Effect of rotational coupling on emission probabilities of Lyman and Werner band systems of the vacuum ultraviolet spectrum of H2

Hervé Abgrall, Françoise Launay, Evelyne Roueff, and JeanYves Roncin

Articles you may be interested in

VUV Fourier-transform absorption study of the Lyman and Werner bands in D2
J. Chem. Phys. 136, 234310 (2012); 10.1063/1.4726457

Electronic transition moments for the Lyman and Werner bands of the H2 molecule
J. Chem. Phys. 82, 4720 (1985); 10.1063/1.448684

Emission spectrum of rare gas dimers in the vacuum UV region. II. Rotational analysis of band system I of Ar2
J. Chem. Phys. 71, 1780 (1979); 10.1063/1.438529

Emission of the Werner Band System and Lymanα Radiation for 0.05–6keV Electrons in H2
J. Chem. Phys. 55, 3829 (1971); 10.1063/1.1676668

Absorption Spectra of H2 in the VacuumUltraviolet Region. I. The Lyman and the Werner Bands
J. Chem. Phys. 40, 3154 (1964); 10.1063/1.1724978

Effect of rotational coupling on emission probabilities of Lyman and Werner band systems of the vacuum ultraviolet spectrum of H₂

Hervé Abgrall,[a] Françoise Launay, and Evelyne Roueff
Observatoire de Paris, Section de Meudon, CNRS, U.A. 812, 92195 Meudon Principal Cédex, France

Jean-Yves Roncin
Equipe de Spectroscopie, CNRS, U.A. 171,[b] Ecole des Mines, 42023 Saint-Etienne Cédex, France

Ratios of emission probabilities of rotational lines of the Lyman and Werner band systems, $B\,^1\Sigma_u^+ \to X\,^1\Sigma_g^+$ and $C\,^1\Pi_u \to X\,^1\Sigma_g^+$, respectively, are calculated by different methods. These theoretical ratios are compared to the experimental intensity ratios of about a hundred lines selected from a vacuum ultraviolet emission spectrum whose intensity is investigated for the first time at high resolution. The computation permits to compare two ways of solving a system of two coupled equations with discrete eigenvalues. In most cases the effect of the mutual rotational perturbation between B and C states is found significant on the ratio of P and R line intensities. Ambiguity in labeling a few B and C levels is discussed.

I. INTRODUCTION

The vacuum ultraviolet spectrum (VUV) of the sunlit hemisphere of outer planets such as Jupiter, Saturn,[1] and Uranus[2] is dominated by emission from atomic and molecular hydrogen, which is known as electro-glow emission. In this context, laboratory spectra of H₂ excited by electron impact have been investigated by Ajello *et al.*[3] In diffuse interstellar clouds, several H₂ absorption lines arising from the first seven rotational levels are observed in the Lyman and Werner band systems $B\,^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ and $C\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$, respectively.[4] The quantitative interpretation of these observations[5] requires detailed knowledge of the absolute values of transition probabilities between many rovibronic levels. Whereas high resolution laboratory experiments provide accurate level energies through the measurements of line wavelengths,[6,7] intensity measurements are quite sparse, especially in the VUV spectral range. It is usually assumed that the line oscillator strength, from which line transition probabilities can be obtained,[8] is the product of the band oscillator strength calculated theoretically, by the rotational Hönl–London factors.[9,10] Such a calculation has been performed by Allison and Dalgarno[11] for the Lyman and Werner band systems of H₂. This procedure neglects the centrifugal term and nonadiabatic effects arising from electron–rotation coupling and can lead to uncontrolled errors. Morton and Dinerstein[4] considered the impact of these factors on some line oscillator strengths in analyzing observations of interstellar molecular hydrogen toward Zeta Puppis.

The purpose of this paper is to perform calculations of line emission transition probabilities in the Lyman and Werner band systems of H₂. This is done in a treatment taking into account the rotational coupling between $B\,^1\Sigma_u^+$ and $C\,^1\Pi_u$, calculated by Ford[12] following a model described by Julienne[13] and Ford.[14] These authors used a matrix method to solve the system of coupled equations. We first have repeated Ford's calculation.[14] Then we have used a direct method more accurate for high v' and J' levels for which significant differences are found. Up to now comparison with the few published experimental intensity measurements[15,16] had not clearly favored the introduction of the coupling. In the present report we compare our calculations with relative intensities, obtained for the first time at high resolution in that spectral range, by means of the National 10 m VUV spectrograph of the Meudon Observatory. We demonstrate that the experimental results are well reproduced by the calculations, as far as no self-absorption occurs. In the meantime we show that some lines are relabeled when one takes into account the percentage of B and C characters of the rovibronic levels.

II. THEORY

The emission probability is given by the expression:

$$A\,^{v'J'}_{v''J''} = \frac{4}{3d\,'\hbar^4 c^3}\,(E\,^{v'J'}_{v''J''})^3 \sum_{d''d''l} |\langle \Phi' er_l \Phi'' \rangle|^2, \qquad (1)$$

where er_l is the dipole operator and Φ', Φ'' are the total wave functions of the upper and the lower states with degeneracy d' and d'', respectively. $E\,^{v'J'}_{v''J''}$ is the transition energy for which only the rovibrational indexes are explicit, $\hbar$ is the Planck constant, c the velocity of light, and e the electron charge.

We introduce a Hund's case (a) molecular basis for the ground and excited state wave functions. In this representation, the nonrelativistic electronic Hamiltonian is diagonal but the rotational Hamiltonian has nonzero off-diagonal terms. The molecular parity is defined with respect to inversion of all particle coordinates and we use the corresponding labeling e and f defined by Brown *et al.*[17]:

$$\Phi'' = \sqrt{\frac{2J''+1}{4\pi}}\,\frac{1}{R}f_{Xv''J''}(R)D\,^{*J''}_{M,0}(\phi,\theta,0)\psi_X(r,R), \quad (2)$$

$$\Phi'_e = \sqrt{\frac{2J'+1}{4\pi}} \frac{1}{R} \left\{ f_{B v'J'}(R) D^{*J'}_{M,0}(\phi,\theta,0)\psi_B(r,R) \right.$$

$$+ \frac{1}{\sqrt{2}} f_{C^+v'J'}(R) [D^{*J'}_{M,1}(\phi,\theta,0)\psi_{C,1}(r,R)$$

$$\left. + D^{*J'}_{M,-1}(\phi,\theta,0)\psi_{C,-1}(r,R)] \right\}, \qquad (3a)$$

$$\Phi'_f = \sqrt{\frac{2J'+1}{4\pi}} \frac{1}{R} \frac{1}{\sqrt{2}} f_{C^-v'J'}(R)$$

$$\times [D^{*J'}_{M,1}(\phi,\theta,0)\psi_{C,1}(r,R)$$

$$- D^{*J'}_{M,-1}(\phi,\theta,0)\psi_{C,-1}(r,R)], \qquad (3b)$$

where the ψ are the Born–Oppenheimer (BO) electronic wave functions calculated at several fixed internuclear distances R, D are the rotation matrices, and f the vibrational wave functions. Φ'' always has the eigenvalues $(-1)^{J''}$ for the inversion of all coordinates, but for Φ' we have distinguished two cases according to whether coordinate inversion gives the factor $(-1)^{J'}$ or $(-1)^{J'+1}$ for the wave function. Φ'_e, which gives $(-1)^{J'}$, is built from the $B\ {}^1\Sigma_u^+$ state and from the component ${}^1\Pi_u^+$ of the state $C\ {}^1\Pi_u$. ϕ'_f, which gives $(-1)^{J'+1}$, is built only from the component ${}^1\Pi_u^-$ which is not coupled with the state $B\ {}^1\Sigma_u^+$.

The integration of the Hamiltonian H over the electronic coordinates r and the angular coordinates θ and ϕ leads to differential equations to calculate the f. For Φ'', $f_{Xv''J''}$ is simply given by

$$\left[\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E_{v''J''} - V_X(R) \right.$$

$$\left. - J''(J''+1) \frac{\hbar^2}{2\mu R^2} \right] f_{Xv''J''}(R) = 0, \qquad (4)$$

where $V_X(R)$ is the adiabatic potential $\langle \psi_X H \psi_X \rangle_{\text{el}}$. For Φ'_e the nonadiabatic rotational coupling between B and C is taken into account. We obtain a coupled system which mixes $B\ {}^1\Sigma_u^+$ and $C\ {}^1\Pi_u^+$ in the following way:

$$\left[\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E_{v'J'} - V_B(R) \right.$$

$$\left. - J'(J'+1) \frac{\hbar^2}{2\mu R^2} \right] f_{Bv'J'}(R)$$

$$= -\frac{\hbar^2}{\mu R^2} \sqrt{J'(J'+1)} S(R) f_{C^+v'J'}, \qquad (5a)$$

$$\left\{ \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E_{v'J'} - V_C(R) \right.$$

$$\left. - [J'(J'+1)-1] \frac{\hbar^2}{2\mu R^2} \right\} f_{C^+v'J'}(R)$$

$$= -\frac{\hbar^2}{\mu R^2} \sqrt{J'(J'+1)} S(R) f_{Bv'J'}, \qquad (5b)$$

with

$$V_B(R) = \langle \psi_B H \psi_B \rangle_{\text{el}},$$
$$V_C(R) = \langle \psi_C H \psi_C \rangle_{\text{el}},$$
$$S(R) = \left\langle \psi_B \frac{L^+}{\sqrt{2}} \psi_{C,-1} \right\rangle_{\text{el}}.$$

Φ'_e is normalized such that

$$n_B = \int f_B^2(R)dR, \quad n_C = \int f_{C^+}^2(R)dR,$$

$$n_B + n_C = 1, \qquad (6)$$

and we have labeled a state as B or C according to the greater value of n_B or n_C. Then independently for each species we have chosen the vibrational index v' following the increasing order of level energies. As the coupling is too small to unsettle the level structure, the index is the same as that of the nearest unperturbed level of the same species (see the last section).

For Φ'_f, as $C\ {}^1\Pi_u^-$ is not rotationally coupled to any other state, $f_{C^-v'J'}$ is the solution of

$$\left\{ \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E^0_{v'J'} - V_C(R) \right.$$

$$\left. - [J'(J'+1)-1] \frac{\hbar^2}{2\mu R^2} \right\} f^0_{C^-v'J'}(R) = 0. \qquad (7)$$

The Λ doubling, which describes the separation of C^+ from C^-, due to the coupling, is $E_{v'J'} - E^0_{v'J'}$.

If after replacing in Eq. (1) ϕ'' and ϕ' by their expressions in Eq. (2) and Eq. (3), respectively, we integrate the expression of the emission probability over electronic and rotational coordinates, we obtain a new form[13] in which the two electronic transition moments appear:

$$M_{BX}(R) = \langle \psi_B er_l \psi_X \rangle_{\text{el}}$$

and

$$M_{CX}(R) = \langle \psi_C er_l \psi_X \rangle_{\text{el}}.$$

Depending on the value of $J' - J''$ there are three expressions for $A^{v'J'}_{v''J''}$:

P branch $J'' = J' + 1$:

$$\frac{4}{3\hbar^4 c^3(2J'+1)} (E^{v'J'}_{v''J''})^3 |\sqrt{J'+1} \langle f_{Xv''J''} M_{BX} f_{Bv'J'} \rangle$$

$$- \sqrt{J'} \langle f_{Xv''J''} M_{CX} f_{C^+v'J'} \rangle|^2, \qquad (8a)$$

R branch $J'' = J' - 1$:

$$\frac{4}{3\hbar^4 c^3(2J'+1)} (E^{v'J'}_{v''J''})^3 |\sqrt{J'} \langle f_{Xv''J''} M_{BX} f_{Bv'J'} \rangle$$

$$+ \sqrt{J'+1} \langle f_{Xv''J''} M_{CX} f_{C^+v'J'} \rangle|^2, \qquad (8b)$$

Q branch $J'' = J'$.

The emitting state $C\ {}^1\Pi_u^-$ is not coupled and the expression is simply

$$\frac{4}{3\hbar^4 c^3} (E^{v'J'}_{v''J''})^3 |\langle f_{Xv''J''} M_{CX} f_{C^-v'J'} \rangle|^2. \qquad (8c)$$

III. CALCULATIONS

In order to obtain the R-dependent electronic quantities we have used previously published results. Details and references are indicated in Sec. IV. We have calculated the vibrational wave functions by integrating the differential equations (4) and (7) with the help of the Numerov algorithm.[18] For the coupled system (5), we have used two methods of computation[13,19,20] with the same potential values.

On the one hand, we have chosen the matrix method described by Julienne[13] and Ford.[14] In this case the vibra-

tional wave functions are expressed in the two sets of basis functions solutions of the system of Eqs. (5) without right-hand sides, that is, the vibrational wave functions of the adiabatic potential. We have restricted the basis to the bound states:

$$f_{Bv'J'} = \sum_s b_s f^0_{BsJ'},$$ (9a)

$$f_{C^+v'J'} = \sum_t c_t f^0_{C^-tJ'}.$$ (9b)

The b_s, c_t, and the eigenvalues $E_{v'j}$ are obtained by diagonalizing a symmetric matrix whose diagonal elements are the adiabatic rovibronic energies $E^0_{BsJ'}$ and $E^0_{CtJ'}$ and the non-diagonal elements are:

$$-\frac{\hbar^2}{\mu}\sqrt{J'(J'+1)}\left\langle f^0_{BsJ'} \frac{S(R)}{R^2} f^0_{C^-tJ'}\right\rangle.$$ (10)

On the other hand we have used a direct method which calculates the eigenvalues and the wave functions, solutions of the system of Eqs. (5), by using the renormalized Numerov algorithm as described by Johnson.[21] This method takes into account the effect of the vibrational continuum and is more reliable, especially for high vibrational states.

Even in the cases where the rotational coupling has no effect ($J' = 0$ or C^-), the published calculated adiabatic potentials do not reproduce the experimental level energies. This may be due to radial nonadiabatic effects or to small inaccuracy of the adiabatic calculation. As a small effect gives a perturbation whose first order term is proportional to $1/(E^0_{BsJ'} - E^0_{CtJ'})$, it is necessary to use accurate zero-order energy in case of near coincidence. For this reason some authors[12,13] have replaced the diagonal elements $E^0_{BsJ'}$ and $E^0_{CtJ'}$ by the experimental level energies. This is not possible for the direct resolution, and following a procedure similar to that of Stwalley,[22] we have chosen to change slightly the potentials in order to fit the experimental levels for $B, J' = 0$ and $C^-, J' = 1$ within 1 cm^{-1}. We have first made a vertical translation of the potential curves until the calculated and experimental vibrational level energies coincide for $v'' = 0$, then we have modified the right turning points within $\Delta R / R = 0.001$ to adjust the other vibrational levels.

IV. CHOICE OF THE ELECTRONIC QUANTITIES

A. Potentials

For the ground state $V_X(R)$ we have used the potential of Bishop and Shih.[23]

For the two upper state adiabatic potentials we have retained the following data:

$V_B(R) 1 < R < 12$ (Ref. 24)

    $12 < R < 20$ (Ref. 25)

    $R < 1$ and $R > 20$ (Refs. 26 and 27)

    (R in atomic unit)

$V_C(R)$ Born–Oppenheimer potential[28] with

    adiabatic corrections.[29]

To calculate the level energies we have set the origin at

D_0, the dissociation limit of H_2 into $H(1s) + H(2p)$. Experimental values are taken with respect to the level $v'' = 0$, $J'' = 0$, and $D_0 = 118\ 377.45\ cm^{-1}$, sum of the ground state dissociation energy[30]: $36\ 118.3\ cm^{-1}$, and of the excitation energy between $H(2p)$ and $H(1s)$.[22]

Tables I and II show that after adjusting the potential curves[37] the agreement with experimental levels is within 1 cm^{-1}.

B. Rotational coupling S(R)

We have used the values calculated by Ford.[12]

C. Electronic transition moments

For $M_{BX}(R)$ and $M_{CX}(R)$ we have used the values given by Dressler and Wolniewicz.[32]

V. RESULTS

A. Transition energies

For most of the emitting rovibronic levels, the two ways of solving the coupled system give close transition energies,

TABLE I. Vibrational level energies E of the state $B\ {}^1\Sigma_u^+$, $J' = 0$ calculated with adiabatic potential whose right-hand side has been slightly modified so as to fit experimental values within 1 cm^{-1}.

v'	E	E_1-E [a]	E_2-E [b]
0	90 203.23	0.35	0.29
1	91 521.39	0.42	0.46
2	92 803.01	0.37	0.34
3	94 049.96	0.05	0.07
4	95 263.01	0.20	0.06
5	96 442.94	0.05	0.12
6	97 590.32	0.25	0.26
7	98 705.54	0.39	0.53
8	99 789.43	0.52	0.54
9	100 842.19	0.52	0.59
10	101 864.52	0.41	0.50
11	102 856.73	0.27	0.35
12	103 819.33	0.04	0.32
13	104 752.52	0.29	0.45
14	105 657.40	0.24	0.50
15	106 534.25	0.09	0.42
16	107 383.63	0.21	0.36
17	108 206.16	0.08	0.09
18	109 002.15	0.14	
19	109 771.71	− 0.21	
20	110 515.09	0.37	
21	111 233.17	0.11	
22	111 926.96	− 0.20	
23	112 596.01	0.04	
24	113 240.02	− 0.34	
25	113 858.98	− 0.30	
26	114 452.59	− 0.13	
27	115 021.00	− 0.09	
28	115 562.39	− 0.22	
29	116 075.17	− 0.09	
30	116 556.94	0.35	
31	117 003.77	− 0.17	
32	117 409.31	0.79	
33	117 765.37	0.49	
34	118 054.69	0.19	
35	118 253.66	0.38	
36	118 336.48	0.46	
37	118 363.99	0.65	

[a] E_1: experimental values of Ref. 31.
[b] E_2: experimental values of Ref. 6.

TABLE II. Vibrational level energies E of the state $C\,{}^1\Pi_u^-$, $J' = 1$ calculated with adiabatic potential whose right-hand side has been slightly modified so as to fit experimental levels within 1 cm^{-1}.

v'	E	$E_1 - E$ [a]	$E_2 - E$ [b]
0	99 150.92	0.02	0.00
1	101 456.78	− 0.21	− 0.39
2	103 628.57	− 0.57	− 0.62
3	105 668.23	− 0.36	0.02
4	107 578.46	0.29	0.31
5	109 360.23	− 0.24	0.02
6	111 011.51	0.17	0.28
7	112 530.22	0.37	0.75
8	113 912.95	0.42	0.48
9	115 151.93	0.31	0.03
10	116 236.00	− 0.03	0.04
11	117 149.90	0.57	− 0.15
12	117 869.28		− 0.59
13	118 349.61		− 0.44

[a] E_1: experimental values of Ref. 7.
[b] E_2: experimental values of Ref. 6.

although they may differ significantly for the higher levels (Tables III and IV). This shows the effect of neglecting the continuum part of the expansion basis.

The direct method is faster when we do computation for only one emitting level but the matrix method allows to obtain all vibrational levels for a given J', and is advantageous to obtain fair data for a set containing nearly all vibrational levels.

Table III shows the upper level energies calculated without and with coupling. For the C state, we have indicated the experimental Λ doubling deduced from the work of Dabrowski.[6] The last column indicates the percentage of B character.

The transition energies listed in Table IV have been obtained by subtracting from the calculated upper level energies the ground state level energies picked out from experimental data of Dabrowski.[6] We see that, at least for direct resolution, the agreement with measured transition energies is always within 1 cm^{-1}.

We must emphasize that until now the levels B (12,4), B (14,1), and C (3,1) have been usually labeled C (2,4), $C(3,1)$, and B (14,1), respectively. This difference indicates that it is sometimes difficult to discriminate between B and C states (see the last section). We can mention a similar occurrence in Table IV of Jungen and Atabek's work.[34] Like Ford we find $\Lambda = 43.3$ cm^{-1} for the C (1,5) level, but had we given the label C (1,5) to its closest counterpart B (10,5), we should have obtained $\Lambda = -26$ cm^{-1} to be compared with the experimental value of -25.95 cm^{-1} deduced from Dabrowski's work.[6] Morton and Dinerstein[4] pointed out these labeling differences between several authors.

B. Transition probabilities

In spite of slightly different potentials, we find the same rotational line strengths as Ford[14] for the lines he compared to the experimental data of Schmoranzer and Geiger[16] resulting from electron impact excitation. As these data concerned only low v' and J' levels, we have found it necessary to

undertake a new experiment in order to look for a more steady improvement for any v' and J'.

In the high resolution spectrum of H_2 emitted between 78 and 118 nm by a low pressure discharge lamp with a magnetic field,[7] among about 5000 lines, we have selected and measured all the isolated $B \to X$ and $C \to X$ lines assigned to single transitions. In order to get realistic intensity measurements, we have replaced the photographic plate holder of the 10 m spectrograph by a scanning photomultiplier or channeltron whose response is linear and not too much wavelength dependent.[35]

To reach the true emission probability we should know the population of the emitting level. In order to get population-free effect on relative intensities we have retained only the cases for which it was possible to select couples of P and R lines originating from one and the same level. In this way the population effect on relative intensity is avoided and the two compared lines are not too far apart. Nevertheless too large a population of the terminating levels $X_{v''J''}$ may produce self-absorption of the light. On our plates this phenomenon strongly shows up and diminishes most of the lines corresponding to transitions terminating to $v'' = 0$ and sometimes to $v'' = 1$, as well. This effect leads us to underestimate the emission towards the lower levels, i.e., an R line with respect to a P line. Therefore, we have left aside the transitions towards $v'' = 0$ which are too much affected by self-absorption.

In Table V the calculated emission probabilities A_P and A_R are listed for sets of P and R lines emitted by the same level. The last two columns contain heights I_P and I_R of peaks recorded with the photomultiplier or channeltron. For each level the two lines have been obtained in the same run, which warrants the same working conditions of the lamp, and, therefore, a good correspondence between peak heights and emission probabilities.

It can be seen that the agreement between the experimental values and the values calculated with coupling is quite good in 71% of cases and that in 76% the agreement is better with coupling than without.

VI. DISCUSSION OF THE THEORETICAL RESULTS

A. Effect of the centrifugal term of the potentials

We have been particularly interested by the ratio A_P/A_R of the two emission probabilities of a rovibronic level. It is often approximated by the ratio of Hönl–London factors $[(J' + 1)/J'$ for a ${}^1\Sigma_g^+$ state and $J'/(J' + 1)$ for a ${}^1\Pi_u$ state]. In Table VI we see discrepancies between ratios of Hönl–London factors and our three calculated ratios. In the no-coupling case this is due to the centrifugal term $J''(J'' + 1)/2\mu R^2$ which induces different vibrational functions of the state $X\,{}^1\Sigma_g^+$ for $J'' = J' + 1$ and $J'' = J' - 1$.

B. Ambiguity in labeling close-lying *B* and *C* levels

Sometimes two zero-order levels $E°_{B v'J'}$ and $E°_{C v'J'}$ are close to each other so that the coupling is stronger. The actual levels have both B and C characters and their label B or C has little physical meaning. In this case the vibrational coef-

TABLE III. Selected rovibronic level energies calculated without coupling (E_{NC}), with matrix method (E_M), with direct method (E_D), experimental Λ doubling and percentage of B character. All energies in cm^{-1}.

	v'	J'	E_{NC}	E_M	E_D	$E_M - E_{NC}$	$E_D - E_{NC}$	Λ^a	$\%B^b$
B	27	4	115 165.35	115 160.16	115 157.74	− 5.19	− 7.61		98.3
B	27	3	115 108.05	115 103.79	115 102.31	− 4.26	− 5.74		98.2
B	27	2	115 064.69	115 061.72	115 061.04	− 2.97	− 3.66		98.4
B	27	1	115 035.60	115 034.30	115 034.07	− 1.31	− 1.54		99.0
B	24	3	113 338.71	113 336.91	113 335.99	− 1.80	− 2.72		99.5
B	22	2	111 980.35	111 978.62	111 978.40	− 1.73	− 1.95		99.8
B	21	2	111 288.48	111 289.46	111 289.32	0.98	0.84		98.6
B	20	4	110 704.35	110 698.37	110 697.98	− 5.98	− 6.38		99.3
B	20	2	110 572.36	110 570.03	110 569.94	− 2.32	− 2.41		99.7
B	19	4	109 967.68	109 969.87	109 969.66	2.19	1.98		96.0
B	19	3	109 889.86	109 889.43	109 889.30	− 0.42	− 0.55		98.8
B	18	3	109 124.47	109 119.24	109 119.16	− 5.23	− 5.31		99.3
B	17	4	108 416.11	108 413.40	108 413.31	− 2.71	− 2.80		98.9
B	17	2	108 269.68	108 268.33	108 268.31	− 1.35	− 1.37		99.8
B	16	6	107 833.64	107 820.12	107 819.95	− 13.53	− 13.70		98.9
B	16	4	107 600.71	107 591.63	107 591.55	− 9.08	− 9.16		98.8
B	14	2	105 727.59	105 717.29	105 717.28	− 10.30	− 10.32		87.0
B	14	1	105 680.86	105 688.87	105 688.86	8.01	8.01		69.2
B	12	4	104 067.09	104 046.35	104 046.30	− 20.74	− 20.79		84.0
B	12	3	103 968.70	103 976.09	103 976.06	7.39	7.35		86.2
B	11	4	103 112.96	103 106.58	103 106.51	− 6.38	− 6.44		99.7
B	11	3	103 011.21	103 007.06	103 007.02	− 4.15	− 4.19		99.8
B	11	2	102 934.26	102 932.04	102 932.02	− 2.22	− 2.24		99.9
B	10	6	102 413.33	102 395.43	102 395.34	− 17.90	− 17.99		96.3
B	10	4	102 129.31	102 128.89	102 128.86	− 0.42	− 0.45		96.4
B	8	6	100 375.99	100 387.76	100 387.76	11.77	11.77		57.3
B	7	3	98 882.13	98 878.45	98 878.45	− 3.68	− 3.68		99.8
B	7	1	98 735.16	98 734.48	98 734.48	− 0.69	− 0.69		100.0
B	6	8	98 647.09	98 633.52	98 633.52	− 13.57	− 13.57		99.7
B	6	6	98 218.06	98 208.85	98 208.85	− 9.21	− 9.21		99.8
B	4	2	95 361.56	95 360.26	95 360.26	− 1.30	− 1.30		100.0
B	3	9	95 502.90	95 491.03	95 491.04	− 11.87	− 11.87		99.8
C	12	2	117 908.42	117 910.92	117 910.31	2.50	1.89	1.95	1.5
C	11	4	117 367.86	117 372.91	117 371.59	5.05	3.72		4.6
C	10	3	116 379.89	116 385.20	116 384.72	5.31	4.82	4.63	2.4
C	9	5	115 599.85	115 606.50	115 605.79	6.65	5.94		7.6
C	9	2	115 217.43	115 221.96	115 221.83	4.53	4.40	4.43	2.0
C	8	4	114 234.72	114 247.03	114 246.81	12.31	12.09	11.93	4.0
C	8	1	113 912.95	113 917.43	113 917.40	4.48	4.45	4.48	7.7
C	7	4	112 880.97	112 900.52	112 900.38	19.54	19.41		8.3
C	7	3	112 726.34	112 749.72	112 749.52	23.38	23.18	22.88	24.7
C	7	2	112 609.05	112 601.69	112 601.60	− 7.36	− 7.45	− 8.10	19.8
C	7	1	112 530.22	112 529.46	112 529.45	− 0.76	− 0.77	− 0.88	2.4
C	6	3	111 223.04	111 222.54	111 222.49	− 0.50	− 0.55	− 0.91	7.0
C	6	1	111 011.51	111 012.28	111 012.27	0.77	0.77	0.71	0.4
C	5	4	109 765.94	109 771.63	109 771.60	5.69	5.66	5.99	5.0
C	5	3	109 586.94	109 592.88	109 592.87	5.93	5.92	6.00	1.9
C	5	2	109 451.32	109 455.07	109 455.07	3.75	3.75	3.80	0.9
C	5	1	109 360.23	109 361.67	109 361.67	1.43	1.43	1.40	0.3
C	4	2	107 675.51	107 681.11	107 681.11	5.60	5.60	5.81	1.3
C	4	1	107 578.46	107 580.67	107 580.67	2.22	2.22	2.98	0.7
C	3	4	106 127.36	106 143.98	106 143.97	16.62	16.62	16.84	3.1
C	3	2	105 771.24	105 783.54	105 783.54	12.30	12.30	12.67	13.1
C	3	1	105 668.23	105 660.92	105 660.92	− 7.30	− 7.31	21.08	30.8
C	2	4	104 114.81	104 141.82	104 141.78	27.01	26.97	− 68.31	16.4
C	0	7	100 739.77	100 768.59	100 768.59	28.82	28.82	28.35	2.4

^{a} Experimental Λ doubling of Dabrowski (Ref. 6), to be compared with $E_M - E_{NC}$ and $E_D - E_{NC}$. Dieke (Ref. 33) found $- 7.4$ cm^{-1} for $C(3,1)$ and 27.25 cm^{-1} for $C(2,4)$. Other values of Λ can be found in Ref. 12.
^{b} $\%B = 100n_B$.

ficients $f_B(R)$ and $f_C(R)$ of the wave function Φ' of expression (3) are of the same order of magnitude; $n_B \simeq n_C \simeq 0.5$.

To see what happens if we let $E^0_{Bs't'}$ vary across $E^0_{Ct'f'}$ we have studied by the direct resolution method the effect of a vertical translation of $V_B(R)$. Figure 1 describes the shift of

$E^0_{B\,12,4}$ with respect to $E^0_{C\,2,4}$ over a range of 400 cm^{-1}. The calculation sets the nearest levels $E^0_{B\,13,4}$ and $E^0_{B\,11,4}$, respectively, at 925.2 cm^{-1} above and 954.1 cm^{-1} below $E^0_{B\,12,4}$. Figure 1(a) shows $E_{B\,12,4} - E^0_{C\,2,4}$ and $E_{C^+2,4} - E^0_{C\,2,4}$ vs $E^0_{B\,12,4} - E^0_{C\,2,4}$. Then we can see the continuous shift of the

TABLE IV. Comparison of a selection of measured and calculated transition energies between (v',J') and (v'',J'') for P and R lines (in cm^{-1}). Calculation without coupling (NC), with matrix method (M), and direct method (D).

	v'	J'	v''	Observed P	Observed R	NC P	NC R	M P	M R	D P	D R
B	27	4	2	105 503.71	106 435.23	7.49	7.42	2.30	2.23	− 0.12	− 0.19
B	27	3	2	105 962.52	106 696.06	5.67	5.70	1.41	1.44	− 0.07	− 0.04
B	27	2	9	85 548.46	85 871.78	3.29	3.27	0.32	0.30	− 0.36	− 0.38
B	27	1	1	110 536.30	110 873.10	1.48	1.36	0.18	0.06	− 0.05	− 0.17
B	24	3	1	108 064.71	108 838.35	2.64	2.54	0.84	0.74	− 0.08	− 0.18
B	22	2	1	107 147.51	107 705.38	1.43	1.22	− 0.30	− 0.51	− 0.52	− 0.73
B	21	2	1	106 458.97	107 016.57	− 1.90	− 1.84	− 0.92	− 0.86	− 1.06	− 1.00
B	20	4	5	90 891.45	91 672.65	5.87	5.69	− 0.11	− 0.29	− 0.50	− 0.68
B	20	2	1	105 738.87	106 296.60	2.08	2.01	− 0.25	− 0.32	− 0.34	− 0.41
B	19	4	1	104 155.77	105 138.52	− 2.04	− 2.25	0.15	− 0.06	− 0.06	− 0.27
B	19	3	4	93 698.65	94 353.45	0.55	0.71	0.12	0.28	− 0.01	0.15
B	18	3	4	92 928.10	93 583.19	5.71	5.58	0.48	0.35	0.40	0.27
B	18	3	6	86 786.11	87 361.98	5.51	5.51	0.28	0.28	0.20	0.20
B	17	4	3	95 148.06	96 029.28	2.78	2.69	0.07	− 0.02	− 0.02	− 0.11
B	17	2	3	95 884.30	96 384.92	1.24	1.25	− 0.11	− 0.10	− 0.13	− 0.12
B	16	6	4	90 011.19	91 170.38	13.69	13.78	0.17	0.26	0.00	0.09
B	16	4	1	101 777.73	102 760.28	9.03	9.02	− 0.05	− 0.06	− 0.13	− 0.14
B	14	2	3	93 333.33	93 833.83	10.12	10.25	− 0.18	− 0.05	− 0.19	− 0.06
B	14	2	4	89 899.04	90 371.55	10.28	10.23	− 0.02	− 0.07	− 0.03	− 0.08
B	14	1	3	93 604.83	93 906.89	− 8.63	− 8.39	− 0.62	− 0.38	− 0.63	− 0.39
B	12	4	2	94 392.29	95 323.18	20.65	21.21	− 0.09	0.47	− 0.14	0.42
B	12	3	1	98 705.08	99 478.71	− 7.74	− 7.83	− 0.35	− 0.44	− 0.38	− 0.47
B	11	4	2	93 452.57	94 383.94	6.24	6.32	− 0.14	− 0.06	− 0.21	− 0.13
B	11	3	1	97 735.75	98 509.31	4.10	4.08	− 0.05	− 0.07	− 0.09	− 0.11
B	11	2	2	94 209.54	94 738.39	2.02	2.06	− 0.20	− 0.16	− 0.22	− 0.18
B	11	2	4	87 114.09	87 586.55	1.90	1.90	− 0.32	− 0.32	− 0.34	− 0.34
B	10	6	0	99 207.75	100 655.03	18.01	18.09	0.11	0.19	0.02	0.10
B	10	4	4	85 479.98	86 311.06	− 0.15	− 0.02	− 0.57	− 0.44	− 0.60	− 0.47
B	8	6	3	85 892.65	87 122.81	− 12.12	− 12.09	− 0.35	− 0.32	− 0.35	− 0.32
B	7	3	1	93 607.47	94 381.03	3.30	3.28	− 0.38	− 0.40	− 0.38	− 0.40
B	7	1	3	86 650.31	86 952.64	0.19	0.16	− 0.49	− 0.52	− 0.49	− 0.52
B	6	8	1	89 725.47	91 446.10	13.34	13.55	− 0.23	− 0.02	− 0.23	− 0.02
B	6	6	0	95 021.40	96 468.85	9.09	9.00	− 0.12	− 0.21	− 0.12	− 0.21
B	4	2	2	86 637.70	87 166.62	1.16	1.13	− 0.14	− 0.17	− 0.14	− 0.17
B	3	9	1	85 607.22	87 483.51	11.89	11.62	0.02	− 0.25	0.03	− 0.24
C	12	2	2	109 186.85	109 715.81	− 1.13	− 1.20	1.37	1.30	0.76	0.69
C	11	4	2	107 716.93	108 648.47	− 3.22	− 3.31	1.83	1.74	0.51	0.42
C	10	3	2	107 244.86	107 978.07	− 4.83	− 4.47	0.48	0.84	0.00	0.36
C	9	5	2	105 345.17	106 464.71	− 6.52	− 4.72	0.13	1.93	− 0.58	1.22
C	9	2	2	106 499.12	107 027.98	− 4.39	− 4.36	0.14	0.17	0.01	0.04
C	8	4	1	108 433.20	109 415.52	− 12.43	− 12.21	− 0.12	0.10	− 0.34	− 0.12
C	8	1	1	109 419.92	109 756.53	− 4.79	− 4.72	− 0.31	− 0.24	− 0.34	− 0.27
C	7	4	1	107 087.34	108 069.78	− 20.32	− 20.22	− 0.77	− 0.67	− 0.91	− 0.81
C	7	3	6	90 417.69	90 993.55	− 24.20	− 24.19	− 0.82	− 0.81	− 1.02	− 1.01
C	7	2	2	103 879.06	104 407.88	7.29	7.36	− 0.07	0.00	− 0.16	− 0.09
C	7	1	2	104 123.72	104 443.04	0.21	0.25	− 0.55	− 0.51	− 0.56	− 0.52
C	7	1	3	100 445.38	100 747.72	0.18	0.14	− 0.58	− 0.62	− 0.59	− 0.63
C	7	1	6	90 773.15	91 024.33	0.09	0.11	− 0.67	− 0.65	− 0.68	− 0.66
C	6	3	1	105 951.08	106 724.62	0.60	0.60	0.10	0.10	0.05	0.05
C	6	1	3	98 927.68	99 230.06	− 0.83	− 0.91	− 0.06	− 0.14	− 0.07	− 0.15
C	5	4	6	87 035.83	87 765.82	− 5.50	− 5.46	0.19	0.23	0.16	0.20
C	5	3	5	90 216.77	90 832.49	− 5.82	− 5.83	0.12	0.11	0.11	0.10
C	5	2	2	100 732.35	101 261.18	− 3.73	− 3.67	0.02	0.08	0.02	0.08
C	5	2	6	87 449.54	87 865.33	− 3.80	− 3.83	− 0.05	− 0.08	− 0.05	− 0.08
C	5	1	6	87 604.69	87 855.97	− 1.44	− 1.52	0.00	− 0.08	0.00	− 0.0
C	4	2	2	98 958.80	99 487.69	− 5.99	− 5.99	− 0.39	− 0.39	− 0.39	− 0.39
C	4	1	1	103 083.14	103 419.78	− 2.50	− 2.46	− 0.29	− 0.25	− 0.29	− 0.25
C	4	1	5	88 820.83	89 089.17	− 2.65	− 2.63	− 0.44	− 0.42	− 0.44	− 0.42
C	3	4	1	100 330.22	101 313.14	− 16.81	− 17.19	− 0.19	− 0.57	− 0.20	− 0.58
C	3	2	5	86 757.88	87 202.23	− 12.65	− 12.70	− 0.35	− 0.40	− 0.35	− 0.40
C	3	1	4	90 125.00	90 410.45	7.53	7.37	0.22	0.06	0.22	0.06
C	0	7	2	89 036.01	90 506.91	− 28.36	− 28.34	0.46	0.48	0.46	0.48

TABLE V. Calculated emission probabilities in 10^7 s^{-1} and measured line intensities.

	v'	J'	v''	Without coupling A_P	A_R	With coupling Matrix A_P	A_R	Direct A_P	A_R	Experiment[a] I_P	I_R
B	27	4	2	1.808	1.365	1.274	1.800	1.159	2.022	2.0	3.0
B	27	3	2	1.856	1.332	1.301	1.807	1.210	1.979	5.0	7.0
B	27	2	9	1.084	0.727	1.051	0.652	1.016	0.690	3.8	2.5
B	27	1	1	1.741	0.920	1.366	1.307	1.341	1.347	2.0	2.0
B	24	3	1	2.124	1.740	2.049	1.812	1.992	1.893	4.0	4.0
B	22	2	1	2.801	1.949	2.539	2.208	2.516	2.242	29.0	14.0
B	21	2	1	3.083	2.120	3.675	1.617	3.657	1.636	47.0	11.5
B	20	4	5	1.008	0.405	0.856	0.504	0.846	0.520	6.0	2.8
B	20	2	1	3.355	2.277	2.888	2.744	2.878	2.761	16.0	10.0
B	19	4	1	3.335	2.675	4.271	1.984	4.260	2.003	11.0	5.0
B	19	3	4	2.345	1.749	2.105	2.062	2.105	2.065	3.3	3.3
B	18	3	4	2.441	1.678	1.983	2.072	1.982	2.072	6.5	5.5
B	18	3	6	1.180	1.255	0.791	1.631	0.791	1.629	1.5	2.9
B	17	4	3	1.389	1.579	1.512	1.533	1.510	1.532	3.5	3.2
B	17	2	3	1.579	1.293	1.538	1.350	1.537	1.350	115.0	105.0
B	16	6	4	1.800	0.817	1.543	0.991	1.541	0.985	5.0	3.0
B	16	4	1	3.650	2.658	2.523	3.724	2.530	3.720	26.0	30.0
B	14	2	3	3.592	2.422	2.176	2.804	2.176	2.801	16.0	22.0
B	14	2	4	0.472	0.140	2.509	0.449	2.510	0.450	38.0	6.5
B	14	1	3[b]	4.006	2.019	3.600	0.964	3.600	0.964	13.5	4.0
B	12	4	2[b]	1.522	1.820	0.014	5.139	0.014	5.129	0.0	38.0
B	12	3	1	2.070	1.158	0.897	2.165	0.894	2.168	11.5	28.5
B	11	4	2	2.750	2.804	2.086	3.505	2.092	3.496	17.0	23.0
B	11	3	1	1.271	0.608	1.130	0.739	1.126	0.741	40.0	22.0
B	11	2	2	3.036	2.337	2.607	2.778	2.610	2.775	14.0	15.0
B	11	2	4	1.361	1.258	1.092	1.542	1.092	1.541	16.0	21.2
B	10	6	0	7.574	6.808	2.897	11.463	2.896	11.468	28.0	41.0
B	10	4	4	2.849	2.926	0.720	6.532	0.720	6.532	2.8	22.0
B	8	6	3	0.308	1.069	2.294	9.292	2.295	9.295	1.7	5.0
B	7	3	1	1.279	1.436	0.857	1.938	0.856	1.936	6.0	11.0
B	7	1	3	2.832	1.636	2.885	1.562	2.884	1.562	22.0	11.5
B	6	8	1	3.618	4.851	2.719	5.694	2.719	5.691	22.0	10.0
B	6	6	0	9.369	7.442	7.913	8.879	7.913	8.879	4.0	3.2
B	4	2	2	0.470	0.560	0.431	0.599	0.431	0.599	10.0	17.0
B	3	9	1	11.858	10.224	10.657	11.486	10.659	11.486	1.8	2.0
C	12	2	2	0.539	0.786	1.490	1.216	1.322	1.316	1.5	1.5
C	11	4	2	0.778	0.887	1.839	1.469	1.638	1.641	2.0	2.0
C	10	3	2	0.892	1.062	2.226	1.704	2.105	1.786	10.0	3.0
C	9	5	2	0.967	0.873	1.795	1.717	1.714	1.860	15.0	8.0
C	9	2	2	0.844	1.115	2.235	1.713	2.176	1.745	19.0	14.0
C	8	4	1	1.580	2.065	4.446	2.767	4.388	2.805	10.0	5.0
C	8	1	1	1.223	2.486	3.985	3.168	3.958	3.175	7.0	6.0
C	7	4	1	1.919	2.384	6.104	2.305	6.050	2.319	25.0	7.0
C	7	3	6	1.162	1.816	1.597	2.508	1.635	2.536	5.5	6.5
C	7	2	2	0.419	0.436	0.065	1.763	0.063	1.803	0.0	22.0
C	7	1	2	0.330	0.531	0.369	1.350	0.366	1.361	1.5	5.0
C	7	1	3	0.358	0.869	0.906	1.505	0.912	1.495	12.0	16.0
C	7	1	6	0.963	2.062	2.328	3.638	2.331	3.626	2.5	3.8
C	6	3	1	2.053	2.589	3.178	5.736	3.169	5.773	23.0	25.0
C	6	1	3	0.961	2.078	2.205	3.862	2.211	3.854	42.0	76.0
C	5	4	6	0.580	0.193	1.337	0.339	1.336	0.335	3.0	0.5
C	5	3	5	1.841	2.720	4.643	4.341	4.639	4.336	75.0	57.0
C	5	2	2	0.063	0.224	0.209	0.336	0.210	0.333	12.5	18.0
C	5	2	6	0.410	0.293	1.049	0.435	1.050	0.434	9.3	3.5
C	5	1	6	0.299	0.383	0.741	0.655	0.741	0.654	3.5	3.0
C	4	2	2	0.896	1.677	2.177	2.865	2.178	2.861	10.5	12.5
C	4	1	1	0.934	1.664	2.385	2.838	2.385	2.840	30.0	23.0
C	4	1	5	1.537	2.751	3.548	4.962	3.547	4.962	20.0	26.0
C	3	4	1	0.326	0.135	0.960	0.110	0.961	0.111	23.0	3.0
C	3	2	5	0.032	0.223	0.089	1.342	0.088	1.341	1.5	17.5
C	3	1	4[b]	2.548	5.103	5.513	5.627	5.513	5.628	137.0	130.0
C	0	7	2	8.610	10.557	17.263	19.918	17.264	19.919	54.0	40.0

[a] Peak heights of photometric trace, in arbitrary unit. The intensities of different sets of lines are not always comparable, due to the use of different detectors.

[b] Levels, respectively, labeled $C(3,1)$, $C(2,4)$, and $B(14,1)$ by Dabrowski (Ref. 6).

TABLE VI. Ratios of emission probabilities of P and R lines calculated from Hönl–London factors (HL), without coupling (NC), with matrix method (M), and with direct method (D). Experimental ratios are given in the last column.

	v'	J'	v''	HL	NC	M	D	Expt.
B	27	4	2	1.250	1.325	0.708	0.573	0.7
B	27	3	2	1.333	1.393	0.720	0.612	0.7
B	27	2	9	1.500	1.492	1.611	1.473	1.5
B	27	1	1	2.000	1.893	1.045	0.996	1.0
B	24	3	1	1.333	1.221	1.130	1.052	1.0
B	22	2	1	1.500	1.437	1.150	1.122	2.1
B	21	2	1	1.500	1.454	2.272	2.235	4.1
B	20	4	5	1.250	2.491	1.698	1.627	2.1
B	20	2	1	1.500	1.473	1.052	1.042	1.6
B	19	4	1	1.250	1.246	2.153	2.127	2.2
B	19	3	4	1.333	1.341	1.021	1.019	1.0
B	18	3	4	1.333	1.454	0.957	0.956	1.2
B	18	3	6	1.333	0.941	0.485	0.486	0.5
B	17	4	3	1.250	0.880	0.986	0.986	1.1
B	17	2	3	1.500	1.221	1.140	1.138	1.1
B	16	6	4	1.167	2.202	1.557	1.565	1.7
B	16	4	1	1.250	1.373	0.677	0.680	0.9
B	14	2	3	1.500	1.483	0.776	0.777	0.7
B	14	2	4	1.500	3.358	5.586	5.579	5.8
B	14	1	3	2.000	1.984	3.733	3.736	3.4
B	12	4	2	1.250	0.836	0.003	0.003	0.0
B	12	3	1	1.333	1.788	0.415	0.412	0.4
B	11	4	2	1.250	0.981	0.595	0.599	0.7
B	11	3	1	1.333	2.089	1.529	1.519	1.8
B	11	2	2	1.500	1.299	0.938	0.941	0.9
B	11	2	4	1.500	1.081	0.708	0.709	0.8
B	10	6	0	1.167	1.113	0.253	0.253	0.7
B	10	4	4	1.250	0.974	0.110	0.110	0.1
B	8	6	3	1.167	0.288	0.247	0.247	0.3
B	7	3	1	1.333	0.891	0.442	0.442	0.5
B	7	1	3	2.000	1.730	1.847	1.846	1.9
B	6	8	1	1.125	0.746	0.477	0.478	2.2
B	6	6	0	1.167	1.259	0.891	0.891	1.3
B	4	2	2	1.500	0.841	0.720	0.719	0.6
B	3	9	1	1.111	1.160	0.928	0.928	0.9
C	12	2	2	0.667	0.685	1.226	1.004	1.0
C	11	4	2	0.800	0.877	1.252	0.998	1.0
C	10	3	2	0.750	0.840	1.306	1.179	3.3
C	9	5	2	0.833	1.107	1.046	0.922	1.9
C	9	2	2	0.667	0.757	1.305	1.247	1.4
C	8	4	1	0.800	0.765	1.607	1.564	2.0
C	8	1	1	0.500	0.492	1.258	1.247	1.2
C	7	4	1	0.800	0.805	2.648	2.609	3.6
C	7	3	6	0.750	0.640	0.637	0.645	0.8
C	7	2	2	0.667	0.960	0.037	0.035	0.0
C	7	1	2	0.500	0.622	0.273	0.269	0.3
C	7	1	3	0.500	0.412	0.602	0.610	0.8
C	7	1	6	0.500	0.467	0.640	0.643	0.7
C	6	3	1	0.750	0.793	0.554	0.549	0.9
C	6	1	3	0.500	0.462	0.571	0.574	0.6
C	5	4	6	0.800	3.008	3.940	3.983	6.0
C	5	3	5	0.750	0.677	1.070	1.070	1.3
C	5	2	2	0.667	0.279	0.622	0.631	0.7
C	5	2	6	0.667	1.398	2.410	2.420	2.7
C	5	1	6	0.500	0.780	1.131	1.134	1.2
C	4	2	2	0.667	0.534	0.760	0.761	0.8
C	4	1	1	0.500	0.561	0.841	0.840	1.3
C	4	1	5	0.500	0.559	0.715	0.715	0.8
C	3	4	1	0.800	2.415	8.731	8.676	7.7
C	3	2	5	0.667	0.141	0.066	0.066	0.1
C	3	1	4	0.500	0.499	0.980	0.980	1.1
C	0	7	2	0.875	0.816	0.867	0.867	1.4

two levels, each of them going smoothly from a B character $n_B = 1$, to a C character $n_B = 0$. The discontinuity of labeling appears only when $n_B = n_C = 0.5$. Figure 1(b) shows the corresponding continuous evolution of the emission probabilities A_P and A_R towards $v'' = 2$. We notice that A_p and A_R cancel once each when the labeling is B, producing two peaks for the logarithmic representation of A_P/A_R in Fig. 1(c). To see the effect of the coupling we can compare in Fig. 1(c) the values of $\log_{10}(A_P/A_R)$ to -0.078 and -0.025 obtained without coupling and to 0.097 and -0.097 when using the Höln–London factors for B and C, respectively.

VII. CONCLUSION

The good agreement between calculation and experiment shows the effect of rotational coupling on intensity calculation. As it appears in Fig. 1, the effect is noticeable even
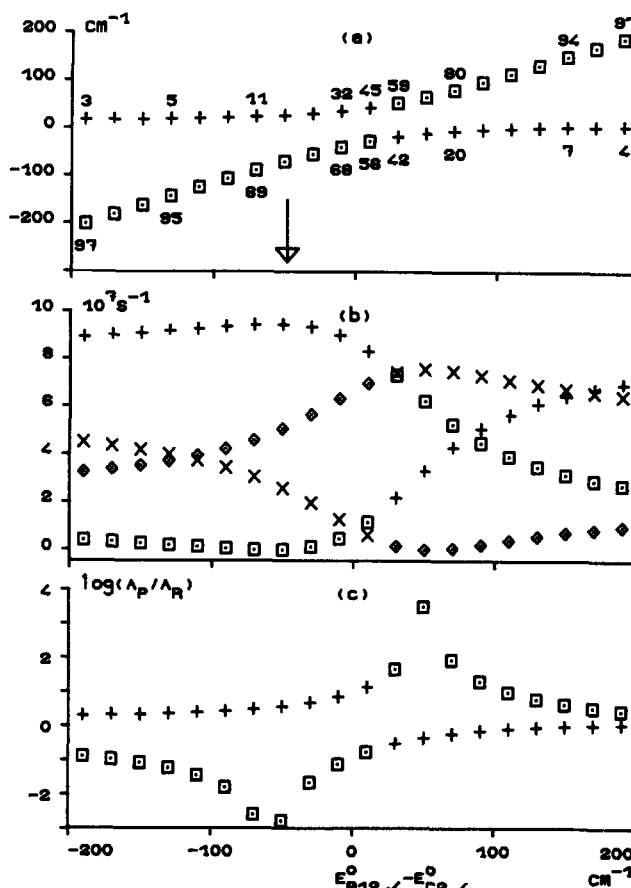

FIG. 1. V_B is translated vertically and V_C remained unchanged to show possible effects of rotational coupling on level positions and emission probabilities when we vary $E^0_{B\,12,4} - E^0_{C\,2,4}$ across 0. The calculation is made with the direct method and includes implicitly the weaker influence of all other zero order vibrational states. The vertical arrow corresponds to the realistic position of V_B used in the present calculations. (a) Level energy shift: for some points we have written the percentage of B character which determines the label. $\square$ and $+$ represent, respectively, $E_{B\,12,4} - E^0_{C\,2,4}$ and $E_{C\,2,4} - E^0_{C\,2,4}$. (b) Emission probabilities from $B(12,4)$ and $C(2,4)$ towards $v'' = 2$: $\square$ and $\diamondsuit$, respectively, for A_P and A_R when the label is B, $+$ and $\times$: respectively, for A_P and A_R when the label is C. (c) $\log_{10}(A_P/A_R)$: $\square$ when the label is B and $+$ when it is C.

if zero order states do not coincide and our calculation clearly defines a level as B or C. This phenomenon is extensively described by Lefebvre-Brion and Field.[36]

The present calculations have been restricted to the coupling between the two lower-lying electronic potential curves related to the states $B\,^1\Sigma_u^+$ and $C\,^1\Pi_u$. However, coupling to other higher-lying electronic states should also be taken into account, particularly for the high excited rovibronic levels of B and C.

ACKNOWLEDGMENTS

[1]A. L. Broadfoot, B. R. Sandel, D. E. Shemansky, J. C. McConnell, G. R. Smith, J. B. Holberg, S. K. Atreya, T. M. Donahue, D. F. Strobel, and J. L. Bertaux, J. Geophys. Res. **86**, 8259 (1981).

[2]A. L. Broadfoot, F. Herbert, J. B. Holberg, D. M. Hunten, S. Kumar, B. R. Sandel, D. E. Shemansky, G. R. Smith, R. V. Yelle, D. F. Strobel, H. W. Moos, T. M. Donahue, S. K. Atreya, J. L. Bertaux, J. E. Blamont, J. C. McConnell, A. J. Dessler, S. Linick, and R. Springer, Science **233**, 74 (1986).

[3]J. M. Ajello, D. E. Shemansky, T. L. Kwok, and Y. L. Yung, Phys. Rev. A **29**, 636 (1984).

[4]D. C. Morton and H. L. Dinerstein, Astrophys. J. **204**, 1 (1976).

[5]Y. P. Viala, Astron. Astrophys. Suppl. Ser. **64**, 391 (1986).

[6]I. Dabrowski, Can. J. Phys. **62**, 1639 (1984).

[7]J.-Y. Roncin, F. Launay, and M. Larzilliére, Can. J. Phys. **62**, 1686 (1984).

[8]M. Larsson, Astron. Astrophys. **128**, 291 (1983).

[9]E. E. Whiting, A. Schadee, J. B. Tatun, J. T. Hougen, and R. W. Nicholls, J. Mol. Spectrosc. **80**, 249 (1980).

[10]A. Schadee, J. Quant. Spectrosc. Radiat. Transfer **19**, 451 (1978).

[11]A. C. Allison and A. Dalgarno, At. Data **1**, 289 (1970).

[12]A. L. Ford, J. Mol. Spectrosc. **53**, 364 (1974).

[13]P. S. Julienne, J. Mol. Spectrosc. **48**, 508 (1973).

[14]A. L. Ford, J. Mol. Spectrosc. **56**, 251 (1975).

[15]W. Fabian and B. R. Lewis, J. Quant. Spectros. Radiat. Transfer **14**, 523 (1974).

[16]H. Schmoranzer and J. Geiger, J. Chem. Phys. **59**, 6153 (1973).

[17]J. M. Brown, J. T. Hougen, K. P. Huber, J. W. C. Johns, I. Kopp, H. Lefebvre-Brion, A. J. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, J. Mol. Spectrosc. **55**, 500 (1975).

[18]J. M. Blatt, J. Comput. Phys. **1**, 382 (1967).

[19]I. H. K. Aldeen, A. C. Allison, and M. J. Jamieson, Mol. Phys. **36**, 931 (1978).

[20]M. Glass-Maujean, P. Quadrelli, and K. Dressler, At. Data Nucl. Data Tables **30**, 273 (1984).

[21]B. R. Johnson, J. Chem. Phys. **69**, 4679 (1978).

[22]W. C. Stwalley, J. Chem. Phys. **58**, 536 (1973).

[23]D. M. Bishop and S. K. Shih, J. Chem. Phys. **64**, 162 (1976).

[24]W. Kolos and L. Wolniewicz, Can. J. Phys. **53**, 2189 (1975).

[25]W. Kolos, Int. J. Quant. Chem. **9**, 133 (1975).

[26]T. L. Stephens and A. Dalgarno, J. Quant. Spectrosc. Rad. Transfer **12**, 569 (1972).

[27]T. L. Stephens and A. Dalgarno, Mol. Phys. **28**, 1049 (1974).

[28]W. Kolos and J. Rychleski, J. Mol. Spectrosc. **62**, 109 (1976).

[29]A. L. Ford, E. M. Greenawalt, and J. C. Browne, J. Chem. Phys. **67**, 983 (1977).

[30]K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, 1979).

[31]P. G. Wilkinson, Can. J. Phys. **46**, 1225 (1968), G. Herzberg and L. L. Howe, Can. J. Phys. **37**, 636 (1959), T. Namioka, J. Chem. Phys. **41**, 2141 (1964), W. C. Stwalley, Chem. Phys. Lett. **6**, 241 (1970), quoted in Ref. 22.

[32]K. Dressler and L. Wolniewicz, J. Chem. Phys. **82**, 4720 (1985).

[33]H. M. Crosswhite, *The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke* (Wiley, New York, 1972).

[34]C. Jungen and O. Atabek, J. Chem. Phys. **66**, 5584 (1977).

[35]F. Launay and F. Rostas (to be published).

[36]H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, New York, 1986).

[37]*Note added in proof:* While the present work was under completion we were aware of the recent calculation of potential energies by Dressler and Wolniewicz [J. Chem. Phys. **85**, 2821 (1986)]. We have checked that, by adjusting their values to experimental data, the matrix method does not lead to significant differences so that the conclusions drawn from Table VI stay the same.