. 1 in Table I), observed outside of the classically allowed wavelength region,¹⁴ can now be clearly and unambiguously confirmed as a rapid oscillation on the dark side of the classical singularity, in the classically forbidden region beyond the minimum in the difference potential. Although the JWKB stationary-phase method had yielded good results, as expected, for analogous spectra in heavy molecules (e.g., halogen dimers¹²), it is very gratifying to see that it also works well in the lightest, least classical molecular system.

A similar measurement for $B, v'=12$, produced the results displayed in Fig. 2. The agreement is again excellent. In this case, however, strong nonadiabatic ("heterogeneous" perturbation) effects on the continuum intensi-

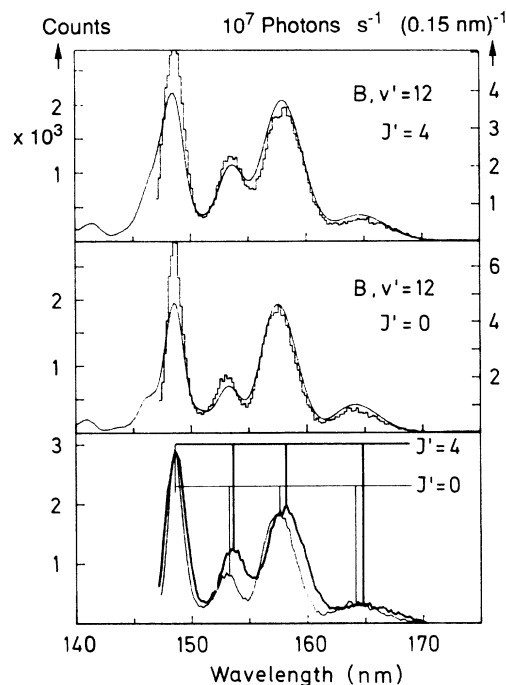


FIG. 2. Continuous fluorescence spectrum of $B, v'=12, J'=0$ and 4. Experiment: stepped curve in upper and central part; both curves in lower part. Theory: smooth curve in upper and central part; close-coupling convolved with experimental resolution function per experimental stepwidth of 0.15 nm. Note that $J'=4$ was reassigned B here according to new findings in contradiction to Ref. 10.

ties are predicted between the $(v'=12, J'=4)$ B state and $(v'=2, J'=4)$ C state, since the levels do not have a pure electronic character.

The vuv fluorescence continua are particularly well suited for investigating these perturbations, because they show the B character of the emitting levels without any

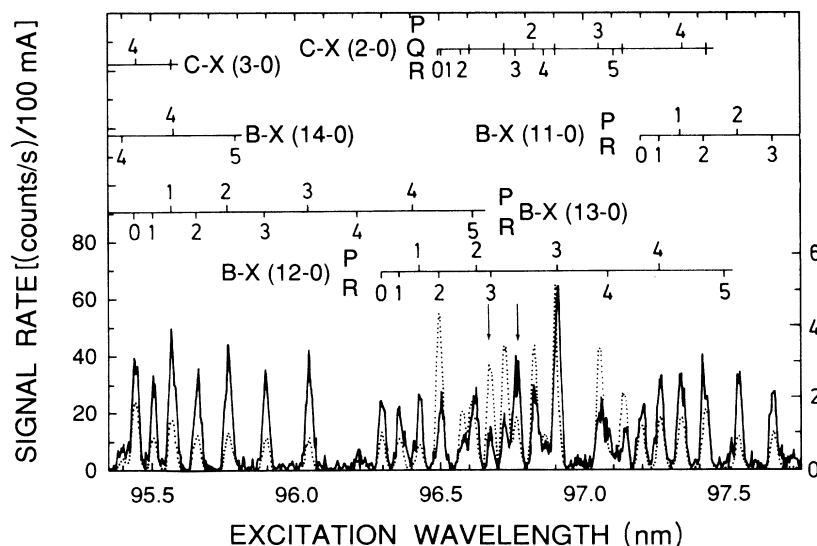


FIG. 3. Fluorescence excitation spectrum in the spectral range of the $B-X(12 \leftarrow 0)$, $B-X(13 \leftarrow 0)$, and $C-X(2 \leftarrow 0)$ bands. Dotted curve, left scale: short-wavelength detection $104 \leq \lambda \leq 130$ nm; solid curve, right scale: long-wavelength detection $123 \leq \lambda \leq 147$ nm.

overlap from the fluorescence radiation of the perturbing C level (in contrast to corresponding studies of discrete transitions^{5,6}), since pure C states of low vibrational quantum numbers do not emit into the longer-wavelength continuum.⁴ Thus, anomalous fluorescence detected in a longer-wavelength window indicates significant mixing or misidentification of levels, in the spirit of separating out mixed absorption systems.¹⁵ To illustrate this technique, consider the fluorescence excitation spectra (Fig. 3) recorded digitally in the spectral excitation range from 95.4 to 97.7 nm, where the $B-X$ ($v'=12 \leftarrow v''=0$), $B-X$ ($13 \leftarrow 0$), and $C-X$ ($2 \leftarrow 0$) absorption bands occur, using both the short-wavelength detector mentioned before (dotted curve) and the long-wavelength detector (solid curve). The identification of rotational lines follows the existing literature,¹⁰ in which the line at 96.767 nm is labeled $C-X$ ($2 \leftarrow 0$) R_3 (see right arrow in Fig. 3). However, the misidentification of this line is easily seen in the excitation spectrum (Fig. 3) because the long-wavelength detection range favors the continuous $B-X$ emission and almost suppresses the $C-X$ emission at shorter wavelengths, whereas the short-wavelength detector clearly favors the $C-X$ emission. The intensity ratio of the two excitation spectra recorded with these two different detection ranges should be nearly constant within a band, e.g., for the R_0 , R_1 , and P_1 lines of $B-X$ ($12 \leftarrow 0$). These lines, which stem from unperturbed B levels, show the long-wavelength detector spectrum to be more intense than the short-wavelength detector spectrum by a factor of about 2.5 on the scale chosen in the figure. The opposite is the case for the so-called R_3 line of the same band (left arrow in Fig. 3), while the so-called R_3 line of $C-X$ ($2 \leftarrow 0$) (right arrow) exhibits the typical intensity ratio for B lines, implying the electronic character of these R_3 lines have been incorrectly identified in the literature.

The close-coupling calculations confirmed that the upper level of this line is, indeed, of prevailing B character (84%), which has been properly renamed in Fig. 2 (upper part). The observable effect of such mixing is clearly seen in Fig. 4, which displays the calculated fluorescence rates for uncoupled B and C states, labeled B^0 and C^0 , and for the actual perturbed levels B and C . Thus, if a so-called C level is perturbed and has some B character mixed in, the

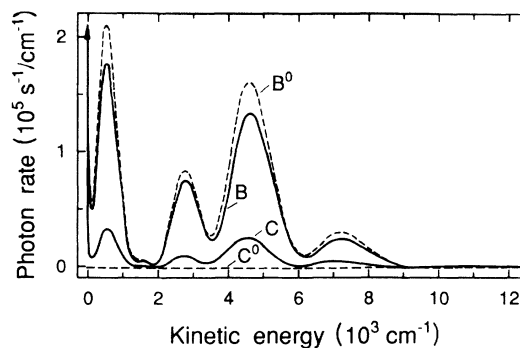


FIG. 4. $P+R$ theoretical dissociative emission probability of $J'=4$ levels of $B(v'=12)$ and $C(v'=2)$ vs kinetic energy. Dotted B^0 and C^0 curves show results without coupling. For C^0 dissociative emission is insignificant. Solid B and C curves take into account rotational coupling. [The labels are different from those of Dabrowski (Ref. 10) and follow our calculated B percentages which are respectively 84.0 and 16.4.] The arrow indicates the quasibound state for $J''=5$, characterized in our calculated profile by a height of $4 \times 10^5 \text{ s}^{-1}/\text{cm}^{-1}$ at 46.5 cm^{-1} and a width at half maximum (Ref. 11) of 27 cm^{-1} . The exit kinetic energy E_k is related to the fluorescence wavelength λ (plotted in Figs. 1 and 2) by $E_k = E_{v',j'} - D_0(\text{H}_2) - (hc/\lambda)$.

perturbation can easily be detected by observing the B -type continuum in a spectral range where no C -type emission occurs, i.e., on a vanishing background.

The investigation of intensity perturbations (instead of energy shifts) in the continuous spectra has proven to be a useful and extremely sensitive method for testing the close-coupling theory of the rotational phenomena.

This work has been funded by the German Minister for Research and Technology under Contract No. 05 352 AXIO. All close-coupling calculations were performed at the "Centre Inter Régional de Calcul Electronique" at the Université Paris-Sud. Département Atomes et Molécules en Astrophysique is "Unité de recherche associée au Centre National de la Recherche Scientifique No. 812." R. J. B. would like to thank the Fulbright Commission of the Federal Republic of Germany for financial support.

*Present address: OSRAM GmbH, D-7922 Herbrechtingen, Germany.

¹H. Schmoranzer and R. Zietz, *Phys. Rev. A* **18**, 1472 (1978).

²H. Schmoranzer, K. Molter, T. Noll, and J. Imschweiler, *Nucl. Instrum. Methods Phys. Res. Sect. A* **246**, 485 (1986).

³T. Noll and H. Schmoranzer, *Phys. Scr.* **36**, 129 (1987).

⁴T. L. Stephens and A. Dalgarno, *J. Quant. Spectrosc. Radiat. Transfer* **12**, 569 (1972); see also A. Dalgarno, G. Herzberg, and T. L. Stephens, *Astrophys. J.* **162**, L49 (1970).

⁵H. Schmoranzer and J. Geiger, *J. Chem. Phys.* **59**, 6153 (1973).

⁶H. Abgrall, F. Launay, E. Roueff, and J.-Y. Roncin, *J. Chem. Phys.* **87**, 2036 (1987).

⁷J. Wörmer, T. Möller, J. Stapelfeldt, G. Zimmerer, D. Haaks, S. Kampf, J. Le Calvé, and M. C. Castex, *Z. Phys. D* **7**, 383 (1988).

⁸H. Abgrall and E. Roueff, *Astron. Astrophys. Suppl.* **79**, 313 (1989).

⁹P. Senn, P. Quadrelli, and K. Dressler, *J. Chem. Phys.* **89**, 7401 (1988); P. Senn, P. Quadrelli, and K. Dressler, *American Institute of Physics Report No. PAPS JCPAS-89-7401-224*, 1989 (unpublished).

¹⁰I. Dabrowski, *Can. J. Phys.* **62**, 1639 (1984).

¹¹R. L. Leroy and R. B. Bernstein, *J. Chem. Phys.* **54**, 5114 (1971).

¹²J. Tellinghuisen, *Adv. Chem. Phys.* **60**, 299 (1985), and references therein; *Can. J. Phys.* **62**, 1933 (1984).

¹³R. J. Bieniek and T. J. Streeter, *Phys. Rev. A* **28**, 3328 (1983).

¹⁴H. Schmoranzer and R. Zietz, in *Proceedings of the Eleventh International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers*, edited by K. Takayanagi and N. Oda (Society of Atomic Collision Research, Kyoto, Japan, 1979), p. 56.

¹⁵R. J. Donovan, M. A. McDonald, K. P. Lawley, A. J. Yencha, and A. Hopkirk, *Chem. Phys. Lett.* **138**, 571 (1987).