

LARGE VIBRATION-ROTATION INTERACTION EFFECTS IN CALCULATED FRANCK-CONDON FACTORS *

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Calculated Franck-Condon factors for the Lyman bands of H_2 are reported which include the previously neglected vibration-rotation interaction effects. Unexpectedly large cancellation effects are found for a number of bands.

* It is generally assumed that vibration-rotation interaction can be neglected in computing Franck-Condon overlap integrals appropriate to electronic transitions in molecules [1]. This assumption is based on the simple physical idea that the *principal* effect of the centrifugal potential can be understood in terms of the rigid rotator approximation. That is, in lowest order, the effect of rotation is merely to shift the potential energy by a constant energy displacement [2]**. However, recent calculations of Franck-Condon factors explicitly including the centrifugal energy have shown, in the case of OH [3] and RbH [4], an appreciable dependence on rotational quantum number (variations of roughly a factor of 2 to a factor of 5 were found). These effects are expected to be particularly large for transitions involving molecules of low reduced mass between appreciably different potential functions [3]. It is the purpose of the present communication to report some extraordinarily large vibration-rotation interaction effects in computed Franck-Condon factors for the Lyman bands of the H_2 molecule. Since the Lyman bands arise from a $\Sigma-\Sigma$ transition, only P and R branches occur and the rotational angular momentum necessarily changes in all transitions of the spectrum. Thus, vibration-rotation interaction effects might be expected to be especially large. Previously re-

ported computations for this system have not included the effects of rotation [5].

The radial equation for nuclear motion of a rotating diatomic molecule in a 1Σ state may be written in the form

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

where the explicit dependence of the wave function on both vibrational and rotational quantum numbers has been developed. The Franck-Condon factor appropriate to the electronic transition $(v', J') \rightarrow (v'', J'')$ is given by the quantity (using single and double primes to refer to the different electronic states)

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

Eigenfunctions of eq. (1) have been obtained for both the $B^1\Sigma_u^+$ (upper) state and the $X^1\Sigma_g^+$ (lower) state of the hydrogen molecule and eq. (2) was then used to compute the appropriate factors. We have used Cooley's method [6] to replace eq. (1) by a difference equation which may be solved numerically. The potential functions $V(R)$ and $V''(R)$ for the B and X states respectively, were those obtained theoretically by Kolos and Wolniewicz [7] and explicitly include diagonal corrections for the nuclear motion. That is, the so-called *adiabatic* potential curves were used and not the Born-Oppenheimer (clamped nucleus) approximation curves. In all of the computations an integration step length of 0.005 atomic units was used and an outer integration limit of 15,000 a.u. could be used when required. Thus, up to 3000 integration points could be included.

Franck-Condon factors were computed for

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** While the authors of ref. [2] recognize that inclusion of the exact centrifugal energy leads to a slight distortion of the potential curve, they argue that this effect is negligible.

Table 1
Computed Franck-Condon factors for Lyman bands of H₂

<i>J</i>	6-0 Band		6-4 Band		6-6 Band	
	<i>P</i> (<i>J</i>)	<i>R</i> (<i>J</i>)	<i>P</i> (<i>J</i>)	<i>R</i> (<i>J</i>)	<i>P</i> (<i>J</i>)	<i>R</i> (<i>J</i>)
0		7.850 -2		1.803 -3		7.115 -4
1	7.998 -2 *	7.760 -2	2.850 -3	1.267 -3	1.975 -4	1.148 -3
2	8.055 -2	7.659 -2	3.293 -3	7.753 -4	7.646 -5	1.729 -3
3	8.101 -2	7.546 -2	3.646 -3	3.720 -4	1.708 -5	2.468 -3
4	8.136 -2	7.422 -2	3.893 -3	1.000 -4	4.319 -8	3.368 -3
5	8.159 -2	7.287 -2	4.024 -3	8.163 -9	9.429 -6	4.424 -3
6	8.170 -2	7.141 -2	4.038 -3	1.067 -4	3.332 -5	5.619 -3
7	8.169 -2	6.984 -2	3.941 -3	4.459 -4	6.403 -5	6.922 -3
8	8.154 -2		3.747 -3		9.790 -5	
9	8.125 -2		3.475 -3		1.351 -4	

* Figures in this column indicate power of ten by which figure in preceding column is to be multiplied.

450 bands of the Lyman system and, except in a very few cases, include factors appropriate to nine P branch lines and eight R branch lines for each band. A few of these results are shown in table 1. The calculations for the 6-0 band show only a small effect due to vibration-rotation interaction. In contrast, the R branch of the 6-4 band and the P branch of the 6-6 band exhibit extremely large variations with increasing rotational quantum numbers: changes of up to *four orders of magnitude* are obtained. Moreover, the variation with increasing rotational quantum number is smooth and systematic as is the case for other bands of the Lyman system where this effect is found. The accuracy of these results has been tested in a variety of ways. One test is illustrated in table 2 where the effect on the cal-

culated Franck-Condon factor for some R(5) branch lines of doubling the integration step length ΔR is shown (this also halves the number of integration points for fixed integration limits). Only the smallest factor shows a significant effect due to this change and in this case it amounts to 1%. Further tests of the accuracy will be reported in a later publication.

In this discussion it is important to note that our results lead to the conclusion that the structure of some of the Lyman bands will be rather unusual as observed, say, in emission spectroscopy. Comparison of our calculated results with the analysis of the Lyman bands reported by Herzberg and Howe [8] shows a good correlation with identified lines in specific bands. Thus, they report only the P(2), P(3) and R(1), R(3) lines of

Table 2
Test calculations: integration step length: adiabatic versus RKR potential

Band	R(5) Branch lines		<i>J</i>	6-10 Band, P Branch lines	
	$\Delta R = 0.005$ a.u.	$\Delta R = 0.010$ a.u.		Adiabatic	RKR
(0, 4)	2.356 -1	2.356 -1	1	1.008 -3	3.568 -3
(2, 4)	1.416 -2	1.416 -2	2	4.279 -4	2.374 -3
(4, 4)	6.279 -2	6.279 -2	3	6.210 -5	1.277 -3
(6, 0)	7.287 -2	7.287 -2	4	4.512 -5	4.286 -4
(6, 4)	8.163 -9	8.087 -9	5	5.360 -4	1.272 -5
(6, 8)	9.239 -3	9.239 -3	6	1.716 -3	2.463 -4
(6, 13)	2.960 -1	2.960 -1	7	3.773 -3	1.369 -3
(11, 8)	1.170 -5	1.172 -5	8	6.857 -3	3.606 -3
(11, 13)	1.447 -5	1.449 -5	9	1.098 -2	7.073 -3

the 6-6 band while for the 6-7 band, calculated by us to show only a very small vibration-rotation interaction effect in intensities, they identified seven P branch lines and seven R branch lines. In addition, these authors report wavelength measurements for several hundred lines which they were unable to assign. We suggest that these difficulties are related to the unusual band intensity patterns predicted by taking into account rotation-vibration interactions.

The sensitivity of this cancellation effect to the detailed features of the potential $V(R)$ is also illustrated in table 2 where Franck-Condon factors for P branch lines of the 6-10 band are shown. These results were calculated using the previously discussed theoretical adiabatic potential curve for the $B^1\Sigma_u^+$ state and, separately, using the "experimental" potential curve for this state constructed by the Rydberg-Klein-Rees method [9]. The two curves are somewhat different, especially in the region of small internuclear separation*. As is evident, the calculated Franck-Condon factors for the 6-10 band are quite different and, in addition, show a greatly different variation with increasing rotational quantum number. Thus, the ratio of these factors for the P(1) and P(3) lines is about 16 when the theoretical adiabatic curve is used, but only 3 for the RKR curve. The great sensitivity of these cancellation effects to the exact form of the molecular potential function might prove to be useful in distinguishing between different alternatives as in the case of the $B^1\Sigma_u^+$ state of H_2 .

These effects have a rather straightforward interpretation. In the framework of the harmonic oscillator approximation it has been shown that a principal effect of vibration-rotation interaction is to shift the minimum of the potential function to larger R values as a function of increasing rotational quantum number [11]. Very approximately, this is given by

$$R_J \cong R_e \left(1 + \frac{4B_e^2}{\omega_e^2} J(J+1) \right) \quad (3)$$

for low rotational quantum numbers. This shift will result in displacement of the radial coordi-

nates of the nodes of a given vibrational eigenfunction. Because the overlap integral, see eq. (2), is sensitive to the relative node position (or relative phase) of the two eigenfunctions, an appreciable effect is expected whenever $4B_e^2/\omega_e^2$ is large as in the case of H_2 . This sensitivity of the value of the integral to the relative position of the nodes and loops of the two eigenfunctions was first recognized by Condon who referred to it as "internal diffraction" although he did not consider the effect of rotation in detail.

Finally, it is important to note that comparison of these computed Franck-Condon factors with experimental determinations of line strengths will not necessarily constitute a quantitative test of deviations from the Franck-Condon principle. That is, some levels of the $B^1\Sigma_u^+$ state are known to be perturbed by levels of the appropriate symmetry of the $C^1\Pi_u$ state [12] and the influence of this perturbation on intensities will also have to be taken into account.

References

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* See especially the discussion by Kolos and Wolniewicz [10]. Possible limitations of the adiabatic approach for the $B^1\Sigma_u^+$ state will be further discussed in a future publication by Kolos and Wolniewicz.