

Vibration-Rotation Interaction Effects in Calculated Franck-Condon Factors. I. The Ionization of H_2 and D_2 *

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Computed Franck-Condon factors for the ionization of H_2 and D_2 are reported which include previously neglected vibration-rotation interaction effects. Eigenfunctions were obtained by direct solution of the Schrödinger equation in which the exact centrifugal potential is explicitly included. Only $v''=0$ and small K'' states of the neutral molecule have been considered and attention is confined to those transitions for which $|K''-K|=0, 2$. The results show a clear dependence of the computed Franck-Condon factor on rotational quantum number. For $K''=K$, this effect is small except for transitions to the uppermost vibrational states of the ion. For $|K''-K|=2$, the effect is substantial even for transitions to low-lying vibrational states of the ion. By using a sum rule, it is shown that the probability of dissociative ionization exhibits a similar dependence on rotational state. Comparison of the present results for the case $K''=K=0$ with previous computation shows that adiabatic corrections for nuclear motion, explicitly included in this work, have a wholly negligible influence on computed Franck-Condon factors.

INTRODUCTION

It has been the common practice to ignore vibration-rotation interaction effects in the calculation of Franck-Condon factors appropriate to electronic transitions in molecules.¹ The assumption that such effects are small is based on the simple physical idea that the rigid-rotator approximation adequately describes the main effect of the centrifugal potential, a shift of the potential energy by an additive constant.² Learner and Gaydon were the first to explicitly show the error resulting from neglect of the centrifugal distortion of the potential curve in analyzing the spectrum of OH.³ More recently, Learner has extended these calculations for OH using approximate eigenfunctions of the rotating Morse oscillator and obtained an appreciable influence of the vibration-rotation interaction.⁴ Similar effects have also been reported in computations for the RbH molecule.⁵ Such departures from the rigid-rotator approximation might be expected to be particularly large for band systems of the H_2 molecule owing to the small reduced mass of this molecule. In a recent communication, we reported some extremely large vibration-rotation interaction effects in calculated Franck-Condon factors for a number of bands of the H_2 Lyman system.⁶

It is the purpose of this paper to report computations of Franck-Condon factors for the ionization of H_2 and D_2 which explicitly include the effects of the exact centrifugal potential. Previous calculations have been

based on potential curves appropriate to nonrotating molecules.⁷⁻¹⁰ These factors are also of interest in connection with recent experimental studies of vibronic structure in H_2 and D_2 ionization.¹¹⁻¹³

METHOD

The radial equation for nuclear motion in the case of H_2^+ has been discussed elsewhere¹⁴ and is

$$-(d^2\phi_{vk}/dR^2) + \{ (M_p/M_e)[1 + (M_e/2M_p)] [E_e(R) + R^{-1} - E_{vk}] + [K(K+1)/R^2] + g_{00}(R) \} \phi_{vk} = 0, \quad (1)$$

where the electronic energy $E_e(R)$ and the nuclear repulsion energy $1/R$ are supplemented by the diagonal correction for nuclear motion $g_{00}(R)$ and by the centrifugal energy. The dependence of the eigenvalues E_{vk} and eigenfunctions ϕ_{vk} on both vibrational and rotational quantum numbers has been explicitly indicated. By including the diagonal corrections for the nuclear motion, the present work is carried out in the adiabatic approximation as distinct from the clamped nucleus (Born-Oppenheimer) approximation used by previous authors.⁹⁻¹⁰ Values of $E_e(R)$ and of the exact diagonal correction term $g_{00}(R)$ were obtained from the tables of Hunter *et al.*¹⁵ A previous computation of the eigenvalues of Eq. (1) included $g_{00}(R)$ values based on approximate electronic eigenfunctions of H_2^+ .¹⁴ Solutions of Eq. (1) for D_2^+ were obtained by replacing M_p with M_D .

The equation appropriate to H_2 has been fully dis-

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¹ See, for example, G. Herzberg, *Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950), 2nd ed., Vol. 1, p. 203.

² G. E. Gibson, O. K. Rice, and N. S. Bayliss, *Phys. Rev.* **44**, 193 (1933).

³ R. C. M. Learner and A. G. Gaydon, *Nature* **183**, 242 (1959).

⁴ R. C. M. Learner, *Proc. Roy. Soc. (London)* **A269**, 311 (1962).

⁵ D. C. Jain and R. C. Sahni, *Proc. Phys. Soc. (London)* **88**, 495 (1966).

⁶ D. Villarejo, R. Stockbauer, and M. G. Inghram, *Chem. Phys. Letters* **2**, 11 (1968).

⁷ M. E. Wacks, *J. Res. Natl. Bur. Std.* **A68**, 631 (1964).

⁸ M. Halman and I. Laulicht, *J. Chem. Phys.* **43**, 1503 (1965).

⁹ G. H. Dunn, *J. Chem. Phys.* **44**, 2592 (1966).

¹⁰ S. Rothenberg and E. R. Davidson, *J. Mol. Spectry.* **22**, 1 (1967).

¹¹ D. W. Turner and D. P. May, *J. Chem. Phys.* **45**, 471 (1966).

¹² J. W. McGowan, M. A. Fineman, E. M. Clarke, and H. P. Hanson, *Phys. Rev.* **167**, 52 (1968). This paper reviews both photon impact and electron impact studies of H_2 ionization.

¹³ D. Villarejo, *J. Chem. Phys.* **48**, 4014 (1968).

¹⁴ H. Wind, *J. Chem. Phys.* **43**, 2956 (1965). We use essentially the same notation as Wind.

¹⁵ G. Hunter, B. F. Gray, and H. O. Pritchard, *J. Chem. Phys.* **45**, 3806 (1966).

TABLE I. Range of integration and step length.

		R_i	R_0	ΔR
H_2^+	$v' = 0-9$	0.35 a.u.	10.00 a.u.	0.005 a.u.
	10-18	0.35	20.00	0.010
	19	0.35	45.00	0.015
D_2^+	$v' = 0-9$	0.35	10.00	0.005
	10-19	0.35	15.00	0.005
	20-25	0.35	30.00	0.010
	26	0.35	45.00	0.015

discussed by Wolniewicz.¹⁶ We have used the clamped nucleus potential calculated by Kolos and Wolniewicz¹⁷ and the diagonal corrections for nuclear motion separately calculated by the same authors.¹⁸ Solutions for D_2 were obtained by scaling the nuclear motion corrections in accordance with the proton-deuteron mass ratio. In all of the present work, we have used $M_p/M_e = 1836.09$.

Eigenfunctions for the states of the molecular ion $\phi_{v'k'}$ and for the states of the neutral molecule $\phi_{v''k''}$ were obtained by solution of the relevant equation using a numerical technique originally developed by Cooley.¹⁹ Zare modified Cooley's procedure for use in a computer program for the calculation of Franck-Condon factors.²⁰ The program we have used is based on simple extensions of Zare's ideas. Franck-Condon factors were calculated from these eigenfunctions according to the expression

$$q(v', K; v'', K'') = \left| \int_{R_i}^{R_0} \phi_{v'k'}(R) \phi_{v''k''}(R) dR \right|^2, \quad (2)$$

where the inner and outer limits of integration, R_i and R_0 , respectively, are chosen to be consistent with the desired accuracy of the result. In the present work, results are reported for $v''=0$ and all v' . Table I shows a summary of the values of R_0 , R_i , and of the integration step length ΔR used in the present work.

RESULTS

The principal results of this calculation are presented in Tables II and III which show the values of $q(v', K; 0, K'')$ for the ionization of H_2 and D_2 , respectively. Only those transitions are considered for which $|K - K''| = 0, 2$ in accordance with the prohibition of

¹⁶ L. Wolniewicz, J. Chem. Phys. **45**, 515 (1966).

¹⁷ W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).

¹⁸ W. Kolos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).

Since this work includes nuclear motion corrections for internuclear separations in the range $0.6 \text{ a.u.} \leq R \leq 3.7 \text{ a.u.}$, while Ref. 17 gives values of the clamped-nucleus potential in the range $0.4 \text{ a.u.} \leq R \leq 10.0 \text{ a.u.}$, it was necessary to use analytic curve fits to obtain $g_{00}(R)$ values for the full range of R . For the region $3.7 \text{ a.u.} \leq R \leq 10.0 \text{ a.u.}$, a fit of the form $g_{00}(R) = A/R^n$ was assumed. By fitting this expression to the values at 3.6 and 3.7 a.u., one obtains $n = 4.922$, $A = 4.060 \times 10^8 \text{ cm}^{-1}$. Note that our usage of $g_{00}(R)$ corresponds to ΔD_{nuc} as used by Kolos and Wolniewicz.

¹⁹ J. W. Cooley, Math. Computation **15**, 363 (1961).

²⁰ R. N. Zare, UCRL-10925, 1963.

ortho-para conversion in optically allowed transitions.²¹ Also shown in the tables are values of $q(v', 0; 0, 0)$ calculated by some other authors. There is an appreciable variation of the computed q 's with rotational quantum number. This variation is only negligible for those transitions with $K''=K$, but even in this case becomes significant for transitions involving the largest v' values. It should be noted that differences between calculated Franck-Condon factors for transitions with $|K''-K|=2$ and those calculated for the case $|K''-K|=0$ are appreciable even for $v'=0$. Also, the effect is larger in H_2 ionization than for D_2 ionization.

Rothenberg and Davidson's values of $q(v', 0; 0, 0)$ for H_2 ionization shown in Table II are based on the clamped nucleus (Born-Oppenheimer) approximation.¹⁰ That is, the only difference between potential curves used by them and the curves used in the present work is our inclusion of the small diagonal corrections for nuclear motion (adiabatic approximation). The very close agreement between the two sets of results for $q(v', 0; 0, 0)$ shows that, for this case, the inclusion of the nuclear motion corrections has a wholly negligible influence on the calculated Franck-Condon factors.

Dunn has calculated $q(v', 0; 0, 0)$ for D_2 ionization as well as for H_2 ionization using a modified Morse potential for the ground state of the neutral and the clamped nucleus potential for the ion.⁹ His results, shown in Table III, differ slightly from the results presented in this paper. The magnitude of these differences is roughly the same as for the comparison of his results with the two sets of results for H_2 ionization. It is likely that this discrepancy may be attributed to the slight differences in potential curves used in the two calculations.

By summing the $q(v', K; 0, K'')$ over all discrete states v' for fixed (K, K'') pairs, one can obtain indirect information about the probability of dissociative ionization. This latter quantity can be obtained using the sum rule

$$\sum_{v'} q(v', K; 0, K'') + \int Q(E', K; 0, K'') dE' = 1, \quad (3)$$

where the range of integration over the Franck-Condon density in the continuum $Q(E')$ extends upward from the ion dissociation limit. Use of the indicated sum in Eq. (3) then permits a determination of the value of the integral in this expression. Results for the various (K'', K) pairs are indicated in Table IV. Once again, the transitions with $K''=K$ show only a small variation of dissociative ionization probability with K'' but values for $|K''-K|=2$ differ appreciably. Also, the effect is greatest for H_2 . Comparing the results for the case $K''=K=0$ with those obtained by previous au-

²¹ This restriction on rotational quantum numbers in the transition was previously suggested in connection with electron impact ionization of H_2 ; see J. W. McGowan and M. A. Fineman, Phys. Rev. Letters **15**, 179 (1965). For photoionization, $K''=K$ would appear to be most probable.

TABLE II. Franck-Condon factors in hydrogen ionization, $q(v', K; 0, K'')$.

v'	K''	$K=0$	1	2	3	4	5	Ref. 10 ($K=0$)
0	0	0.09079	...	0.08564	0.09076
	1	...	0.09072	...	0.08231
	2	0.09597	...	0.09059	...	0.07907
	3	...	0.09943	...	0.09038	...	0.07593	...
1	0	0.1599	...	0.1537	0.15986
	1	...	0.1598	...	0.1496
	2	0.1659	...	0.1596	...	0.1455
	3	...	0.1698	...	0.1594	...	0.1414	...
2	0	0.1739	...	0.1700	0.17380
	1	...	0.1738	...	0.1673
	2	0.1774	...	0.1737	...	0.1646
	3	...	0.1796	...	0.1734	...	0.1617	...
3	0	0.1525	...	0.1515	0.15244
	1	...	0.1525	...	0.1507
	2	0.1532	...	0.1524	...	0.1497
	3	...	0.1535	...	0.1523	...	0.1486	...
4	0	0.1194	...	0.1203	0.11934
	1	...	0.1194	...	0.1208
	2	0.1182	...	0.1194	...	0.1212
	3	...	0.1174	...	0.1193	...	0.1214	...
5	0	0.08767	...	0.08954	0.08768
	1	...	0.08769	...	0.09070
	2	0.08573	...	0.08772	...	0.09179
	3	...	0.08440	...	0.08777	...	0.09279	...
6	0	0.06218	...	0.06428	0.06220
	1	...	0.06220	...	0.06566
	2	0.06008	...	0.06225	...	0.06699
	3	...	0.05870	...	0.06233	...	0.06827	...
7	0	0.04332	...	0.04530	0.04336
	1	...	0.04335	...	0.04662
	2	0.04141	...	0.04340	...	0.04792
	3	...	0.04018	...	0.04349	...	0.04920	...
8	0	0.02998	...	0.03168	0.03002
	1	...	0.03000	...	0.03282
	2	0.02837	...	0.03006	...	0.03397
	3	...	0.02735	...	0.03013	...	0.03512	...
9	0	0.02075	...	0.02213	0.02078
	1	...	0.02077	...	0.02308
	2	0.01946	...	0.02081	...	0.02404
	3	...	0.01865	...	0.02088	...	0.02500	...
10	0	0.01442	...	0.01551	0.01445
	1	...	0.01444	...	0.01627
	2	0.01341	...	0.01447	...	0.01704
	3	...	0.01279	...	0.01453	...	0.01702	...
11	0	0.01008	...	0.01093	0.01010
	1	...	0.01009	...	0.01151
	2	0.00931	...	0.01012	...	0.01213
	3	...	0.00883	...	0.01016	...	0.01273	...
12	0	0.00708	...	0.00773	0.00710
	1	...	0.00710	...	0.00818
	2	0.00650	...	0.00712	...	0.00864
	3	...	0.00614	...	0.00715	...	0.00911	...
13	0	0.00499	...	0.00547	0.00500
	1	...	0.00500	...	0.00581
	2	0.00455	...	0.00501	...	0.00615
	3	...	0.00428	...	0.00503	...	0.00650	...
14	0	0.00349	...	0.00384	0.00350
	1	...	0.00350	...	0.00408
	2	0.00317	...	0.00350	...	0.00433
	3	...	0.00297	...	0.00351	...	0.00457	...

TABLE II. (Continued)

v'	K''	$K=0$	1	2	3	4	5	Ref. 10 ($K=0$)
15	0	0.00239	...	0.00263	0.00240
	1	...	0.00239	...	0.00279
	2	0.00216	...	0.00239	...	0.00295
	3	...	0.00202	...	0.00238	...	0.00309	...
16	0	0.00154	...	0.00168	0.00154
	1	...	0.00153	...	0.00178
	2	0.00139	...	0.00152	...	0.00184
	3	...	0.00129	...	0.00150	...	0.00190	...
17	0	0.00084	...	0.00089	0.00084
	1	...	0.00083	...	0.00091
	2	0.00075	...	0.00081	...	0.00090
	3	...	0.00069	...	0.00077	...	0.00084	...
18	0	0.00025	...	0.00023	0.00025
	1	...	0.00024	...	0.00018
	2	0.00023	...	0.00020	...	a
	3	...	0.00020	...	0.00016	...	a	...
19	0	0.000015	...	a	Not calculated
	1	...	0.000010	...	a
	2	0.000013	...	a	...	a
	3	...	0.000008	...	a	...	a	...

* This state of the ion is not bound.

thors, it is evident that the agreement with Rothenberg and Davidson for H_2 is very good. For D_2 , however, the present result differs from that obtained by Dunn by about 15%. Comparison of the present results with electron impact experimental determinations of the dissociative ionization probability²² indicates fair agreement for the case of hydrogen and some disagreement in the case of deuterium.

ACCURACY OF THE CALCULATION

The accuracy of the calculated Franck-Condon factors may be tested in several ways. First, energy eigenvalues as well as eigenfunctions have been determined. These may be compared with the results of other highly accurate calculations. Second, it is possible to perform simple tests of the numerical solution technique by determining the dependence of the overlap integral on the integration step length, the range of integration, etc. Also, the influence of neglected interactions (such as relativistic corrections to the electron energy) must be considered.

Some of the rotationless energy levels of H_2^+ and of D_2^+ are shown in Table V, where they are compared with the results of Wind¹⁴ and of Dunn,⁹ respectively. Since Wind's levels for H_2^+ correspond to the adiabatic potential curve, essentially exact agreement is expected for this case. Indeed, the energy difference in all cases amounts to less than 0.2 cm^{-1} and decreases rapidly with increasing v' . The small differences in Table V are regarded as significant and are attributed by us to the

²² O. A. Schaeffer and J. M. Hastings, *J. Chem. Phys.* **18**, 1048 (1950).

fact that Wind used an approximate diagonal correction function $g_{v0}(R)$. Comparison of this approximate expression, originally computed by Cohen *et al.*,²³ with the exact values obtained by Hunter *et al.*,²⁴ shows, at $R=2.00 \text{ a.u.}$, for example, a difference of about -0.19 cm^{-1} (the difference asymptotically approaches zero as R increases). This is in satisfactory agreement with the difference -0.16 cm^{-1} between Wind's value for the energy of the ground vibrational state and the result of the present work. Further confirmation of this interpretation is obtained by comparing the adiabatic energies for $v'=0, 1$ state of H_2^+ ($K=0$) calculated by Hunter and Pritchard²⁴ with the results shown in Table V. The differences are 0.03 cm^{-1} and 0.00 cm^{-1} , respectively. In the case of D_2^+ , there is considerable disagreement with the energy levels calculated by Dunn (a systematic difference of about 40 cm^{-1}) whereas the highly accurate D_2^+ ground-state binding energy reported by Hunter and Pritchard²⁴ is within 0.03 cm^{-1} of our value. In part, the differences with Dunn's energies for D_2^+ may be attributed to the inclusion of nuclear motion correction in the present work. On the basis of these considerations, it is concluded that the eigenfunctions calculated in this work refer to energy levels that are within 0.1 cm^{-1} of the exact nonrelativistic adiabatic values.

²³ S. Cohen, D. L. Judd, and R. J. Riddell, University of California, Lawrence Radiation Laboratory, UCRL 8802. The results are discussed, but not tabulated, in S. Cohen, D. L. Judd, and R. J. Riddell, *Phys. Rev.* **119**, 384 (1960).

²⁴ G. Hunter and H. O. Pritchard, *J. Chem. Phys.* **46**, 2153 (1967).

TABLE III. Franck-Condon factors in deuterium ionization, $q(v', K; 0, K'')$.

v'	K''	$K=0$	1	2	3	4	5	6	Ref. 9 ($K=0$)
0	0	0.03442	...	0.03303	0.03278
	1	...	0.03440	...	0.03212
	2	0.03580	...	0.03436	...	0.03122
	3	...	0.03671	...	0.03431	...	0.03033
	4	0.03763	...	0.03423	...	0.02946	...
1	0	0.08585	...	0.08318	0.08286
	1	...	0.08581	...	0.08140
	2	0.08845	...	0.08573	...	0.07962
	3	...	0.09017	...	0.08561	...	0.07786
	4	0.09184	...	0.08545	...	0.07610	...
2	0	0.1246	...	0.1218	0.12168
	1	...	0.1246	...	0.1199
	2	0.1273	...	0.1245	...	0.1180
	3	...	0.1290	...	0.1243	...	0.1161
	4	0.1307	...	0.1242	...	0.1142	...
3	0	0.1389	...	0.1369	0.13699
	1	...	0.1389	...	0.1356
	2	0.1407	...	0.1388	...	0.1342
	3	...	0.1419	...	0.1387	...	0.1327
	4	0.1429	...	0.1385	...	0.1313	...
4	0	0.1325	...	0.1317	0.13181
	1	...	0.1325	...	0.1311
	2	0.1332	...	0.1324	...	0.1304
	3	...	0.1336	...	0.1324	...	0.1297
	4	0.1340	...	0.1323	...	0.1289	...
5	0	0.1145	...	0.1146	0.11473
	1	...	0.1145	...	0.1147
	2	0.1143	...	0.1145	...	0.1147
	3	...	0.1141	...	0.1144	...	0.1146
	4	0.1139	...	0.1144	...	0.1145	...
6	0	0.09262	...	0.09338	0.09343
	1	...	0.09263	...	0.09386
	2	0.09182	...	0.09264	...	0.09432
	3	...	0.09127	...	0.09266	...	0.09475
	4	0.09072	...	0.09268	...	0.09514	...
7	0	0.07171	...	0.07278	0.07277
	1	...	0.07172	...	0.07349
	2	0.07064	...	0.07175	...	0.07418
	3	...	0.06993	...	0.07179	...	0.07486
	4	0.06922	...	0.07184	...	0.07552	...
8	0	0.05392	...	0.05507	0.05503
	1	...	0.05393	...	0.05585
	2	0.05279	...	0.05397	...	0.05662
	3	...	0.05206	...	0.05402	...	0.05739
	4	0.05134	...	0.05408	...	0.05815	...
9	0	0.03978	...	0.04088	0.04082
	1	...	0.03980	...	0.04162
	2	0.03873	...	0.03983	...	0.04237
	3	...	0.03805	...	0.03989	...	0.04312
	4	0.03740	...	0.03995	...	0.04388	...
10	0	0.02902	...	0.02999	0.02994
	1	...	0.02904	...	0.03065
	2	0.02811	...	0.02907	...	0.03133
	3	...	0.02752	...	0.02912	...	0.03201
	4	0.02696	...	0.02918	...	0.03270	...
11	0	0.02105	...	0.02187	0.02184
	1	...	0.02106	...	0.02243
	2	0.02028	...	0.02109	...	0.02301
	3	...	0.01980	...	0.02114	...	0.02360
	4	0.01933	...	0.02120	...	0.02420	...

TABLE III. (Continued)

v'	K''	$K=0$	1	2	3	4	5	6	Ref. 9 ($K=0$)
12	0	0.01524	...	0.01592	0.01590
	1	...	0.01525	...	0.01638	
	2	0.01462	...	0.01528	...	0.01686	
	3	...	0.01422	...	0.01532	...	0.01736	...	
	4	0.01385	...	0.01537	...	0.01786	
13	0	0.01105	...	0.01159	0.01159
	1	...	0.01106	...	0.01197	
	2	0.01055	...	0.01108	...	0.01236	
	3	...	0.01024	...	0.01111	...	0.01277	...	
	4	0.00994	...	0.01116	...	0.01319	
14	0	0.00804	...	0.00847	0.00848
	1	...	0.00805	...	0.00878	
	2	0.00765	...	0.00807	...	0.00909	
	3	...	0.00740	...	0.00809	...	0.00942	...	
	4	0.00717	...	0.00813	...	0.00976	
15	0	0.00588	...	0.00622	0.00624
	1	...	0.00589	...	0.00646	
	2	0.00557	...	0.00590	...	0.00671	
	3	...	0.00538	...	0.00592	...	0.00698	...	
	4	0.00520	...	0.00595	...	0.00725	
16	0	0.00432	...	0.00459	0.00462
	1	...	0.00433	...	0.00478	
	2	0.00408	...	0.00434	...	0.00498	
	3	...	0.00393	...	0.00436	...	0.00519	...	
	4	0.00379	...	0.00438	...	0.00540	
17	0	0.00320	...	0.00341	0.00343
	1	...	0.00320	...	0.00356	
	2	0.00301	...	0.00321	...	0.00372	
	3	...	0.00289	...	0.00322	...	0.00388	...	
	4	0.00278	...	0.00324	...	0.00405	
18	0	0.00238	...	0.00254	0.00257
	1	...	0.00238	...	0.00266	
	2	0.00223	...	0.00239	...	0.00278	
	3	...	0.00214	...	0.00240	...	0.00291	...	
	4	0.00206	...	0.00241	...	0.00304	
19	0	0.00177	...	0.00190	0.00192
	1	...	0.00178	...	0.00199	
	2	0.00166	...	0.00178	...	0.00209	
	3	...	0.00159	...	0.00179	...	0.00219	...	
	4	0.00153	...	0.00180	...	0.00229	
20	0	0.00132	...	0.00142	0.00144
	1	...	0.00132	...	0.00149	
	2	0.00124	...	0.00133	...	0.00156	
	3	...	0.00118	...	0.00133	...	0.00164	...	
	4	0.00113	...	0.00134	...	0.00172	
21	0	0.00098	...	0.00106	0.00107
	1	...	0.00098	...	0.00111	
	2	0.00091	...	0.00098	...	0.00116	
	3	...	0.00087	...	0.00099	...	0.00122	...	
	4	0.00083	...	0.00099	...	0.00127	
22	0	0.00072	...	0.00077	0.00078
	1	...	0.00072	...	0.00081	
	2	0.00067	...	0.00072	...	0.00084	
	3	...	0.00063	...	0.00072	...	0.00088	...	
	4	0.00060	...	0.00072	...	0.00092	
23	0	0.00050	...	0.00054	0.00054
	1	...	0.00050	...	0.00056	
	2	0.00047	...	0.00050	...	0.00059	
	3	...	0.00044	...	0.00050	...	0.00061	...	
	4	0.00042	...	0.00050	...	0.00063	

TABLE III. (Continued)

ν'	K''	$K=0$	1	2	3	4	5	6	Ref. 9 ($K=0$)
24	0	0.00032	...	0.00034	0.00034
	1	...	0.00032	...	0.00036	
	2	0.00030	...	0.00032	...	0.00037	
	3	...	0.00028	...	0.00032	...	0.00037	...	
25	0	0.00017	...	0.00018	0.00016
	1	...	0.00017	...	0.00018	
	2	0.00016	...	0.00016	...	0.00017	
	3	...	0.00015	...	0.00016	...	0.00016	...	
26	0	0.00005	...	0.00005	0.00004
	1	...	0.00005	...	0.00004	
	2	0.00005	...	0.00004	...	a	
	3	...	0.00004	...	0.00003	...	a	...	
	4	0.00004	...	a	...	a	...

^a This state of the ion is not bound.

To test the calculation method, Franck-Condon factors for H_2 ionization corresponding to the case $K''=K=0$ were computed using an integration step length twice as large as that shown in Table I. The integration limits were kept fixed so that only half as many integration points were used. For all states with $\nu' \leq 11$, the computed Franck-Condon factors differed by less than one part in 10^4 . For the states with $12 \leq \nu' \leq 16$, the deviation was less than three parts in 10^4 , while for $\nu' = 17, 18$ the change was as large as four parts in 10^3 . As a further test of the method, the outer integration limits were decreased by 30% from the values shown in Table I using the smaller integration step length. Except for the $\nu' = 19$ state, the changes in calculated Franck-Condon factors $q(\nu', 0; 0, 0)$ were smaller than the changes resulting from using the

larger integration step length quoted above. To test the sensitivity of the final results to small errors in the interpolated potential curve, two of the original 61 points for H_2^+ were omitted (those at $R=1.25$ a.u. and at $R=4.50$ a.u.). The interpolated potential curve resulting from this change is regarded as somewhat less accurate than the curve resulting from use of the full set of points. Nevertheless, the computed values of $q(\nu', 0; 0, 0)$ were unchanged from the values shown in Table II. On the basis of these and other tests, we conclude that the computed Franck-Condon factors presented in Tables II-IV represent the results of the nonrelativistic adiabatic approximation to an accuracy of at least one part in the last quoted decimal place.

Comparison of the theoretical nonrelativistic electronic energy of the hydrogen atom with the experi-

TABLE IV. Probability of dissociative ionization, $1 - \sum_{\nu'} q(\nu', K; 0, K'')$.

		Hydrogen					Ref. 10 ($K=0$)
$K''=0$	$K=0$	1	2	3	4	5	
	0.0145	...	0.0172	0.0146
1	...	0.0147	...	0.0188
2	0.0126	...	0.0150	...	0.0214
3	...	0.0118	...	0.0154	...	0.0249	...
Experiment (electron impact) ^a —0.0159							
		Deuterium					Ref. 9 ($K=0$)
$K''=0$	$K=0$	1	2	3	4	5	6
	0.0052	...	0.0058
1	...	0.0051	...	0.0062
2	0.0047	...	0.0052	...	0.0067
3	...	0.0045	...	0.0054	...	0.0074	...
4	0.0043	...	0.0055	...	0.0080
Experiment (electron impact) ^a —0.0072							

^a Reference 22.

TABLE V. Molecular ion vibrational levels ($K=0$).^a

H_2^+		
v'	This work (cm^{-1})	Ref. 14 (cm^{-1})
0	-21 379.20	-21 379.36
1	-19 187.85	-19 188.02
2	-17 123.76	-17 123.91
3	-15 182.66	-15 182.80
4	-13 361.01	-13 361.15
5	-11 655.88	-11 656.01
6	-10 064.98	-10 065.10
7	-8 586.65	-8 586.76
8	-7 219.90	-7 219.99
9	-5 964.38	-5 964.48

D_2^+		
v'	This work (cm^{-1})	Ref. 9 (cm^{-1})
0	-21 711.46	-21 669
1	-20 134.29	-20 092
2	-18 621.83	-18 581
3	-17 172.42	-17 131
4	-15 784.61	-15 744
5	-14 457.09	-14 417
6	-13 188.73	-13 149
7	-11 978.54	-11 938
8	-10 825.71	-10 786
9	-9 729.57	-9 690

^a Energy in cm^{-1} with respect to the dissociation limit.

mental ground-state energy shows that about 1 cm^{-1} must be attributed to relativistic and radiative (Lamb shift) corrections neglected in the nonrelativistic theory. For the $R=0$ limit of H_2^+ , these corrections amount to about 20 cm^{-1} . At intermediate R values it is expected that these corrections to the electron energy $E_e(R)$ will vary smoothly between the two limiting values. It is evident, then, that the total effect on the H_2^+ potential curve will be significantly smaller than the changes resulting from the inclusion of the diagonal corrections for nuclear motion $g_{00}(R)$ in the adiabatic representation we have used. As previously noted, Franck-Condon factors calculated in the clamped nucleus (Born-Oppenheimer) approximation are not significantly modified by the adiabatic corrections. On the basis of these considerations and the argument of the preceding paragraph, we suggest that the results presented in Tables II-IV will not be altered beyond the quoted uncertainty by either the inclusion of relativistic and radiative corrections to the adiabatic potential curve or by a more accurate solution technique for the adiabatic problem.

DISCUSSION

It is possible to make a simplified analysis of the effects of vibration-rotation interaction within the framework of the harmonic-oscillator approximation.

While the systems under consideration are known to be strongly anharmonic, this analysis is, nevertheless, instructive and provides the central qualitative ideas of the discussion which follows. Because a full treatment of the harmonic case is readily accessible elsewhere,²⁵ only the central points are mentioned here.

The oscillator potential, including the centrifugal term, may be written in the form

$$V(R) = (\omega_e^2/4B_e R_e^2)(R - R_e)^2 + [K(K+1)B_e R_e^2/R^2]. \quad (4)$$

Expanding the second term in powers of the displacement from equilibrium $\eta = R - R_e$ one obtains

$$V(\eta) \cong \frac{\omega_e^2}{4B_e R_e^2} \eta^2 + K(K+1)B_e \left(1 - \frac{2\eta}{R_e} + \frac{3\eta^2}{R_e^2}\right), \quad (5)$$

where the expansion is truncated with the term representing the second-order displacement from equilibrium. By means of a change of variable, the linear term in displacement may be eliminated yielding an harmonic-oscillator form. This new effective potential has a minimum at

$$R_{\min} = \left[1 + \frac{K(K+1)}{3K(K+1) + (\omega_e^2/4B_e^2)}\right] R_e, \quad (6)$$

which, for small K values, may be approximated in the form

$$R_{\min} \cong R_e + (4B_e^2/\omega_e^2) R_e K(K+1). \quad (7)$$

Thus, a principal effect of vibration-rotation interaction is the displacement of the radial coordinate of the minimum to larger R values with increasing rotational quantum number. In the harmonic approximation, this displacement is proportional to $K(K+1)$ and to B_e^2/ω_e^2 . As a consequence, the radial coordinates of

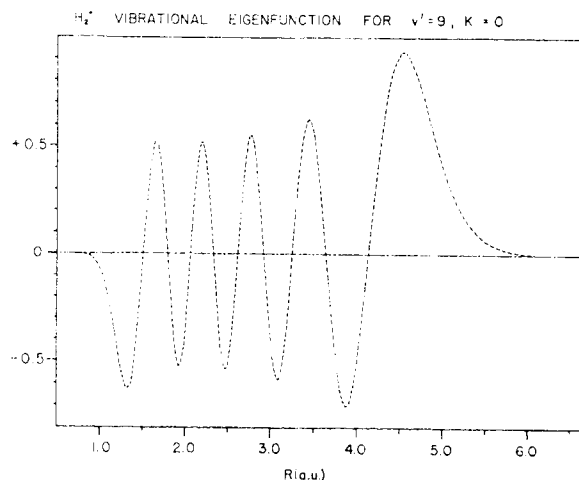


FIG. 1. H_2^+ vibrational eigenfunction for $v'=9$, $K=0$.

²⁵ See, for example, L. Pauling, and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., New York, 1935), p. 269.

nodes and loops of the vibrational eigenfunction are also expected to be displaced in quantitative correspondence to the shift of the potential minimum. Since the overlap integral, Eq. (2), is sensitive to the relative node position of two distinct eigenfunctions, an appreciable cancellation effect might be expected for some bands. Using harmonic-oscillator functions applied to H_2 ionization, this effect has been found.¹³

The influence of the exact centrifugal potential for a realistic oscillator model can be directly studied by comparing features of the computed eigenfunctions as they vary with increasing rotational quantum number. In the following, we quantitatively describe some features of the computed H_2^+ vibrational eigenfunctions from this point of view. Figure 1 shows the $v'=9$, $K=0$ eigenfunction of the hydrogen molecular ion as

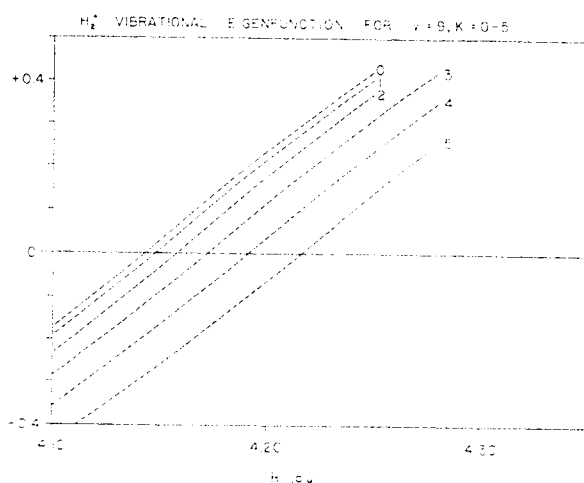


FIG. 2. Outermost node of H_2^+ vibrational eigenfunction, variation with increasing rotational quantum number K . Note the expanded scale of the abscissa.

computed in this work. One property which may be unambiguously examined is the behavior of the radial coordinate of each node as a function of K . This behavior for the outermost node of the $v'=9$ eigenfunction is shown in Fig. 2, where only the relevant part of the eigenfunction for each value of K is plotted using a much expanded scale. The displacement of the node to larger R values with increasing K value is evident as is the increasing magnitude of the displacement. As an aid in deducing the systematics of this node displacement, we define the dimensionless quantity $\rho(K)$ by the relation

$$\rho(K) \equiv R(K)/R(0), \quad (8)$$

where $R(K)$ is the node coordinate for rotational quantum number K and $R(0)$ is the coordinate for $K=0$. This quantity is uniquely defined for each node of each vibrational eigenfunction. For convenience, the nodes may be indexed in order of occurrence with increasing radial coordinate (thus, Fig. 2 shows the behavior of node 9 of the $v'=9$ eigenfunction). The behavior of

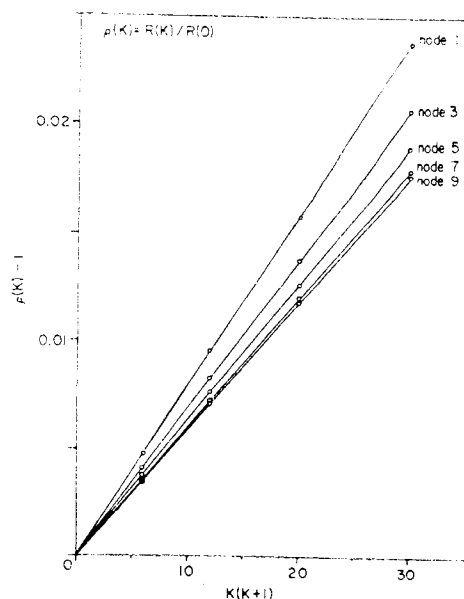


FIG. 3. Dependence of reduced node coordinate $\rho(K)$ on rotational quantum number for five nodes of $v'=9$ H_2^+ vibrational eigenfunction.

$\rho(K)$ is illustrated in Fig. 3, where the quantity $\rho(K) - 1$ is plotted as a function of $K(K+1)$ for five nodes of the $v'=9$ eigenfunction. For clarity, the graphs of the even nodes, which fall between the corresponding graphs of the odd nodes, have been omitted. From this and similar graphs for other v' values, $\rho(K)$ is found to be well represented by the expression

$$\rho(K) = 1 + [\Delta R/R(0)]K(K+1) \quad (9)$$

for all nodes of all v' values and for the range of K values considered in this paper. Thus, even for the strongly anharmonic potential functions here considered, the representation of Eq. (9), analogous in form to Eq. (7), holds to the accuracy of the determination of the node coordinate. The quantitative behavior

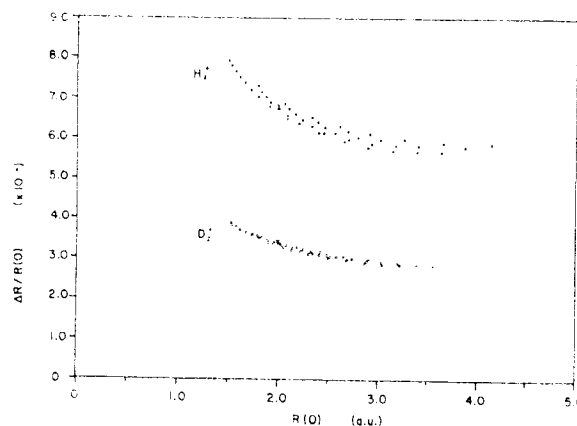


FIG. 4. Dependence of rate of change of reduced node coordinate $[d/d(K(K+1))] \rho(K)$ on node coordinate for $K=0$. Shown are values for all nodes of $v'=1-9$ vibrational eigenfunctions of H_2^+ and D_2^+ .

of $\Delta R/R(0)$ and its relation to the predictions of the harmonic-oscillator model are considered next.

Using the representation of Eq. (9), a value of $\Delta R/R(0)$ may be determined from the slopes of graphs like Fig. 3 for each node of each v' eigenfunction. Since each node is correlated with some definite value of $R(0)$, the behavior of the complete set of calculated $\Delta R/R(0)$ values can be studied as a function of $R(0)$. A graph of all such values for $v'=1$ through $v'=9$ is shown in Fig. 4 for both H_2^+ and for D_2^+ . Several features are evident from this graph: the relative insensitivity of $\Delta R/R(0)$ values to v' ; the small dependence of $\Delta R/R(0)$ on $R(0)$; and the obvious isotope effect (in the inverse ratio of the molecular reduced masses). An additional feature which is not quite as apparent concerns the magnitude of the $\Delta R/R(0)$ values. Recalling the form of Eq. (7), we note that the lowest order vibration-rotation interaction constant α_e is, in the harmonic-oscillator approximation, given by

$$\alpha_e \cong -6B_e^2/\omega_e, \quad (10)$$

which is of the right order of magnitude but of the wrong sign as compared with empirically determined values. Nevertheless, as a first approximation, one might expect that by analogy

$$\Delta R/R(0) \cong C\alpha_e/\omega_e, \quad (11)$$

Values of α_e/ω_e for H_2^+ and D_2^+ , determined from the computed energy levels, are shown as crosses in Fig. 4 where they are plotted at $R(0) = R_e$. Evidently, for this case, C is close to unity. The very good approximation represented by Eq. (9) with $\Delta R/R(0)$ given by α_e/ω_e provides the logical extension of the preceding discussion based on the harmonic-oscillator model.

While this representation of the displacement of R_e is seen to be quantitatively accurate, it is important to realize that it is the *relative* displacement of the minima of two distinct potential curves as a function of increasing rotational quantum number that will determine the magnitude of variations in the Franck-Condon factors. Only when this relative displacement

becomes an appreciable fraction of the de Broglie wavelength of the vibrational eigenfunction will significant variations be obtained in the corresponding overlap integrals. From this point of view, one must consider the quantity

$$\delta R_{v'K''} = [R_e'(K) - R_e''(K'')] - (R_e' - R_e'') \quad (12a)$$

$$= (\alpha_e'/\omega_e') R_e' K(K+1) - (\alpha_e''/\omega_e'') R_e'' K''(K''+1), \quad (12b)$$

where the singly primed molecular constants refer to the ion and doubly primed to the neutral. To illustrate the magnitude involved, consider transitions between the state $K''=3$ and the states $K=5, 3, 1$. Equation (12b) gives relative shifts of $+0.0157$, $+0.0025$, and -0.0048 Å, respectively, which are a small fraction of the de Broglie wavelength of the molecular ground-state vibration ($\lambda \cong 0.78$ Å). Thus, a relatively small variation with rotational state of computed Franck-Condon factor is expected for transitions originating in this vibrational level. But note that for higher vibrational states, the de Broglie wavelength is decreased and a larger effect is predicted. The sensitivity of Franck-Condon factors to small displacements of the separation of the potential minima for transitions between vibrationally excited states has been emphasized in the highly accurate calculations of Zare.²⁶ The application of the ideas developed in this paragraph to band systems of H_2 and to other molecular systems is discussed elsewhere.²⁷

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²⁶ R. N. Zare, J. Chem. Phys. **40**, 1934 (1964).

²⁷ D. Villarejo, R. Stockbauer, and M. G. Inghram, "Vibration-Rotation Interaction Effects in Calculated Franck-Condon Factors. II. Hydrogen Lyman and Fulcher Bands," J. Chem. Phys. (to be published).