

Franck-Condon Factors for the Ionization of H₂O and D₂O

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(February 11, 1969)

Franck-Condon factors have been calculated for vertical transitions of H₂O and D₂O involving both bond length and angle changes. It is shown that even in the harmonic oscillator approximation different Franck-Condon factors are obtained for positive and negative angle changes. The results are used to obtain the geometry of the ion ground state. Satisfactory agreement is obtained for the isotope effect on the vibrational transition probabilities. The effects of anharmonicity are discussed semi-quantitatively.

Key words: D₂O; Franck-Condon principle; geometry; H₂O; ion; photoionization; photoelectron spectroscopy.

1. Introduction

In recent years there has been growing interest in the quantitative formulation and application of the Franck-Condon principle to a variety of vertical transition processes in polyatomic molecules, including electronic absorption spectra, photoionization and photoelectron spectroscopy [1–11].¹ One of the major objectives of these studies has been to determine the structure of excited and ionized molecules from experimentally determined vibrational transition probabilities. In one case, the C(¹B₁) Rydberg state of water, the results obtained by this method were in rather good accord with the geometry obtained by rotational analysis [4]. All these studies have in common the assumption of constant electronic transition moment, thus reducing the problem to an evaluation of vibrational overlap integrals, and a further simplification of using harmonic oscillator wave functions [12]. Three distinct approaches to the problem have been employed. First, consideration of only one progression of a totally symmetric vibration [1], second, consideration of all totally symmetric vibrations combined with a simplified normal coordinate transformation and an iterative procedure [2] and last, use of the method of generating functions [13] extended to n dimensions with considera-

tion of all normal modes and including the possibility of symmetry as well as geometry differences between the initial and final states [9].

One application of the last method was an approximate determination of the water molecule-ion geometry from experimental Franck-Condon factors (hereafter called FCF) obtained from the staircase structure observed near threshold in the photoionization yield curve [11, 14]. The calculations reported in that study were based on a simplified normal coordinate transformation and, in addition, the extent and accuracy of the experimental data were limited to an unknown degree by interference from autoionization near threshold [11, 15]. Recently the FCF for both H₂O and D₂O ions have been determined by Brundle and Turner [16] with much greater accuracy and completeness by means of photoelectron spectroscopy. We report here new and more complete calculations based on their work, along with some new results concerning sign ambiguities in geometry determination, rough considerations concerning anharmonicity effects, and a comparison of the ion geometry with that of the C(¹B₁) Rydberg state.

2. Method

The generating function method has already been described in detail elsewhere [9–10]. The basic problem in the polyatomic case is the determination of the transformation relating the normal coordinates

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¹ Figures in brackets indicate the literature references at the end of this paper.

of the initial and final states. As first pointed out by Duschinsky [17], this is in the most general case a linear matrix transformation relating initial and final state normal coordinate vectors \mathbf{Q} and \mathbf{Q}' . It has the form

$$\mathbf{Q}' = \mathbf{J}\mathbf{Q} + \mathbf{K}$$

where \mathbf{J} is a matrix and \mathbf{K} a vector. From symmetry considerations it follows that \mathbf{K} has nonvanishing components only for totally symmetric modes. As a result, only totally symmetric vibrations are strongly excited in the vertical transition [18–19]. In the diatomic case there is an analogous transformation in which \mathbf{J} incorporates the effect of frequency changes and \mathbf{K} the effect of bond length change.

In the diatomic case, in the harmonic oscillator approximation, one obtains the same FCF for bond length changes of equal magnitude but opposite sign. This follows directly from the symmetry properties of the harmonic oscillator wave functions and the fact that the FCF is the square of the vibrational overlap integral. Consequently, one cannot directly determine the sign of the bond length change by working backwards from observed vibrational intensities. This ambiguity, of course, disappears when anharmonicity is taken into account. In the polyatomic case, on the other hand, this ambiguity disappears in the harmonic approximation if there is more than one totally symmetric mode and if the transformation relating the initial and final state totally symmetric modes involves a rotation in normal coordinate space, i.e., if the \mathbf{J} matrix has off-diagonal elements. An illustration is given below.

The detailed form of the normal coordinate transformation given above is conveniently found starting with internal symmetry coordinates S and S' for the two states. With the choice of a force field, such as a simple valence force field, the normal coordinates are obtained by solving the vibrational eigenvalue problem from which one obtains matrices \mathbf{L} and \mathbf{L}' relating the respective normal coordinates to the internal symmetry coordinates

$$\mathbf{S} = \mathbf{L}\mathbf{Q} \text{ and } \mathbf{S}' = \mathbf{L}'\mathbf{Q}'.$$

The most general transformation relating the internal symmetry coordinates of the two states is again of the form

$$\mathbf{S}' = \mathbf{Z}\mathbf{S} + \mathbf{R}$$

from which it follows that

$$\mathbf{J} = \mathbf{L}'^{-1}\mathbf{Z}\mathbf{L} \text{ and } \mathbf{K} = \mathbf{L}'^{-1}\mathbf{R}$$

Using conventional stretching and bending internal symmetry coordinates, the relation between these coordinates for two states of bond angles 2β and $2\beta'$ and bond length r and r' , respectively, is readily written down. (It is often convenient to work this out via cartesian displacement coordinates.)

$$S'_1 = \cos(\beta - \beta') \cdot S_1 - \frac{r}{\sqrt{2}}$$

$$\sin(\beta - \beta') \cdot S_2 + \sqrt{2}(r \cos(\beta - \beta') - r')$$

$$S'_2 = \frac{\sqrt{2}}{r'} \sin(\beta - \beta') \cdot S_1 + \frac{r}{r'}$$

$$\cos(\beta - \beta') \cdot S_2 + \frac{2r}{r'} \sin(\beta - \beta')$$

$$S'_3 = \frac{\sin \beta'}{\sin \beta} \cdot S_3$$

where the subscripts 1, 2, and 3 refer (throughout) to the symmetric stretching, symmetric bending and antisymmetric stretching coordinate. It is seen from this transformation that the off-diagonal elements of the \mathbf{Z} matrix will have different sign depending on the sign of the bond angle change. Further, inspection of the \mathbf{L}' matrix elements also shows an unsymmetric behavior with respect to positive or negative bond angle differences compared to the other state. Consequently, a bond angle difference between the initial and final state will lead to somewhat different FCF depending on the sign of the difference. The \mathbf{L} and \mathbf{L}' matrices depend, of course, on the normal coordinates which, in turn depend on the assumed force field. However, these remarks are qualitatively correct.

A second effect of the mixing to stretching and bending normal modes in the transformation is that the FCF of the stretching mode is somewhat dependent on the angle change and, conversely, the FCF of the bending mode is dependent also on the bond length change.

3. Results and Discussion

3.1. Ambiguity of Sign

In order to illustrate the unsymmetric behavior with respect to geometry changes as discussed above, calculations were carried out for an idealized case. FCF were calculated for a transition of the water molecule in which the upper state had geometry but not frequency changes with respect to the lower state. For the initial state parameters, the geometry and the totally symmetric mode frequencies of the ground state water molecule were used. A simple valence force field was used to determine the antisymmetric stretching frequency and the normal modes. In table 1 are shown the FCF calculated at various geometries corresponding to all combinations of up to two increments of $\pm 0.0400 \text{ \AA}$ and $\pm 5.00 \text{ deg}$ geometry change with respect to the initial state. The sum of the FCF for any given geometry may not equal unity because of contributions from higher overtone and combination transitions which are not tabulated. It is seen that when there is only a bond length change the sign ambiguity is still present, i.e., one obtains exactly the same transition probabilities. However, when angle changes occur one obtains numerically different values depending on the sign of both the angle and bond length change. Further, the dependence of stretching excita-

TABLE 1. Franck-Condon Factors for Positive and Negative Geometry Changes in H₂O^a

$\frac{2\beta}{r}$	94.52°	99.52°	104.52°	109.52°	114.52°
P (000-000)					
0.8772Å	0.37639	0.47072	0.51071	0.48097	0.39331
.9172	.62016	.78023	.84537	.78929	.63530
.9572	.73212	.92512	1.00000	.92530	.73326
.9972	.61925	.78468	0.84537	.77494	.60477
1.0372	.37529	.47610	.51071	.46364	.35643
P (100-000)					
0.8772	0.23236	0.30657	0.34243	0.32415	0.26006
.9172	.08916	.12400	.14170	.13347	.10363
.9572	.00055	.00009	.00000	.00000	.00002
.9972	.11662	.13713	.14170	.12914	.10398
1.0372	.26512	.32515	.34243	.31019	.24196
P (010-000)					
0.8772	0.14774	0.05205	0.00075	0.03155	0.11911
.9172	.21706	.07276	.00031	.05627	.19417
.9572	.22690	.07161	.00000	.07146	.22618
.9972	.16861	.04947	.00031	.06463	.18826
1.0372	.08897	.02387	.00075	.04163	.11197
P (110-000)					
0.8772	0.07781	0.02928	0.00050	0.01758	0.06590
.9172	.02162	.00824	.00005	.00649	.02177
.9572	.00204	.00043	.00000	.00032	.00124
.9972	.04317	.01205	.00005	.01454	.04392
1.0372	.07493	.01982	.00050	.03237	.08909

^a Ground state $r=0.9572\text{Å}$ $2\beta=104.52^\circ$, G. Herzberg, Electronic Spectra of Polyatomic Molecules (D. Van Nostrand, New York, 1966).

ν_1 —Symmetric stretching mode.
 ν_2 —Symmetric bending mode.
 ν_3 —Antisymmetric stretching mode.

tion on angle change and vice versa is clearly demonstrated by inspecting rows and columns. The results of including frequency differences as well as geometry differences are not very much different. For upper state frequencies corresponding to the Rydberg state of the ion (see table 3) there is a slight distortion of the FCF surfaces.

From a practical standpoint, this asymmetry effect is too small to be of use in this range of geometry variation. However, for still larger angle changes the effect will be quite pronounced. An extreme case of this type is the pyramidal planar-transition of NH₃ [20].

3.2. Franck-Condon Factors for Ionization

In table 2a are shown the experimental FCF for H₂O and D₂O determined by Brundle and Turner [16] by photoelectron spectroscopy. In table 2b are listed the FCF relative to the zero-zero transition computed

TABLE 2a. Experimental Franck-Condon Factors for the ionization of H₂O and D₂O from photoelectron spectroscopy^a

Transition	H ₂ O	D ₂ O
000-000	0.757 ± 0.005	0.702 ± 0.005
100-000	.143 ± .005	.148 ± .005
200-000	.018 ± .002	.025 ± .002
300-000	^b < .008
010-000	.069 ± .005	.087 ± 0.005
110-000	.013 ± .002	.034 ± .002
210-000	> .002	.004 ± .002

^a Turner and Brundle, ref. [16].

^b Detection limit; not observed.

^c Throughout this paper indicated numerical error limits represent subjective estimates, by the authors cited or by the present writers, of probable limits of error.

from the photoelectron spectroscopy data along with other ratios obtained from photoionization experiments by Dibeler [11] and Brehm [15] and, for comparison, the results for the Rydberg C and D states determined spectroscopically by Bell [4]. It is seen that the photoionization data are in only moderate agreement with the photoelectron results. Both photoionization experiments show clear indication of autoionization structure just above the (100-000) step, and it is probable that there is interference from autoionization near threshold as well. In table 3 are listed the frequencies for the ground state, ion state, and the C and D Rydberg states determined by various workers. There is a very close correspondence between the ion frequencies and those of the Rydberg C state for both isotopic species. This, of course, leads to the expectation of very similar geometries for both states.

The FCF were calculated for both molecules as a function of both bond distance and angle, using the Rydberg C state frequencies for the upper state. Calculations were carried out for both a simple valence force field and for one with a potential interaction constant between the stretching and bending coordinate. The two gave essentially identical results. The ground state geometry is given in table 4. In figures 1 and 2 are shown the results in the region of interest corresponding to an increase in both angle and length. The curves may be visualized as cuts through the Franck-Condon surfaces at three different values of the bond length, and the tenfold difference in ordinate scale for both 000 and 100 should be kept in mind. Also shown are the experimental points for all transitions measured by Brundle and Turner [16]. The measure of agreement is whether all points lie on the same vertical line. It is clear that the agreement is only moderately good, with some deviation for 110 and 210. Noteworthy is the fact that the results for both ions lie at almost exactly the same geometry, that the significant deviations from ideal are in the same direction for the same transitions and, most important, that there is a major discrepancy in both cases for the 200-000 transition, with the experimental values several times as large as the calculated values. Also, inspection of the cuts at 0.99 and 1.01 Å shows that the disagreement cannot be resolved

TABLE 2b. Ratio of experimental Franck-Condon factors by different methods relative to the 000-000 transition

		Photo-electron spectroscopy [16]	Photoionization ^a		Rydberg C State [4]	Rydberg D State [4]
			ref. 11	ref. 15		
H ₂ O	100-000	0.189	0.18 ± 0.03	0.20 ± 0.03	0.6 ± 0.2	0.60 ± 0.15
H ₂ O	010-000	.091		.14 ± .03		
D ₂ O	100-000	.222	0.18 ± 0.03	.18 ± .03	0.6 ± 0.2	0.60 ± 0.15
D ₂ O	010-000	.124		.14 ± .03		

^a The values given are estimated from the published curves. Both sets of photoionization values are subject to error due to autoionization.

TABLE 3. Frequencies for various states of H₂O and D₂O, in cm⁻¹

	Ground State ^(a)	C Rydberg State		D Rydberg State ref. 4	Ion Ground State	
		ref. 4	ref. 22		P. I. ref. 15	P.E.S. ref. 16
H ₂ Oν ₁	3652	3179	3170	3268	3190 ± 50	3200 ± 50
H ₂ Oν ₂	1595	1407	^b (1422)	1636	1420 ± 50	1380 ± 50
H ₂ Oν ₃	3756	(3238)	(3224)			
D ₂ Oν ₁	2666	2338	(2290)	2381	2280 ± 50	2310 ± 50
D ₂ Oν ₂	1179	1041	1038	1223	1050 ± 50	980 ± 50
D ₂ Oν ₃	2784	(2427)	(2365)	(2483)		

^a G. Herzberg, Infrared and Raman Spectra, New York (1945).

In the FCF calculations a value of ν₁ = 3699 was used. This has no effect on the results.

^b All quantities in brackets have been calculated from simple valence force fields.

TABLE 4. Geometry of various water states

	Ground state [19]	C State rotational analysis [22]	C State FCF [4]	D State FCF [4]	Ion FCF ^a	Ion SCF calc. [23]
<i>r</i>	0.9512 Å	1.013	1.022 ± 0.01	1.024 ± 0.01	0.995 ± 0.005	119
2β	104.52°	106.7	109.7 ± 1.8	113.0 ± 1.8	^b < 109	

^a This work.

^b The value 110° is obtained for a harmonic oscillator calculation. The consideration of anharmonicity would decrease this value by perhaps several degrees, see text.

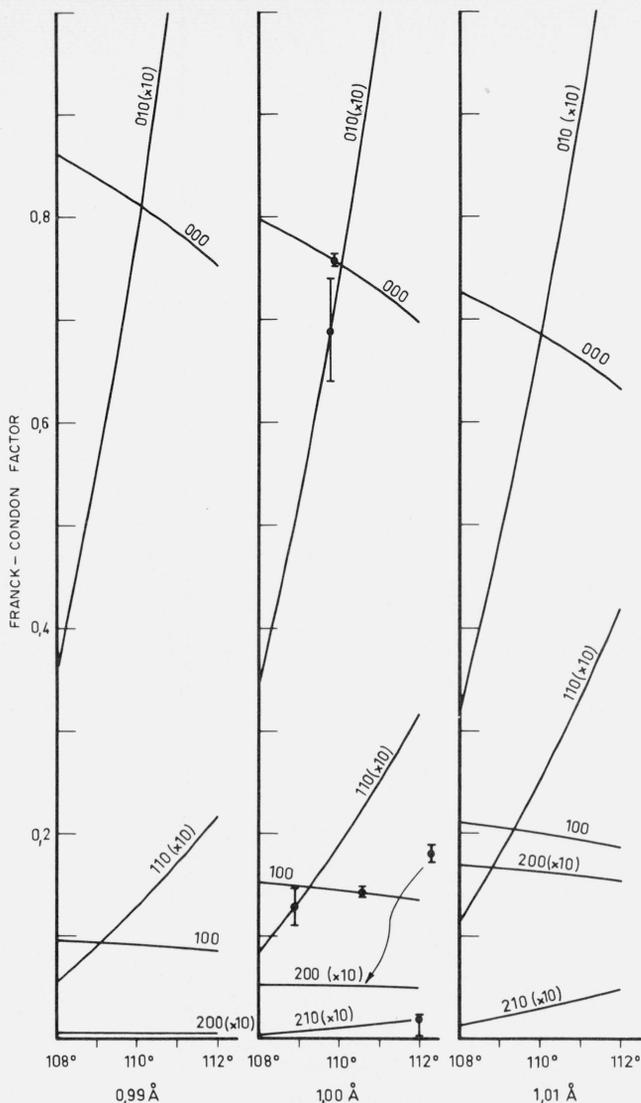


FIGURE 1. Franck Condon factors for H_2O as a function of bond angle at three bond distances for the ion state.

Experimental points with error bars are the photoelectron spectroscopy results of Brundle and Turner [16].

by a slight geometry change. Thus, at first sight one has established a geometry estimate of 1.00 Å and 110 deg. with astoundingly good precision. The large deviations are due to anharmonicity, and the precision is a little deceptive.

3.3. Anharmonicity Effects

Before considering anharmonicity, one other factor has to be considered. In the H_2O and D_2O molecules and ions the frequencies of the antisymmetric stretching mode are quite close to the symmetric stretching frequencies. For the ions this is based purely on simple valence force field calculations which, as seen from table 3 give reasonably good results for the C Rydberg state. Comparing the values with those of the molecule ground state one has a decrease of about 500 and 300

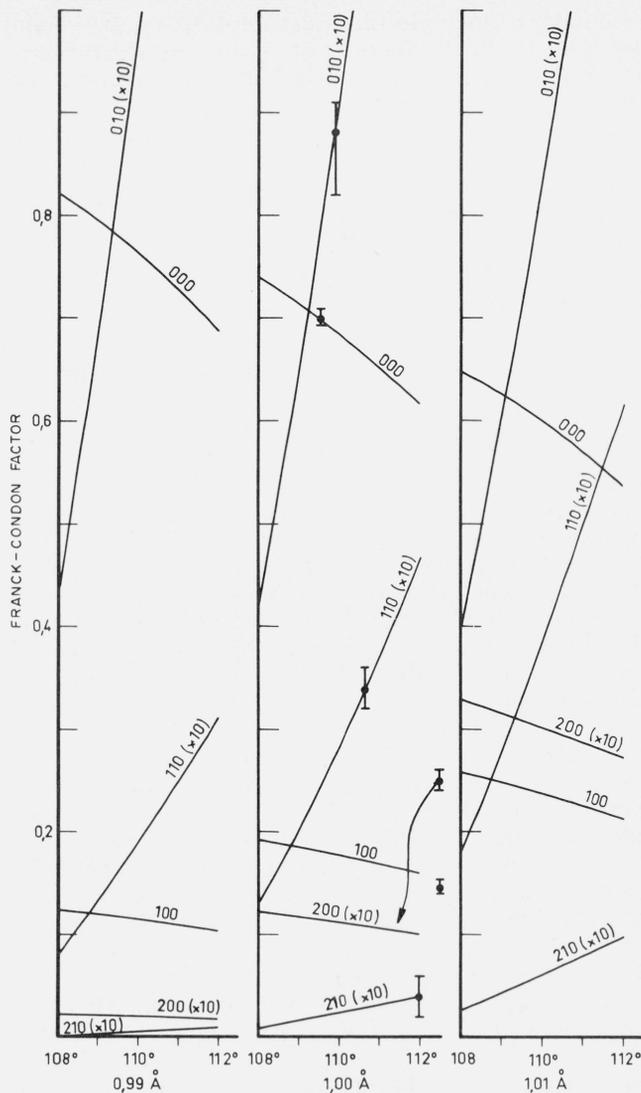


FIGURE 2. Franck-Condon factors for D_2O as a function of bond angle at three bond distances for the ion state.

Experimental points with error bars are the photoelectron spectroscopy results of Brundle and Turner [16].

cm^{-1} for the H_2O and D_2O ions, respectively. This is sufficient to produce a small excitation of the even overtones of the antisymmetric stretching modes, and it is very probable that the results of Brundle and Turner for the 200-000 transition include contributions from 002-000 as well. The calculated transition probability is about 0.001 for both H_2O and D_2O . Another possible interference is the (120-100) transition which would lie only several hundred wave numbers away from the (200-000) transition. The FCF for this transition depends on the geometry but, in this range has a value of about 0.003 to 0.004 for H_2O and 0.001 for D_2O . Thus the difference between the calculated and measured FCF is quite real, although the experimental value might be somewhat lower than stated.

There is no direct indication of the magnitude of

the anharmonicity in the water ions. Again, the results of Bell on the Rydberg C state are suggestive since they show first differences in both the stretching and bending progression [4]. However, they are far too fragmentary for a determination of anharmonicity. In view of this we have carried out only the very simplest one dimensional perturbed harmonic oscillator calculation corresponding to a cubic term in the potential for both the symmetric stretching and bending mode. For this model perturbation theory yields for the wave function

$$\psi_n = \psi_n^0 + \frac{\sqrt{X_e}}{3\sqrt{30}} \left\{ -[n(n-1)(n-2)]^{1/2} \psi_{n-3}^0 - 9n^{3/2} \psi_{n-1}^0 + 9(n+1)^{3/2} \psi_{n+1}^0 + [(n+3)(n+2)(n+1)]^{1/2} \psi_{n+3}^0 \right\}$$

where x_e is the anharmonicity constant and n is the vibrational quantum number. In the absence of better information we note the remark of Bates [21] that in many diatomic molecules x_e has values of the order of magnitude 10^{-2} . Using the perturbed wave functions for the stretching normal mode it is a straightforward matter to recalculate the FCF using the overlap integrals previously calculated for that geometry. The results are shown in figure 3. The dashed lines show the anharmonic FCF as a function of $x_e^{1/2}$. They are shown for a geometry of 1.00 Å and 110 deg. The 000-000 transition probability decreases somewhat and both the 100-000 and 200-000 transition probabilities increase. The great slope difference between the latter two is again due to the tenfold difference in ordinate scale. It is interesting to note that a reasonable value of the anharmonicity parameter accounts for the intensity discrepancy in 200-000. At a slightly lower value of $r=0.995$ Å one can bring all three transitions into accord with a value of x_e of about 0.008-0.009. The dependence of the FCF on the anharmonicity coefficient at that geometry is very similar to that shown for 1.00 Å. Further, with this value of anharmonicity one can calculate the effect on 300-000 as well, although at this transition the first order perturbed wave function is of doubtful utility. In any even the FCF calculated with the perturbed wave function did not exceed the upperbound determined experimentally.

It is evident that a similar situation holds for the bending vibration as well. A similar parametrized calculation indicates that for an anharmonicity of 0.01 the same FCF is obtained at 109 deg instead of 110, and for an anharmonicity of 0.04 at 108 deg. There is little question that the bending mode is anharmonic, and these results indicate that the accuracy as well as the precision of the bending angle estimate is somewhat lower than appears from the FCF curves and the small probable error of the experimental FCF.

3.4. Geometry of Water States

In table 4 are given the geometries of the various states determined spectroscopically [22] and by spec-

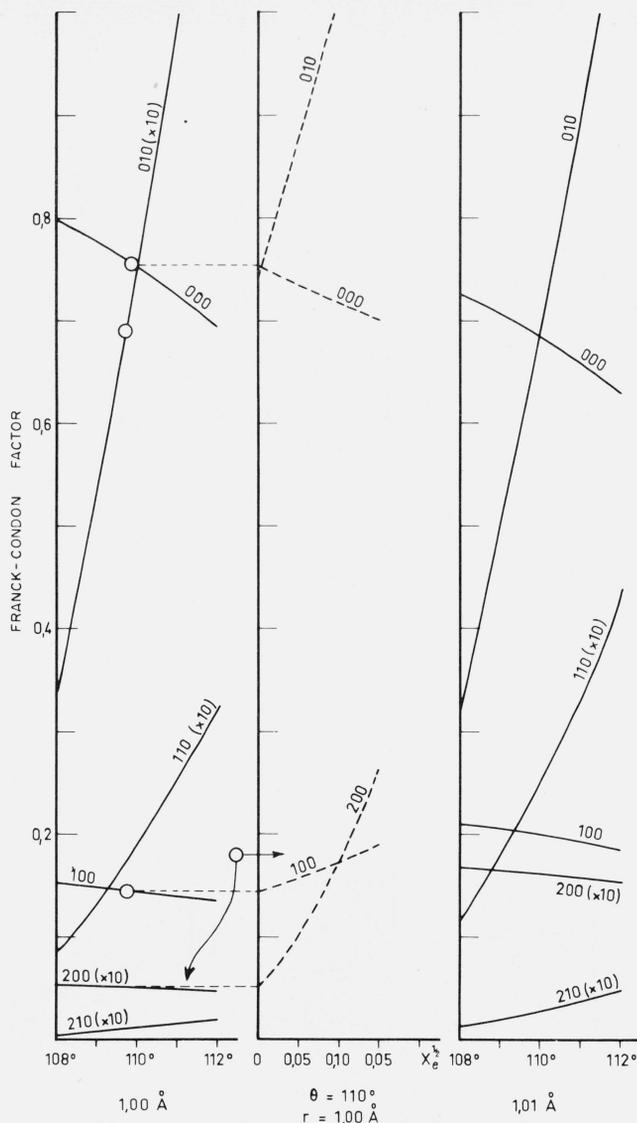


FIGURE 3. Dependence of Franck-Condon factors for H_2O on the anharmonicity parameter $x_e^{1/2}$, for an upper state geometry of 1.00 Å and 110°.

Left-hand and right-hand graphs give the dependence on geometry for comparison.

troscopic FC and photoelectron spectroscopic FC methods and the results of a SCF calculation by Krauss [23]. On the basis of the crude discussion of anharmonicity effects, one can suggest that at least part of the angle discrepancy between the FCF results of Bell and the rotational analysis of Johns is due to anharmonicity. In the harmonic approximation we obtained the same results as Bell. Further, in comparing the bond length of the C state and the ion state we note that the bond length of the ion is smaller. In addition, the ambiguity of geometry change determination which is still effectively present in the harmonic approximation is in fact removed by the anharmonicity assumptions required to account for the abnormally high 200-000 FCF. The analogous anharmonic calculations for a decrease of bond

length of equivalent magnitude *below* the neutral molecule value would have led to an opposite effect on the "corrected" transition probability. Lastly, the bond angle estimate for the ion is of only moderate value. It may in fact be equal to, or even lower than that of the C state. The answer to that question will depend on improved knowledge of anharmonicity.

We thank D. W. Turner and C. R. Brundle for sending their results prior to publication and for helpful correspondence.

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(Paper 73A3-555)