

Vibration-Rotation Interaction Effects in Calculated Franck-Condon Factors. II. Hydrogen Lyman and Fulcher Bands*

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Calculated Franck-Condon factors, explicitly including previously neglected vibration-rotation interaction effects, are reported for 450 Lyman and 24 Fulcher bands of the hydrogen molecule. Large cancellation effects, depending on rotational quantum number, are found for a number of Lyman bands. Where comparison is possible, the results show good qualitative agreement with experimentally determined intensity distributions. Using alternative representations of the $B\ ^1\Sigma_u^+$ potential curve (upper state of the Lyman bands) it is shown that the calculated intensity distribution for some bands are highly sensitive to detailed features of the molecular potential curves.

INTRODUCTION

In a recent communication we reported some unusually large vibration-rotation interaction effects in calculated Franck-Condon factors for the H_2 Lyman bands.¹ In a subsequent paper similar, though quantitatively smaller, variations were reported in calculations pertinent to the ionization of H_2 and D_2 .² It is the purpose of the present paper to amplify the preliminary report concerning the Lyman bands and, in addition, to report results for the H_2 Fulcher bands.

When the centrifugal potential is explicitly taken into account the Franck-Condon factor appropriate to the electronic transition $(v', J') \rightarrow (v'', J'')$ is given by

$$q(v', J'; v'', J'') = \left| \int \phi'_{v'J'}(R) \phi''_{v''J''}(R) dR \right|^2, \quad (1)$$

where $\phi'_{v'J'}(R)$ and $\phi''_{v''J''}(R)$ are eigenfunctions of the nuclear motion for the two states. For $^1\Sigma$ states, the eigenfunctions are solutions of the Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \phi_{vJ}}{dR^2} + \left[V(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] \phi_{vJ} = E_{vJ} \phi_{vJ}, \quad (2)$$

in which μ is the molecular reduced mass and E_{vJ} is the energy eigenvalue appropriate to ϕ_{vJ} . Previous computations for the Lyman bands, whether based on the use of Morse potential functions^{3,4} or on potential curves constructed by the Rydberg-Klein-Rees method,⁵ have not included the effects of the centrifugal potential. That is, it has been tacitly assumed that the *principal* effect of the rotational energy is a shift of the potential curve by a constant energy displacement.⁶

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¹ D. Villarejo, R. Stockbauer, and M. G. Ingram, Chem. Phys. Letters **2**, 11 (1968).

² D. Villarejo, "Vibration-Rotation Interaction Effects in Calculated Franck-Condon Factors. I. Ionization of H_2 and D_2 ," J. Chem. Phys. (to be published).

³ R. W. Nicholls, Astrophys. J. **141**, 819 (1965).

⁴ M. Halmann and I. Laulicht, J. Chem. Phys. **44**, 2398 (1966).

⁵ M. Halmann and I. Laulicht, J. Chem. Phys. **46**, 2684 (1967).

⁶ G. E. Gibson, O. K. Rice, and N. S. Bayliss, Phys. Rev. **44**, 193 (1933). While these authors recognize that inclusion of the exact centrifugal energy leads to a slight distortion of the potential curve, they argue that this effect is negligible.

This assumption, equivalent to the rigid-rotator approximation, is most severely tested in calculations of Franck-Condon factors for electronic transitions of light molecules, and especially if the transition involves states with appreciably different potential curves.⁷ Not only are the $B\ ^1\Sigma_u^+$ (excited-state) and the $X\ ^1\Sigma_g^+$ (ground-state) curves of the Lyman system quite different but, since this is a Σ - Σ transition, only P and R branches occur. The rotational angular momentum necessarily changes in all transitions of the spectrum tending to emphasize further vibration-rotation interaction effects. By way of contrast, the Fulcher bands arise from the transition $d\ ^3\Pi_u \rightarrow a\ ^3\Sigma_g^+$ for which the potential curves are quite similar.⁸ For this band system somewhat smaller vibration-rotation interaction effects in intensities are expected. Previous computations have not included the centrifugal potential.⁹

METHOD

Solutions of the Schrödinger equation were obtained by replacing Eq. (2) with the equivalent finite difference equation which is solved numerically by a computer procedure. The computer program we have used is discussed in Ref. 2. For all of the computed Franck-Condon factors we have used an integration step length of 0.005 atomic units. Inner and outer integration limits for Eq. (1) were specified consistent with accuracy in the result. These are summarized in Table I where we also indicate the range of (v', v'') values for which computations have been completed. Since results were obtained for several hundred bands of the Lyman system and, except for a few bands, included 17 lines for each band, it proved convenient to have the computer punch the results on cards as well as list them in the output. A separate program, called SORT, uses these cards as input and will command a partial or complete listing in any specified order. Photographic copies of

⁷ R. C. M. Learner, Proc. Roy. Soc. (London) **A269**, 311 (1962).

⁸ Compare, for example, the published molecular constants in G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950), 2nd ed., pp. 530-531.

⁹ W. C. Price, Proc. Roy. Soc. (London) **A136**, 264 (1932).

the complete listing are available.¹⁰ It is believed that by using this procedure the possibility of manual copying errors has been eliminated. Because computations for the Fulcher bands involved only a few bands, this procedure was not used.

Potential functions for the $B^1\Sigma_u^+$ (upper) and the $X^1\Sigma_g^+$ (lower) electronic states of the Lyman system were those calculated theoretically by Kołos and Wolniewicz and include the diagonal corrections for nuclear motion.¹¹ That is, the present work is carried out in the adiabatic approximation as distinct from the clamped-nucleus, or Born-Oppenheimer, approximation. It should be noted that a previous calculation of Franck-Condon factors for the Lyman bands,⁵ which did not include the effects of the centrifugal potential, was based on potential functions constructed from the experimental data using the Rydberg-Klein-Rees method.¹² While the theoretical adiabatic and the RKR curves for the $X^1\Sigma_g^+$ ground state are in excellent agreement, the corresponding curves for the $B^1\Sigma_u^+$ state are known to differ somewhat, particularly in the region of small internuclear separation.¹³ In a completely separate calculation we have computed Franck-Condon factors for selected Lyman bands, including vibration-rotation interaction effects, using the RKR curve for the B state. The comparison of these results with those obtained using the theoretical adiabatic curve for the B state is discussed in a later section of this paper. However, it should be noted that the RKR curve shows a defect at the innermost turning points which casts doubts on its reliability for vibrational states near the dissociation limit. For these highly excited vibrational levels the inner turning points exhibit an anomalous increase in value with increasing vibrational quantum number. This physically unreasonable result would appear to be related to uncertainties in the experi-

TABLE I. Limits of integration for the Lyman bands.

	Inner limit	Outer limit
$v'=0-19; v''=0-13$	0.35 a.u.	10.00 a.u.
$v'=20-29; v''=0-14$	0.35 a.u.	15.30 a.u.
$v'=0; v''=14$	0.35 a.u.	15.30 a.u.
Limits of integration for the Fulcher bands		
$v'=0-3; v''=0-5$	0.50 a.u.	10.00 a.u.

¹⁰ Tables are being deposited as Document NAPS-00163 at ASIS National Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N.Y.; please remit \$1.00 for microfiche and \$3.00 for photocopies.

¹¹ W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663 (1964); **43**, 2429 (1965); **45**, 509 (1966).

¹² For the $B^1\Sigma_u^+$ state see T. Namioka, *J. Chem. Phys.* **43**, 1636 (1965).

¹³ See the discussion in W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **45**, 509 (1966). Possible limitations of the adiabatic approach for the $B^1\Sigma_u^+$ state are further discussed elsewhere: W. Kołos and L. Wolniewicz (unpublished).

TABLE II. Spectroscopic constants used to construct RKR potential curve, $d^3\Pi_u^-$ state.

Rotational constants ^a	Vibrational constants ^b
$B_e=30.364 \text{ cm}^{-1}$	$\omega_e=2373.18 \text{ cm}^{-1}$
$\alpha_e=1.545$	$\omega_e x_e=66.324$
$\gamma_e=0.00131$	$\omega_e y_e=0.903$
	$\omega_e z_e=0.029$

^a B_e and α_e values obtained from G. H. Dieke and R. W. Blue, *Phys. Rev.* **47**, 261 (1935). The γ_e value was estimated by analysis of the energy levels for this state listed in G. H. Dieke, *J. Mol. Spectry.* **2**, 494 (1955).

^b Obtained from O. W. Richardson, *Molecular Hydrogen and Its Spectra*, (Yale University Press, New Haven, Conn., 1934), p. 361. Richardson gives an expression for A_e in powers of v . This expression was transformed to the more usual $G(v)$ to obtain the constants listed above. These constants differ slightly from those reported by Dieke and Blue.

mental data upon which the method is based.¹⁴ To overcome this defect we have modified the RKR curve by fitting an analytic power law to that portion of the curve corresponding to lower v' states and extrapolating that function through the uncertain portion.

In the case of the Fulcher bands we have used the theoretical adiabatic potential calculated by Kołos and Wolniewicz¹⁵ for the $a^3\Sigma_g^+$ state while for the $d^3\Pi_u^-$ state it proved necessary to construct a potential curve using the RKR method.¹⁶ The spectroscopic constants used in this calculation are listed in Table II and the potential curve constructed in this manner is shown in Fig. 1. Also shown in this figure is the curve for the $a^3\Sigma_g^+$ state. By contrast with the Lyman system, for which both upper and lower states are Σ states, the upper state of the Fulcher bands is a Π state. For this system there will be Q branches as well as P and R branches. Moreover, although the states are triplet states, we make the identification $J \rightarrow K$ where K is the quantum number of the total molecular angular momentum excluding spin (case b coupling). For the Π state it is necessary to supplement the centrifugal term in Eq. (2) with the additional term $-\Lambda^2 \hbar^2 / 2\mu R^2$ with $\Lambda = 1$.

RESULTS

The principal results of this work are contained in tables of Franck-Condon factors for 450 bands of the Lyman system and 24 bands of the Fulcher system.¹⁰ Selected results are shown in Tables II-V. The quantities shown for each entry are a decimal number and an integer. The integer is the power of 10 by which the decimal number is to be multiplied. The dominant

¹⁴ This point has been emphasized by M. L. Ginter and R. Battino, *J. Chem. Phys.* **42**, 3222 (1965).

¹⁵ W. Kołos and L. Wolniewicz (unpublished). We thank Professors Kołos and Wolniewicz for making these results available to us in advance of publication.

¹⁶ Spectroscopic data appropriate to the $^3\Pi_u^-$ component of the d state was used in this computation since it is known that $^3\Pi_u^-$ component levels are perturbed by the $b^3\Sigma_u^+$ state.

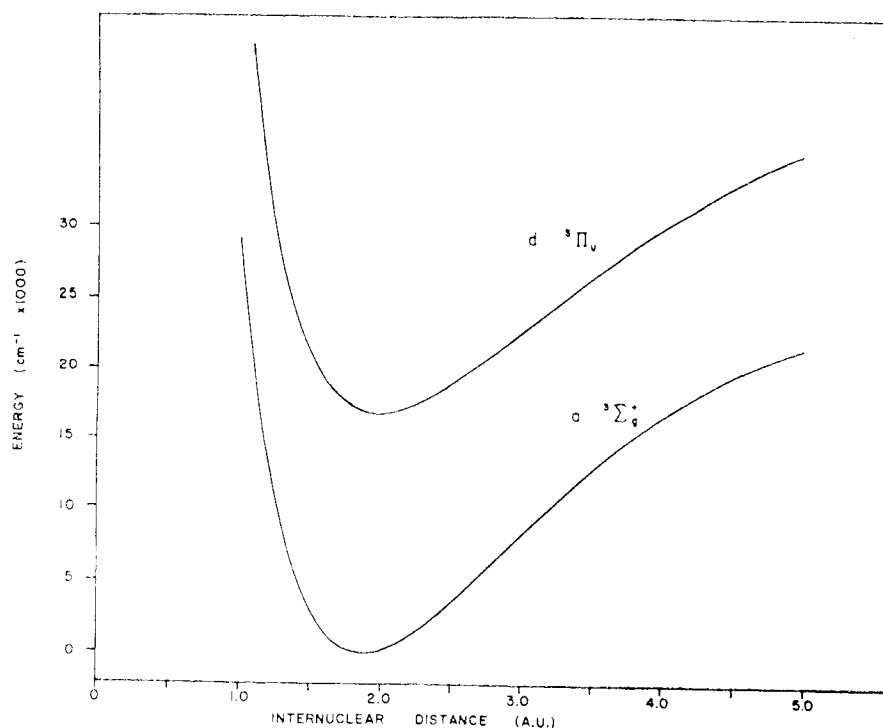


FIG. 1. Potential curves for the Fulcher bands of H_2 . The $d\ ^3\Pi_u$ curve was constructed by the RKR procedure in the present work while the $a\ ^3\Sigma_u^+$ curve is that calculated theoretically by Kolos and Wolniewicz.

influence of vibration-rotation interaction in the results for a number of the Lyman bands is well illustrated by reference to Fig. 2 where the value of the overlap integral for each of nine P branch lines of the 7-12 band is plotted as a function of J'' . The overlap integral is seen to decrease with increasing rotational quantum number and actually changes sign when J'' increases from 6 to 7. With further increase of J'' up to 9, the largest value used in the present calculation, the integral becomes more negative. Because the Franck-Condon factor is equal to the square of the overlap integral, this variation with J'' will manifest itself as a rapid decrease in the Franck-Condon factor followed

by a subsequent rapid increase. This is illustrated in Table III where the results for the 7-12 band are listed and compared with similar results for the 7-11 and 7-13 bands. The two-order-of-magnitude variation in calculated Franck-Condon factor obtained in both 7-11 and 7-12 P -branch lines is easily recognized as simply a cancellation effect. That is, the integral in Eq. (1) passes through a zero (changes sign) as a function of increasing J'' .

Large cancellation effects, of one order of magnitude or more, are obtained for roughly one-fourth of the Lyman bands for which calculations have been completed. Some examples with $v'=6$, namely the 6-4, 6-6, and 6-10 bands, were discussed previously.¹ In all of

TABLE III. Franck-Condon factors for P -branch lines of selected Lyman bands.

J	7-11 band	7-12 band	7-13 band
0			
1	7.383-3	2.794-2	3.018-1
2	5.543-3	2.435-2	3.288-1
3	3.666-3	1.901-2	3.621-1
4	1.961-3	1.220-2	3.956-1
5	6.712-4	5.033-3	4.173-1
6	3.542-5	2.570-4	4.069-1
7	2.094-4	3.323-3	3.364-1
8	1.109-3	2.314-2	a
9	2.200-3	7.006-2	a

a Not calculated.

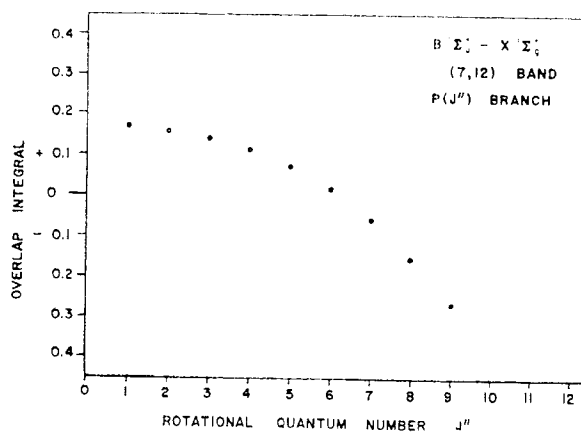


FIG. 2. Variation of the Franck-Condon overlap integral for the 7-12 Lyman band P branch with rotational quantum number: J'' .

the cases where these large effects are found the variation of the calculated Franck-Condon factors with increasing rotational quantum number is both smooth and systematic as in the examples discussed above.

By way of contrast with these results for the Lyman system, calculated Franck-Condon factors for the Fulcher system show only a small effect of vibration-rotation interaction. This is illustrated in Table VI where results for the 3-3 and 3-4 Fulcher bands are listed. In these examples, which are typical of the calculated results for this band system, variations of only 25%-50% are obtained. As in the case of the results for the Lyman system, the dependence of the result on increasing rotation quantum number is smooth and systematic. The very different magnitudes of vibration-rotation interaction effects obtained in the calculated Franck-Condon factors for these two-band systems is further discussed in a later section of this paper.

As mentioned previously, the theoretical adiabatic potential curve for the $B^1\Sigma_u^+$ state we have used in the Lyman band calculations differs somewhat from the potential curve constructed from the experimental data by the Rydberg-Klein-Rees method. This uncertainty in the B state is important only for the inner limit of the potential curve ($R < R_e$). However, because the equilibrium internuclear separation of the ground state is about 1.40 a.u. while that of the B state is 2.44 a.u., it is precisely the small R portion of the upper-state

TABLE IV. Franck-Condon factors for some bands of the Fulcher system.

K	$R(K)$	3-3 band	
		$Q(K)$	$P(K)$
0	5.409-1
1	5.265-1	5.550-1	...
2	5.120-1	5.546-1	5.830-1
3	4.975-1	5.539-1	5.963-1
4	4.830-1	5.530-1	6.091-1
5	4.686-1	5.518-1	6.213-1
6	...	5.502-1	6.327-1
7	6.434-1
		3-4 band	
0	2.790-1
1	2.877-1	2.704-1	...
2	2.963-1	2.706-1	2.533-1
3	3.050-1	2.709-1	2.451-1
4	3.136-1	2.714-1	2.374-1
5	3.221-1	2.720-1	2.297-1
6	...	2.729-1	2.226-1
7	2.159-1

TABLE V. Comparison of Franck-Condon factors for Lyman system using alternative representations of potential curve for $B^1\Sigma_u^+$ state.

J	Theoretical adiabatic potential		Rydberg-Klein-Rees potential	
	$P(J)$	$R(J)$	$P(J)$	$R(J)$
	6-8 band			
0	...	4.435-3	...	8.430-3
1	2.767-3	5.376-3	6.710-3	9.582-3
2	2.062-3	6.360-3	5.100-3	1.072-2
3	1.451-3	7.359-3	4.090-3	1.180-2
4	9.373-4	8.335-3	3.151-3	1.280-2
5	5.242-4	9.239-3	2.294-3	1.367-2
6	2.194-4	1.002-2	1.533-3	1.436-2
7	3.836-5	1.060-2	8.848-4	1.481-2
8	1.005-5	...	3.802-4	...
9	1.834-4	...	6.677-5	...
	Rigid-rotator approximation using RKR potential curves: 6.954-3 (Ref. 17)			
	6-6 band			
0	...	7.115-4	...	2.684-3
1	1.975-4	1.148-3	1.572-3	3.419-3
2	7.646-5	1.729-3	1.172-3	4.281-3
3	1.708-5	2.468-3	8.596-4	5.273-3
4	4.319-8	3.368-3	6.200-4	6.388-3
5	9.429-6	4.424-3	4.396-4	7.616-3
6	3.332-5	5.619-3	3.057-4	8.935-3
7	6.403-5	6.922-3	2.067-4	1.031-2
8	9.790-5	...	1.333-4	...
9	1.351-4	...	7.817-5	...
	Rigid-rotator approximation using RKR potential curve: 2.017-3 (Ref. 17)			

curve that plays a crucial role in determining the relevant overlap integrals. This is shown in Fig. 3 where the two potential curves are plotted. Clearly, it is the inner limb of the upper-state potential curve which lies within the Franck-Condon region for all vibrational states of the ground electronic state. We have calculated some Franck-Condon factors for bands of the Lyman system using the RKR curve for the excited state. A few of these results are listed in Table V where they are compared with those obtained using the theoretical adiabatic potential curve for the excited state. In addition, we show results obtained by Halmann and Laulicht which were calculated using RKR potential curves appropriate to nonrotating mole-

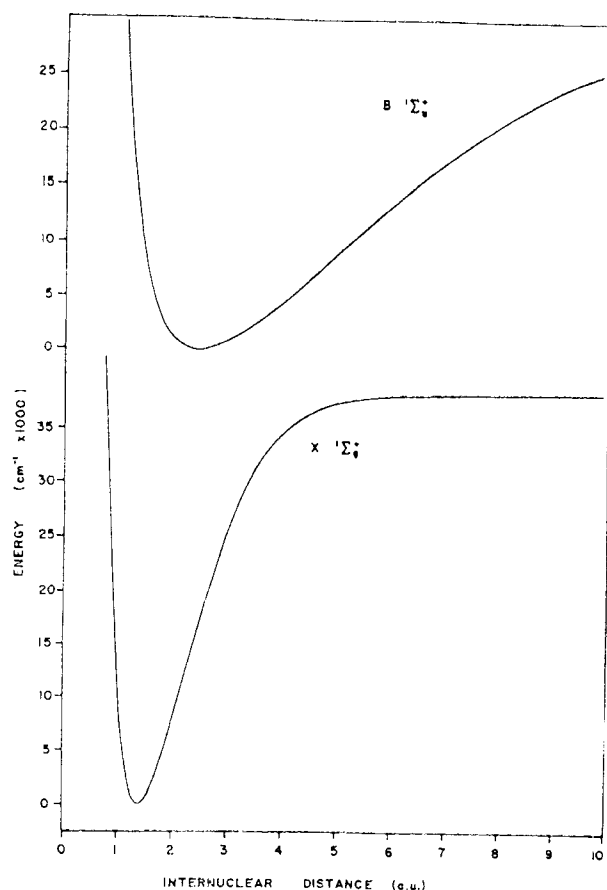


Fig. 3. Potential curves for the $B^1\Sigma_u^+$ and $X^1\Sigma_g^+$ state of H_2 . The upper curve position relative to the lower state has been altered to clarify the presentation. In fact, the minima are separated by about $91\,700\text{ cm}^{-1}$.

cules.¹⁷ Great differences in calculated Franck-Condon factors resulting from the use of alternative representations of the $B^1\Sigma_u^+$ state are evident as is the very different variation of these factors with increasing rotational quantum number. This latter feature might prove to be useful in determining which of several slightly different potential functions most adequately describes a given state, as in the present case. To illustrate this large sensitivity we note that the ratio of Franck-Condon factors for the $P(1)$ and $P(3)$ branch lines is nearly 2 when using the RKR curve for the B state but is larger than 11 when the theoretical adiabatic curve is used. A similar large effect for P -branch lines of the 6-10 band was noted in the earlier communication.¹

ACCURACY OF THE RESULTS

It is possible to infer conclusions concerning the accuracy of the calculated Franck-Condon factors in

¹⁷ M. Halmann and I. Laulicht, "Supplementary Material to: Isotope Effects on Franck-Condon Factors. VII. Vibrational Intensity Distributions in H_2 Lyman, H_2 Werner, O_2 Schumann-Runge, N_2 First Positive, N_2 Vegard-Kaplan, and $LiH(A-X)$ Systems Based on RKR Potentials. Tables of Franck-Condon Factors." Document No. 9287, ADI Auxiliary Publications Project, Library of Congress, Washington, D.C. 20225.

several ways. First, energy levels as well as eigenfunctions have been computed. These may be compared with other accurate calculations. Second, several tests have been carried out which permit one to estimate the magnitude of errors resulting from the use of the approximate numerical integration technique. Finally, from comparison of the computed results obtained using alternative representations of the molecular potential functions, it is possible to infer the order of magnitude of errors attributable to uncertainties in the potential curves.

With regard to the accuracy of the computed energy levels, we show in Table VI some eigenvalues obtained in this work together with the results of another accurate calculation. Small differences are noted amounting to 1 cm^{-1} , or less, in most cases. It is believed that these differences likely reflect different computational procedures.¹⁸

TABLE VI. Computed energy levels in hydrogen (binding energy with respect to the dissociation limit).

J'	This work	Kolos and Wolniewicz ^a
	$B^1\Sigma_u^+, v'=0$	
	cm^{-1}	
0	-28 167.34	-28 167.29
1	28 128.23	28 128.16
2	28 050.40	28.050.28
3	27 934.61	27 934.42
4	27 781.97	27 781.70
5	27 593.93	27 593.54
6	27 372.16	27 371.66
7	27 118.61	27 117.96
8	26 835.34	26 834.54
	$a^2\Sigma_u^-, v'=0$	
0	-23 297.85	-23 297.38
1	23 231.21	23 230.71
2	23 098.46	23 097.89
3	22 900.63	22 899.96
4	22 639.26	22 638.46
5	22 316.30	22 315.35
6	21 934.13	21 933.00
7	21 495.47	21 494.14

^a W. Kolos and L. Wolniewicz, "Tables of Vibrational and Rotational Energies for the $B^1\Sigma_u^+$, $C^1\Pi_u$, and $a^2\Sigma_u^-$ States of the Hydrogen Molecule" (unpublished).

¹⁸ As a point of interest we note that we have used $m_p/m_e = 1836.09$ while Kolos and Wolniewicz used the value 1836.12. In a trial computation for H_2^+ we used a value of m_p/m_e differing by 6 parts in 10^8 from the latter value and obtain a shift in the binding energy of the $v'=0, J'=0$ state of 0.22 cm^{-1} while the energy of the $v'=9, J'=0$ state was shifted by 0.47 cm^{-1} . Possible uncertainties in this fundamental ratio may in fact contribute small errors to the final result.

The computational method has been tested in several ways. With fixed integration step length the outer integration limit of 10.00 a.u. was extended to 15.00 a.u. for some transitions of the Lyman system involving (v' , v'') in the range (0-19, 0-13). Except for transitions involving rotational states of $v'' = 13$ very near to the dissociation limit, none of the calculated Franck-Condon factors differed by as much as 0.5% from the values computed with the smaller outer limit of integration. In a separate test, the limits of integration were kept fixed and the integration step length was doubled to 0.010 a.u. Selected results for the Lyman bands are shown in Table VII. These computations, as well as similar test calculations for this system published previously, suggest that inaccuracies attributable to the numerical approximation scheme are likely of order 1%, or less, in the most unfavorable cases and very likely smaller in most of the results for the Lyman system. Since the calculations for the Fulcher system pertain only to low-lying vibrational states, it is likely that the computational accuracy is greater for these bands.

The greatest single source of uncertainty in this work is in the potential curves actually used for the $B^1\Sigma_u^+$ state and for the $d^3\Pi_u$ state. From the comparison of the calculated Franck-Condon factors using, separately, two alternative representations of the B -state curve, it is evident that uncertainties in the results for some lines of some of the Lyman bands may be as great as several orders of magnitude. Typically, though, the uncertainty is a good bit smaller. Nevertheless, as is clear in Table V, cancellation effects, attributable to vibration-rotation interaction, are present independent of which curve is actually used. For the d state of the Fulcher bands, theoretical potential curves are not yet available. As a consequence, uncertainties are limited at present by the accuracy of the RKR curve we have constructed. However, because of the great similarity of the d - and

TABLE VII. Selected Franck-Condon factors of the Lyman system calculated with differing integration step length.

Band	$P(3)$ -branch lines	
	$\Delta R = 0.005$ a.u.	$\Delta R = 0.010$ a.u.
(0, 6)	1.388-1	1.388-1
(6, 6)	1.708-5	1.709-5
(20, 6)	1.505-3	1.505-3
(25, 6)	5.508-3	5.508-3
(29, 6)	9.363-3	9.363-3
(6, 14)	4.550-2	4.550-2
(20, 14)	8.296-3	8.296-3
(22, 14)	1.253-3	1.253-3
(25, 14)	6.013-3	6.013-3
(26, 14)	3.870-6	3.882-6
(27, 14)	2.980-3	2.980-3
(29, 14)	1.017-3	1.071-3

TABLE VIII. Calculated band strengths and experimental intensities for the (v' , 0) Lyman bands.

Band	This work (adiabatic) ^a	Exptl. ^b	This work (RKR) ^c	Ref. 17 ^d
(1, 0)	0.179	0.25	0.173	0.175
(3, 0)	0.580	0.60	0.566	0.576
(5, 0)	0.906	0.98	0.892	0.895
(7, 0)	1.000	0.92	1.000	1.000
(9, 0)	0.911	0.69	0.930	0.925
(11, 0)	0.739	0.50	0.779	0.770
(13, 0)	0.560	0.36	0.613	0.603
(15, 0)	0.407	0.22	0.465	0.455
(17, 0)	0.288	0.10	0.346	0.341
(19, 0)	0.202	0.06	0.254	...

^a Based on calculated Franck-Condon factors using a theoretical adiabatic potential curve for the $B^1\Sigma_u^+$ state.

^b Reference 20. Normalized so that (6, 0) band intensity is equal to 1.00.

^c Based on calculated Franck-Condon factors using an RKR potential curve for the $B^1\Sigma_u^+$ state.

^d Based on calculated Franck-Condon factors using RKR potential curves for nonrotating states of the molecule.

a -state curves, small uncertainties in the equilibrium constants will likely lead to comparatively small uncertainties in the calculated Franck-Condon factors.

COMPARISON WITH EXPERIMENT

The calculated results for the Lyman bands are of particular interest even though experimental determinations of relative line intensities are not available. The analysis of these bands, as observed in emission, presents some difficulties. Herzberg and Howe's extensive study of this band system included wavelength determinations for several hundred lines which they were unable to assign.¹⁹ It is possible that these difficulties are related to the unusual intensity patterns predicted by taking account of vibration-rotation interaction. For those bands which are now only partially analyzed, there is a good correlation with the results of the present calculation. For example, a large cancellation effect is calculated for both P and R branch lines of the 8-13 band. The predicted intensity pattern indicates very small Franck-Condon factors for those lines with small J'' but much larger factors at higher J'' values. The analysis of Ref. 19 shows just $R(3)$ and $P(4)$ identified.

An additional comparison of our results for the Lyman system with experiment is possible. The relative intensity of twenty (v' , 0) bands have been measured by electron-impact spectroscopy.²⁰ None of these bands show an appreciable cancellation effect in the present calculation. Band strengths, based on a room-temperature (300°K.) distribution of H_2 rotational states, are shown in Table VIII along with the experimental

¹⁹ G. Herzberg and L. L. Howe, Can. J. Phys. 37, 636 (1959).

²⁰ J. Geiger and M. Topschowsky, Z. Naturforsch. 21a, 626 (1966).

TABLE IX. Relative intensities of $R(K-1)$ and $P(K+1)$ lines of some Fulcher bands.

Band	K	Exptl.*	Ratio of line strengths	This work
(0, 0)	4	0.85	1.25	1.22
	6	0.74	1.17	1.13
(1, 1)	2	1.35	1.50	1.43
(2, 2)	1	1.55	2.00	1.90
	2	1.08	1.50	1.38
	4	0.82	1.25	1.08
(3, 3)	1	1.51	2.00	1.86
	2	1.00	1.50	1.32
	3	0.84	1.33	1.12

* Reference 21. A more recent unpublished determination shows some small differences from these results. This is discussed more fully in Ref. 22 which also contains data for five additional line pairs.

results. Also shown are band strengths calculated by us which are based on the RKR potential curve for the $B^1\Sigma_u^+$ state as well as results which do not include vibration-rotation interaction effects. The relative Franck-Condon factors based on the theoretical adiabatic potential curves agree better with the measured intensities than do the calculated results based on the RKR curve. Nevertheless, there is a substantial systematic disagreement between the results of the Franck-Condon model and experiment, especially at high vibrational quantum numbers. Possible alternative theoretical descriptions are discussed in a later section of this paper.

In the case of the Fulcher bands a direct comparison of the calculated results with experimental determination for some individual lines is possible. Ginsburg and Dieke have made extensive intensity measurements of a large number of lines of the H_2 Fulcher-band system.²¹ These measurements were extended to the D_2 Fulcher bands using modern techniques by Dimock who also repeated many of the earlier measurements in H_2 .²² The principal result of these investigations was the finding that for virtually all lines of these band systems the observed intensities could not be related in a simple way to the predictions of the elementary theory. In large part these departures from the theoretical model were attributable to complex excitation and de-excitation mechanisms active in the gas discharge used to excite the desired spectrum. To circumvent this diffi-

culty measurements were made of the ratio of intensities of $R(J-1)$ and $P(J+1)$ lines of selected bands. Since these lines originate in the same upper level, the ratio of the observed intensities are expected to be independent of discharge conditions (i.e., population and de-activation mechanisms). For some ten cases this was found to be true while in other cases unresolved blends evidently contributed to an irregular dependence on discharge conditions.²¹ Under the assumption that the Franck-Condon factors are identical for all lines of a given band (rigid-rotator approximation), the intensity ratios considered should be given by the ratio of the corresponding line strengths, or Honl-London formulas

$$I[R(J-1)]/I[P(J+1)] = (J+1)/J, \quad (3)$$

where we have ignored the ν^4 frequency factor for lines of a definite band. In none of the ten cases mentioned above did the experimental ratios agree with Eq. (3). By taking account of vibration-rotation interaction the results of the present paper show that it is necessary to modify Eq. (3) to the form

$$\frac{I[R(J-1)]}{I[P(J+1)]} = \frac{J+1}{J} \frac{q(v', J; v'', J-1)}{q(v', J; v'', J+1)}. \quad (4)$$

The experimental ratios are compared with the predictions of Eq. (3) in Table IX. All of the measured ratios are smaller than the ratios indicated from Eq. (3). This is in good qualitative agreement with the fact that the corresponding ratios of the calculated Franck-Condon factors are less than unity. On the other hand, the measured intensity ratio is still somewhat smaller than what is expected from the use of Eq. (4). Though the discrepancy is only in the range of 6%-50% between the Franck-Condon model predictions based on our calculations and the experimental determinations, it appears that, as for the Lyman bands, this simple model will not account for the observations.

DISCUSSION

The fact that substantial cancellation effects are found for the Lyman bands but not for the Fulcher bands may be understood within the framework of the semiempirical discussion of Ref. 2. That is, addition of the exact centrifugal potential to the molecular potential appropriate to the nonrotating molecule leads to an effective potential with a minimum displaced to larger internuclear separations. The magnitude of this displacement was found to be $(\alpha_e/\omega_e)K(K+1)R_e$, where K is the rotational quantum number and the other constants have their usual significance.²³ For an electronic transition one expects an appreciable can-

²¹ N. Ginsburg and G. H. Dieke, Phys. Rev. **59**, 632 (1941).
²² D. L. Dimock, "The Intensity Distribution in Some Bands of Deuterium," thesis, Johns Hopkins University, 1957 (unpublished).

²³ These quantities are defined and discussed in Ref. 8.

cancellation effect in intensities if the *relative* displacement of the minima of the potential curves of the two states is an appreciable fraction of the molecular de Broglie wavelength. From the discussion this relative displacement of the minima is given by

$$\delta R = (\alpha_e'/\omega_e') K'(K'+1) R_e' - (\alpha_e''/\omega_e'') K''(K''+1) R_e'', \quad (5)$$

which leads to

$$\delta R = K''(K''+1) [(\alpha_e'/\omega_e') R_e' - (\alpha_e''/\omega_e'') R_e''] \\ + \begin{cases} 2(K''+1)(\alpha_e'/\omega_e') R_e' & \text{R branch} \\ 0 & \text{Q branch} \\ -2K''(\alpha_e'/\omega_e') R_e' & \text{P branch.} \end{cases} \quad (6)$$

Unless the potential curves are quite similar the coefficient of the term quadratic in K'' will control the variation of δR with increasing K'' . In the case of the Fulcher bands the potential curves are similar and the bracketed difference is given by

Fulcher bands:

$$(\alpha_e'/\omega_e') R_e' - (\alpha_e''/\omega_e'') R_e'' \cong 1.1 \times 10^{-4} \text{ a.u.}, \quad (7)$$

while for the Lyman bands this quantity is

Lyman bands:

$$(\alpha_e'/\omega_e') R_e' - (\alpha_e''/\omega_e'') R_e'' \cong 1.3 \times 10^{-3} \text{ a.u.}, \quad (8)$$

more than a factor of 11 larger.

To examine this criterion more closely we compare, for both band systems, the shift in minima calculated from Eq. (6) with a typical de Broglie wavelength. For $v''=3$ of the H_2 ground electronic state the de Broglie wavelength is roughly 0.64 a.u. From Eq. (6) the δR value corresponding to R(6) branch lines of the Lyman system is about 0.089 a.u., an appreciable fraction of a wavelength [this amounts to a shift of the relative phase of eigenfunctions of about $(2/7)\pi$]. For higher v'' levels, corresponding to smaller de Broglie wavelengths, an even larger phase shift is obtained. On the other hand, consider the Fulcher-band system. For $v''=3$ of the $a^3\Sigma_g^+$ state the de Broglie wavelength is about 0.74 a.u. and the δR values corresponding to P(6), Q(6), and R(6) branch lines are -0.010 , $+0.003$, and $+0.023$ a.u., respectively. These δR values are a much smaller fraction of a wavelength and a cancellation effect is not expected at low rotational quantum numbers. Also, from the very small δR value for the Q branch lines one expects that Franck-Condon factors for Fulcher-band Q-branch lines will be nearly inde-

pendent of rotational quantum number. This is in excellent agreement with the calculated results.

Using the criterion discussed above it is possible to examine experimental molecular constants and suggest other band systems of H_2 as well as band systems of other molecules in which vibration-rotation interaction effects on intensities may be significant. Some systems expected on this basis to exhibit cancellation effects of this kind are the $\text{H}_2 f \rightarrow a$, $\text{AlH } A \leftrightarrow X$, $\text{CH}^+ A \rightarrow X$, $\text{LiH } A \leftrightarrow X$, $\text{NH } c \rightarrow a$, and $\text{TlH } c \rightarrow X$ bands. It is likely that other band systems of hydride molecules, for which α_e values have not been determined, also show these unusual intensity distributions.

While the preceding discussion provides a straightforward basis for understanding the significant features of the calculated Franck-Condon factors, it is suggested that comparison of these results with experiment will not, by itself, constitute a quantitative test of departures from the Franck-Condon principle. That is, states of the appropriate symmetry severely perturb the $B^1\Sigma_u^+$ and $d^3\Pi_u$ (plus component) states.^{24,25} The influence of these perturbations on the intensity distribution is not, at present, known and could be significant. This point has been previously suggested to account for the departure of the intensities observed in the Fulcher bands from the simple theoretical model.²² As yet there have not been calculations to check this possibility.

We wish to point out that the cancellation effects in calculated Franck-Condon factors discussed in this paper are precisely of the form discussed by Condon and referred to as "internal diffraction" by him.²⁶ The present work can be regarded as an extension of this idea by including previously neglected vibration-rotation interaction effects which are important in light molecules.

As a final point it should be noted that in this work we have discussed the calculation of the distribution of intensity in molecular band systems in the limit of a strictly valid Franck-Condon principle, i.e., the molecular electronic dipole moment does not depend on internuclear separation. It is known that this is not strictly true and that, in fact, there may well be an appreciable variation with internuclear distance in some systems. James has considered this situation and has derived results which show that small variations of dipole moment with internuclear distance tend to be amplified if vibration-rotation interaction effects are appreciable.²⁷ Applied to the present work, if $\mu(R)$ represents the dipole moment function, then expansion of $\mu(R)$

²⁴ For the $B^1\Sigma_u^+$ state see A. Monfils, Acad. Roy. Belg. Bull. Classe Sci. **47**, 585 (1961); and also T. Namioka, J. Chem. Phys. **40**, 3154 (1964).

²⁵ For the $d^3\Sigma_g^+$ state see O. W. Richardson and K. Das, Proc. Roy. Soc. (London) **A122**, 688 (1929), and also G. H. Dieke and R. W. Blue, Phys. Rev. **47**, 261 (1935).

²⁶ E. U. Condon, Am. J. Phys. **15**, 365 (1947).

²⁷ T. C. James, J. Chem. Phys. **32**, 1770 (1960).

around $R=0$ leads to

$$\begin{aligned} & \int \phi'_{\nu'J'}(R)\mu(R)\phi''_{\nu''J''}(R)dR \\ & = \mu_0 \int \phi'_{\nu'J'}(R)\phi''_{\nu''J''}(R)dR \\ & + \mu_1 \int \phi'_{\nu'J'}(R)R\phi''_{\nu''J''}(R)dR + \dots \quad (9) \end{aligned}$$

Clearly, if the overlap integral (first term) vanishes, or is very small, then the higher-order terms involving μ_1 , etc., will dominate. It is the function of the present paper to point out that the overlap integral may in fact vanish for reasons that have not been previously suspected. A more complete theoretical treatment will necessarily involve inclusion of an explicit dipole moment function as well the effect of perturbations mentioned previously.