

VALIDITY OF FRANCK–CONDON ANALYSIS PROCEDURES FOR DEDUCTION OF EXCITED-STATE AND IONIC GEOMETRIES

Part II. The X^2B_1 and A^2A_1 states of hydrogen oxide and hydrogen sulphur

FOO TIM CHAU

Department of Applied Science, Hong Kong Polytechnic, Hung Hom (Hong Kong)

(Received 21 October 1986)

ABSTRACT

The vibrational intensity distributions observed in the first two photoelectron bands of H_2O , D_2O and H_2S were adopted in studying the validity and limitations of different methods for carrying out Franck–Condon analyses. These methods include the generating function method, Coon et al.'s method, the Duschinsky matrix method and the two approximate methods involving the use of the vibrational quantum number with the maximum intensity as well as vertical and adiabatic ionization potentials within a progression. The geometries thus deduced for the H_2O^+ and H_2S^+ ions in the X^2B_1 and A^2A_1 states are in good agreement with observed values. Various criteria for the prediction of signs for changes in bond lengths and bond angles were discussed. Furthermore, the Badger's rule and the electrostatic force model were utilized to estimate quantitatively the changes in bond length on ionization.

INTRODUCTION

Considerable attention has been devoted to quantitative applications of the Franck–Condon principle to vibrational fine structures in molecular photoelectron spectra [1, 2]. Geometries of ions thus derived provides valuable information on the bonding properties and the chemical dynamics involving the parent molecules. The validity of the approach for the determination of ionic geometries for polyatomic molecules other than diatomic molecules has been tested only for a limited number of cases [1, 3, 4].

The He(I) photoelectron spectra of H_2O and its isotopic species have been studied by a number of workers [5–9]. The first photoelectron band of water exhibits vibrational fine structure which can be attributed to the symmetric O–H stretching ν_1 and the angle bending ν_2 modes. There is no change in molecular symmetry (C_{2v}) upon the corresponding $X^2B_1 \leftarrow X^1A_1$ ionization process. However, the second band consists of extended progression in the angle bending mode with no excitation of other vibrations. It has generally been interpreted as a transition from the bent X^1A_1 ground state to the linear A^2A_1 state of H_2O^+ [5–8, 10, 11].

A number of Franck–Condon analyses [6, 8, 9, 12, 13] with different degrees of sophistication have been carried out on the vibrational intensity

distribution observed in the first photoelectron band of H_2O and the ionic geometries obtained from these works are in good agreement with experimental values deduced from emission spectra [10, 11].

Recently, ionic geometries of nitrogen(1) oxide in the $X^2\pi$ and $A^2\Sigma^+$ states has been investigated [4] by adopting high-resolution photoelectron data by Dehmer and Dehmer [14] as well as ionic frequencies obtained from an emission spectroscopic study [15]. Three Franck-Condon analysis procedures, namely the generating function method [16], Coon et al.'s method [17] and the Duschinsky matrix method [4] incorporated the pattern search optimization technique [18] were employed in this work. Although the two stretching modes of nitrogen(I) oxide are found to couple with each other to an appreciable extent in the electronic states under study, the structural parameters for N_2O^+ in the two ionic states agree favorably with experimental data [15].

In the present work, the three methods of Franck-Condon analysis as mentioned previously were applied to compute geometries of H_2O^+ in the X^2B_1 and the A^2A_1 states with the aim of checking the validity of these methods for hydrides. Since the photoelectron spectrum of H_2S [6, 19-21] is similar to that of H_2O in many aspects, Franck-Condon analyses were also performed on the vibrational fine structures of the first two photoelectron bands of H_2S . The results of the calculations were compared with experimental values obtained from emission studies [22, 23].

The second photoelectron bands of H_2O and H_2S molecules show extensive progression of ν_2 . Thus, the approximate methods originally devised for Franck-Condon analysis of diatomic molecules or for single progressions arising from individual vibrational modes with large changes in structural parameters upon ionization were also employed in geometry calculations. Moreover, various guidelines for predicting signs as well as magnitudes of geometric changes upon photoionization are discussed in detail.

THEORY AND METHODS OF CALCULATION

Quantitative applications of the Franck-Condon principle to vibrational intensity distributions accompanying photoionization processes usually assume the validity of the Born-Oppenheimer approximation, the constancy of the photoionization cross-section and the harmonic oscillator approximation. Thus the relative intensities are proportional to the square of the vibrational overlap integrals, i.e., the Franck-Condon factor (FCF).

To evaluate the overlap integrals, normal coordinates in the ionic state Q' are expressed in terms of those in the ground state Q through the transformation [24]

$$Q' = J Q + D \quad (1)$$

with J being the Duschinsky rotation matrix and D a column vector with elements d_i representing the separation of origins of the two coordinate

systems. The two matrices are related to the internal symmetry displacement coordinates [25] S' and S by

$$J = (L_s'^{-1}) L_s \quad (2)$$

$$D = (L_s'^{-1}) \Delta S \text{ or } \Delta S = L_s' D \quad (3)$$

The L_s matrix is defined as

$$S = L_s Q \quad (4)$$

For a two-mode system of Q_1 and Q_2 for the bent H_2O and H_2S molecules and their ions, the Duschinsky rotation matrix J can also be expressed as [26]

$$J = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \quad (5)$$

with θ being the rotation angle between normal coordinates of the ground and ionic states. In this approach, the matrix J can be evaluated without the use of L_s matrices as given in eqn. (2).

In the present work, Franck-Condon analyses were carried out on the first two photoelectron bands of H_2O and H_2S by invoking the generating function method [16], Coon et al.'s method [17] and the Duschinsky matrix method [4] with the use of eqn. (5) to generate the J matrix, designated as methods A, B and C, respectively. Details of these methods are described in ref. 4 and are not repeated here.

L_s' and L_s matrices as well as molecular force constants in the various electronic states of H_2O and H_2S were obtained through normal coordinate analyses by adopting the least-square-fit technique similar to that developed by Overend and Scherer [27]. However, in some ionic states, the number of available vibrational frequencies are not sufficient to carry out full normal coordinate analyses. Two approximate force constant methods were adopted in this work to evaluate the L_s matrices and approximate force constants. Details of the two methods are given below.

Herranz and Castano [28] proposed the characteristic set method (method G1) for the computation of approximate L_s matrices as well as force constants. In the treatment, the symmetrized inverse kinetic energy matrix G_s [25] of a species which depends only on molecular geometry and atomic masses of the constituting atoms can be diagonalized in the form

$$G_s A = A \Gamma \quad (6)$$

with

$$L_s^{-1} = A \Gamma^{-1/2} A^t \quad (7)$$

A^t is the transpose of matrix A . The L_s^{-1} and hence L_s are symmetric matrices. The approximate force constant matrix F_s can be obtained through

$$\mathbf{F}_s = (\mathbf{L}_s^{-1})^t \wedge \mathbf{L}_s^{-1} \quad (8)$$

\wedge is the diagonal matrix with diagonal elements λ_i being equal to $4\pi^2 C^2 \nu_i^2$.

The extremal properties of force constants have been studied extensively by a number of workers [29–31]. For molecules with $\nu_1 > \nu_2$ the force constants of a 2×2 \mathbf{F}_s matrix are well approximated by the condition that the matrix element $(\mathbf{F}_s)_{22}$ is a minimum with respect to $(\mathbf{F}_s)_{12}$ or with $(\mathbf{L}_s)_{12} = 0$. In this approach, the \mathbf{F}_s matrix elements are readily evaluated by using simple algebraic expressions without solution of the secular equation. This \mathbf{L}_s matrix method (method G2) is also adopted in the present work for approximate force constant calculations. However, it should be mentioned that the \mathbf{L}_s matrix obtained from this method is always an unitary matrix and thus is not useful in Franck–Condon calculations on ionic geometries.

RESULTS AND DISCUSSIONS

The molecular force constants of H₂O and H₂S in various electronic states

The observed vibrational frequencies of H₂O, D₂O and H₂S in the X^1A_1 , X^2B_1 , A^2A_1 and C^1B_1 Rydberg states [7, 11, 21, 32–34] are shown in Table 1. ν_1 , ν_2 and ν_3 are respectively the symmetric bond stretching, angle bending and antisymmetric stretching mode of the H₂X molecules with C_{2v} symmetry. Both the ν_1 and ν_2 modes belong to the a_1 representation while the ν_3 mode belongs to the b_1 representation. However, for linear H₂O⁺ ion in the A^2A_1 state, ν_1 , ν_2 and ν_3 are of σ_g^+ , π_u and σ_u^+ representation, respectively with $D_{\infty h}$ molecular symmetry.

The force constant matrix of a bent H₂X molecule in the general valence force field (GVFF) can be expressed as [35]

$$\mathbf{F}_s = \begin{bmatrix} f_r + f_{rr} & \sqrt{2} f_{r\alpha} & 0 \\ \sqrt{2} f_{r\alpha} & f_\alpha & 0 \\ 0 & 0 & f_r - f_{rr} \end{bmatrix} \quad (9)$$

f_r , f_α , f_{rr} and $f_{r\alpha}$ are, respectively, the bond stretching, angle bending, stretching–stretching and stretching–bending interaction force constants. In addition, the simple valence force field (SVFF) with the use of only f_r and f_α has been attempted to investigate the effect of interaction force constants in force constant computation.

Normal coordinate analyses invoking the GVFF and SVFF as well as the two approximate force constant calculation methods G1 and G2 were performed on molecules of H₂O and D₂O as well as H₂S and D₂S in the X^1A_1 , X^2B_1 , A^2A_1 and C^1B_1 state. The results of calculations are given in Table 2. For both H₂O and H₂S in the neutral ground state X^1A_1 , convergence were obtained in the refinement of force constants invoking both the GVFF and SVFF. The discrepancies between the calculated and observed

TABLE 1

Observed vibrational frequencies^a (in cm^{-1}) of H_2O , D_2O and H_2S in various electronic states

		Ground state ^b	Ionic state		Rydberg state ^g
		X^1A_1	X^2B_1	A^2A_1	C^1B_1
<hr/>					
H ₂ O					
	ν_1	3656.65	3241 ± 17^c	—	3179
	ν_2	1594.59	1431.2^d	1006 ± 60^c	1407
	ν_3	3755.79	—	—	3255 ^h
D ₂ O					
	ν_1	2671.46	2362 ± 17^c	—	2338
	ν_2	1178.33	1064 ± 17^c	731 ± 60^c	1041
	ν_3	2788.05	—	—	2389 ^h
H ₂ S					
	ν_1	2614.6	2564 ± 34^e	—	
	ν_2	1182.7	1250 ± 50^f	1120 ± 50^f	
	ν_3	2626	—	—	

^a ν_1 , ν_2 and ν_3 are, respectively, the symmetric bond stretching, angle bending and anti-symmetric stretching mode of H_2O or H_2S with C_{2v} molecular symmetry. ^bSee ref. 22.

^cSee ref. 7. ^dFundamental frequency derived from ref. 11. ^eEstimated from ref. 21. ^fSee ref. 34. ^gSee ref. 33. ^h ν_3 frequencies are calculated from GVFF as given in Table 2.

frequencies in both force fields are within 1% for H_2O and 3% for H_2S .

The ν_3 frequencies are not available for the X^2B_1 states of H_2O and H_2S as well as the C^1B_1 state of H_2O . This leads to the fact that only convergence were obtained in force constant computations in the SVFF for these species. However, in the X^2B_1 state of H_2O^+ ion, the modified GVFF with the value of f_{rr} fixed arbitrarily to be zero were adopted in a normal coordinate analysis and convergence was obtained. The overall results of calculations are listed in Table 2. In the C^1B_1 state of H_2O^+ , the agreement between the calculated and observed frequencies is within 1%. For the ground ionic states of H_2O^+ and H_2S^+ , the agreement is within 5% with the consideration of large uncertainties in the experimental ionic frequencies.

It should be mentioned that the values of f_r and f_α of H_2O and H_2S . In both GVFF and SVFF are close to one another within 2%. This indicates that the interaction force constants of the hydrides although not small in magnitude compared to f_α tend to cancel their contributions to vibrational frequencies in some way.

Peacock and Muller [31] have applied both the characteristic set method and the L_s matrix method to a number of non-hydride compounds. In general, the latter method is found to be superior to the former one by giving force constants, especially off-diagonal ones in the F_s matrices in agreement with force constants obtained from normal coordinate analyses. Moreover, it is physically unreasonable for the matrix element $(L_s)_{12}$ to be

TABLE 2

Calculated force constants^a (in md Å⁻¹) of H₂O and H₂S in different electronic states

	Ground state X ¹ A ₁				Ionic state X ² B ₁				Rydberg state C ¹ B ₁			
	GVFF	SVFF	method G1	method G2	GVFF ^b	SVFF	method G1	method G2	SVFF	method G1	method G2	
H ₂ O												
<i>f_r</i>	7.7754	7.7541	7.6834	7.5861	6.0763	6.0252	5.9978	5.9852	5.7722	5.7722	5.7601	
<i>f_α</i>	0.7123	0.7121	0.7055	0.7021	0.5837	0.5732	0.5655	0.5631	0.5465	0.5465	0.5441	
<i>f_{rα}</i>	0.1269	—	-0.1435	0.0409	0.2125	—	-0.1107	0.0322	—	-0.1064	0.0311	
<i>f_{rr}</i>	-0.0804	—	-0.0804	—	—	—	—	—	—	—	—	
H ₂ S												
<i>f_r</i>	4.0710	4.0745	3.9541	3.9407		3.7681	3.7935	3.7912				
<i>f_α</i>	0.4084	0.4052	0.4030	0.4025		0.4594	0.4499	0.4495				
<i>f_{rα}</i>	-0.0598	—	-0.0402	0.0123		—	-0.0395	0.0137				
<i>f_{rr}</i>	-0.1089	—	-0.0109	—		—	—	—				

^aThe general valence force constants *f_r*, *f_α*, *f_{rr}* and *f_{rα}* are the bond stretching, angle bending, stretching—stretching and stretching—bending interaction force constants, respectively. ^b*f_{rr}* is fixed at zero in carrying out a normal coordinate analysis on the X²B₁ states of H₂O⁺.

equal to $(L_s)_{21}$ in a 2×2 L_s matrix. In general, $(L_s)_{12}$ is found to be much less than $(L_s)_{21}$.

We studied the validity of the characteristic set method and the L_s matrix method with hydride compounds including BH_3 , BH_4^- , CH_4 and NH_4^+ and their deuterated species. We found that method F1 is not bad at all with diagonal matrix elements obtained for the F_s matrix having a deviation within 8% from those determined by force constant calculations. However, the off-diagonal matrix elements may deviate considerably.

With regard to method F2, Peacock and Muller [31] suggested that the atomic mass of atom Y should be less than that of X for the XY_n type molecule. By comparing results of calculations from method G2 with those from normal coordinate analyses, it is found that the F_s matrix elements obtained are generally in better agreement than those evaluated through method G1, especially for the off-diagonal matrix elements.

In the present study, both methods G1 and G2 were applied to compute approximate force constants of H_2O and H_2S in various electronic states. The calculated values of f_r and f_α from both methods agree very well with one another (see Table 2) and even with those from the GVFF though the agreement on interaction force constants is not so good.

Geometries of H_2O and H_2S in the X^2B_1 and C^1B_1 states

The generating function method, Coon et al.'s method and the Duschinsky matrix method were applied to the vibrational fine structures observed in the first photoelectron bands of H_2O and H_2S to deduce ionic geometries in the corresponding states. In the computation, the vibrational intensities of H_2O reported by Dixon et al. [8] were adopted while those of H_2S were estimated from Karlsson et al.'s spectrum [21] by utilizing deconvolution techniques. The bond lengths r_e of H_2O , D_2O and H_2S in the neutral ground states [36, 37] were employed in evaluating bond lengths of these molecules in various ionic and excited states.

Among the three methods A, B and C used in the study, method C gives the best intensity fit while method B gives the worst. The same observation applies to Franck-Condon analyses on N_2O [4]. It is due to the appropriate introduction of the off-diagonal J matrix elements in method C and to a less extent method A to account better for intensities of overtones and combination bands.

Table 3 shows the ionic geometric of H_2O^+ and H_2S^+ in the X^2B_1 state obtained by using methods A, B and C with the use of L_s and L'_s matrices derived from GVFF (see Table 2). The theoretical geometries are close to those obtained by other workers [6, 8, 9, 12, 13] including those by Botter and Carlier [9] (see column 5 of Table 3) on H_2O^+ and D_2O^+ ions and agree well with experimental values (within 1.5%) derived from rotational analyses of emission spectra of H_2O [10, 11] and H_2S [22, 23].

Table 4 gives the computed structural parameters of H_2O^+ in the X^2B_1

TABLE 3

Calculated and observed bond lengths r (in Å) and bond angles (in degrees) of H_2O^+ and H_2S^+ in the X^2B_1 states

	Calculated ionic geometry		Calculated ionic geometry ^d	Observed ionic geometry
	Method A	Method B	Method C	
H_2O				
r_{OH}	1.006 ± 0.001	1.000 ± 0.001	0.993 ± 0.001^a	0.9988^e
$\angle \text{HOH}$	110.4 ± 0.3	110.4 ± 0.2	109.4 ± 0.2^a	110.46^e
D_2O				
r_{OD}	0.998 ± 0.001	0.993 ± 0.001	0.989 ± 0.001^b	0.9995 ± 0.0015
$\angle \text{DOD}$	109.9 ± 0.2	109.8 ± 0.6	108.6 ± 0.1^b	109.8 ± 0.2
H_2S				
r_{SH}	1.349 ± 0.002	1.349 ± 0.002	1.344 ± 0.001^c	1.358^f
$\angle \text{HSH}$	92.9 ± 0.1	92.8 ± 0.1	92.8 ± 0.1^c	92.9^f
				1.365^h
				92.94^h

^aThe rotation angle θ takes the value of -0.5° . ^bThe rotation angle θ takes the value of -3.5° . ^cThe rotation angle θ takes the value of $+3.5^\circ$. ^dIonic geometries obtained by Botter and Carlier (see ref. 9). ^eSee ref. 11. ^fSee ref. 22. ^gSee ref. 10. ^hSee ref. 23.

TABLE 4

Calculated bond lengths r (in Å) and bond angles α (in degrees) as well as relative deviations (in %) of r and α from experimental values of H_2O^+ ion in the X^2B_1 state by employing the \mathbf{D} matrix from method B and \mathbf{L}_s matrices from different force constant calculations

	Observed value ^a	\mathbf{L}'_s matrix derived from ^b			\mathbf{L}_s matrix derived from ^b	
		GVFF	SVFF	Method G1	GVFF	SVFF
r	1.010	1.000	1.005	1.006	1.003	1.005
$(r - r_{\text{obs}})/r_{\text{obs}}$		-1.0	-0.5	-0.4	-0.7	-0.5
α	108.8	110.4	109.8	110.3	110.0	109.8
$(\alpha - \alpha_{\text{obs}})/\alpha_{\text{obs}}$		+1.5	+0.9	+1.4	+1.1	+0.9

^a Observed structural parameters of H_2O^+ is chosen arbitrarily from ref. 10. ^b \mathbf{L}'_s and \mathbf{L}_s matrices were determined from force constant calculations involving the use of the force constants given in Table 2.

state by employing the \mathbf{D} matrix from Coon et al.'s method and the various \mathbf{L}_s matrices from different force constant calculations. It can be seen that the \mathbf{L}'_s matrices from GVFF, SVFF and the characteristic set method of G1 as well as \mathbf{L}_s matrices from the GVFF and SVFF all give small discrepancies (within 1.5%) between calculated and experimental bond lengths and bond angles [10]. The same conclusion is observable for the theoretical structural parameters of H_2S^+ in the X^2B_1 state by employing different \mathbf{L}_s and \mathbf{L}'_s matrices in Franck-Condon analyses although the results are not presented here. It should be mentioned that the stretching and angle bending vibrations couple only to a very small extent with each other as indicated from the potential energy distribution matrix [35].

In the case of nitrogen(I) oxide [4], the geometries of N_2O^+ ions in the $X^2\pi$ and $A^2\Sigma^+$ state were determined by invoking \mathbf{L}'_s and \mathbf{L}_s matrices from GVFF. The resultant ionic geometries are close to one another and agree well with observed data. This is mainly due to the fact the \mathbf{L}_s matrices of the two ionic states deviate only slightly from those of the neutral ground state. However, \mathbf{L}'_s and \mathbf{L}_s matrices from SVFF had not been attempted in computing theoretical ionic geometries of N_2O^+ owing to the fact that the NN and NO stretching modes couple with each other to an appreciable extent in the electronic states under study and the force constants obtained from SVFF have unreasonable values in comparison with other studies.

Both methods B and C cannot determine the signs of the changes in normal coordinates \mathbf{D} and hence, in the present work, the signs for the changes in bond lengths Δr and bond angles $\Delta\alpha$ upon photoionization were chosen to follow the signs as well as magnitudes of the experimental data as close as possible.

In the course of this work, the geometry of H_2O in the C^1B_1 Rydberg

state has also been studied to test the validity of the Franck—Condon analysis procedures. Since only the intensities of 1_0^0 , 1_0^1 and 2_0^1 transitions were reported [33], only Coon et al.'s method together with the L'_s matrix in the GVFF as shown in Table 2 was employed. The bond length and bond angle of the Rydberg state are found to be 1.025 ± 0.010 and $109.8 \pm 0.8^\circ \text{ \AA}$, respectively compared to the theoretical values of $1.022 \pm 0.010 \text{ \AA}$ and $109.7 \pm 1.8^\circ$ by Bell [33]. Again the calculated structural parameters agree favourably with the observed length of $1.002 \pm 0.004 \text{ \AA}$ and the bond angle of $108.7 \pm 0.4^\circ$ [38].

Geometries of H_2O^+ and H_2S^+ ions in the A^2A_1 state

The second photoelectron band of H_2O consists mainly of a long progression of the ν_2 mode. Potts and Price [6] estimated the geometry of H_2O^+ in the corresponding A^2A_1 state to be linear based on a simple Franck—Condon factor calculation as well as vibrational spacings observed within the band. Later Dixon et al. [8] analysed the second band by adopting a model calculation with a large amplitude hamiltonian with reasonable success. The geometry of H_2O^+ is found to be linear. Jungen et al. [10] carried out a rotational analysis on the emission spectra of H_2O corresponding to the $X^2B_1 \leftarrow A^2A_1$ transition. The barrier height of the upper state is found to be zero and the ion is confirmed to be linear.

Both the generating function method and the Duschinsky matrix method were applied to account for the vibrational intensity distribution of the second photoelectron bands of H_2O and H_2S without success. This is not surprising because Franck—Condon factor calculations involving harmonic oscillators tend to give short progressions with an intensity spread of not more than eight vibrational components [39]. In treating a single vibrational progression, the Coon et al. method renders to a one-dimensional case and the iterative one-dimensional Franck—Condon analysis procedure invoking the dichotomous search technique (method D) [2, 40] is applicable.

An approximate method (method E) for long progressions makes use of the formula

$$d^2 = (2m' + 1)/\alpha^2 \quad (10)$$

with

$$\alpha^2 = 4\pi^2 c\nu/h \quad (11)$$

where c is the speed of light, h is Planck's constant, and m' is the vibrational quantum number of the component with maximum intensity. Another approximate method (method F) utilizes the classical interpretation of the Franck—Condon principle with

$$d^2 = (I_v - I_a)/2\pi^2\nu'^2 \quad (12)$$

where I_v and I_a denote the vertical and adiabatic ionization potential, respectively of a photoelectron band.

All the three methods D, E and F are employed in the determination of the ionic geometry of H_2O in the A^2A_1 state based on the vibrational intensities estimated from Karlsson et al.'s spectrum of H_2O [7]. Both the Σ and π vibronic components are considered in the analyses. The results of the calculation are shown in Table 5. The method E1 utilized the $(L'_2)_{22}$ matrix element only for the bending mode in computing bond angles while method E2 utilized the whole L'_s matrix in computation. In addition, the H_2O^+ ion is linear in the A^2A_1 state, leading to diagonal G_s and F_s matrices. In such a case, the L'_s matrix is simply equal to $(G_s)^{1/2}$. Since no 1_n^0 transitional intensities are available from the second photoelectron band of H_2O and the nature of the L'_s matrix in the A^2A_1 state, the bond length of the H_2O^+ ion is found to be the same as that in the ground state. It can be seen in Table 5 that the H_2O^+ ion is found to be close to linearity. It should be mentioned that in these calculations, no consideration on the change in the vibrational degree of freedom was made for the bent-to-linear electronic transition.

The a^2A_1 band system of H_2S has similar envelopes to that of H_2O , but only a single vibrational progression in the ν_2 mode appears clearly on the low energy side of the system. Each member of this progression is accompanied by weaker bands on its high energy side. However, past the maximum of the system, the vibrational spacing is suddenly reduced to about 60% of its value [6, 21]. The general feature of the band was interpreted in terms of the bent-to-bent transition but with appreciable Renner effect in the upper state. Duxbury et al. [22, 23] analysed the emission spectra of the

TABLE 5

Calculated and observed bond lengths r (in Å) and bond angles α (in degrees) of H_2O^+ and H_2S^+ in the A^2A_1 state

	Method D	Method		Method F	Observed structural parameters	
		E1	E2			
<hr/>						
H₂O						
<i>r</i>	0.9572	—	0.9572	—	0.997 ^a	
(<i>r</i> − <i>r</i> _{obs})/ <i>r</i> _{obs}	−4%	—	−4%	—		
α	183	173	173	167	180 ^a	
(α − α _{obs})/α _{obs} (%)	+2	−4	−4	−7		
H₂S						
<i>r</i>	1.334	—	1.333	—	1.369 ^b	1.375 ^c
(<i>r</i> − <i>r</i> _{obs})/ <i>r</i> _{obs} ^d	−3%	—	−3%	—		
α	130	123	124	118	127 ^b	126 ^c
(α − α _{obs})/α _{obs} ^d (%)	+3	−2	−2	−6		

^aSee ref. 10. ^bSee ref. 22. ^cSee ref. 23. ^dThe relative deviations are evaluated by using the observed ionic geometry as given in ref. 23.

$X^2B_1 \leftarrow A^2A_1$ transition and deduced the ionic geometries of the H_2S^+ ion in the A^2A_1 state as shown in Table 5.

The three methods D, E and F for Franck—Condon analyses were also carried out on the second photoelectron band of H_2S and the resultant ionic geometries are tabulated in Table 5. Since there is no change in molecular symmetry upon the photoionization process, observed ionic frequencies are not sufficient to carry out normal coordinate analyses and hence the characteristic set method is used to derive the L'_s and the approximate F_s matrices. The calculated bond lengths and bond angles of the H_2S^+ ion in the A^2A_1 state are in good agreement with observed values (see Table 5). This further supports the use of approximate L_s matrices from the characteristic set method in Franck—Condon analyses for molecular systems where vibrations are coupled with one another only to a small extent. It should be mentioned that for both methods E1 and F, the observed ionic bond length is adopted in bond angle calculations. Use of the bond length in the neutral ground state gives ionic bond angles in even better agreement with experimental values [22, 23].

Predicted signs and magnitudes for changes in bond lengths and bond angles of molecules upon ionization

Both Coon et al.'s method and the generating function method as well as the approximate methods E and F give the set of changes in normal coordinates D from observed vibrational intensities. However, the signs of d_i cannot be determined from the calculations because they are evaluated from square roots of observed Franck—Condon factors. For the H_2O type molecule, the bond stretching mode and the angle bending mode give four different sets of d_{OH} and d_{HOH} , leading to four different sets of Δr and $\Delta \alpha$ for an ionic state.

There are several criteria proposed to predict the sign of Δr upon ionization [1, 4, 41, 42]. They are briefly summarized as follows:

(1) the sign of Δr follows the variation in the corresponding vibrational frequency $\Delta \nu (= \nu - \nu')$ between the two combining states;

(2) the sign of Δr is the same as that of the difference in the corresponding stretching force constant $\Delta f (= f - f')$;

(3) the change in bond distance of a particular bond is related in a reverse manner to the difference of the corresponding overlap population [43] ΔP between the cation and the neutral molecule.

With regard to the change in bond angle $\Delta \alpha$, a criterion was proposed [41] making use of the nodal repulsive forces model [44]. The second highest occupied molecular orbital of H_2O or H_2S possesses a small amount of $H \cdots H$ bonding character. Therefore, the force between the two non-bonding hydrogen atoms is attractive. When an electron is removed from the orbital, the attractive force is weakened, leading to angle widening. The change in overlap population ΔP_{HH} in the triatomic hydride can be used as

a measure of the forces. Moreover, other models such as the valence-shell—electron-pair-repulsion (VSEPR) theory, the Walsh diagram and the electrostatic force (ESF) theory can be applied to predict the variation of the bond angles in triatomic systems qualitatively [45, 46].

Table 6 lists the predicted signs for Δr and $\Delta\alpha$ of H_2O in the X^2B_1 and A^2A_1 states by applying the various criteria as mentioned previously. For the X^2B_1 state, both the changes in stretching frequency $\Delta\nu$ and force constant Δf lead to a correct prediction of the signs of Δr owing to the fact that the stretching and bending vibrations of H_2O do not couple with each other to an appreciable extent. This is further confirmed by the fact that both $\Delta\nu$ and Δf related to the stretching mode predict the right sign for Δr and H_2O in the C^1B_1 Rydberg state. However, there is no simple quantitative relationship obtained between $\Delta\nu$ or Δf and Δr partly due to the uncertainties in the ionic frequencies observed in the X^2B_1 state. In addition, it should be pointed out that the sign obtained from $\Delta\nu$ or Δf for angle bending correctly predicts the sign of $\Delta\alpha$ as seen in Table 6.

As for the criterion invoking changes in overlap population upon photo-

TABLE 6

Signs predicted for the changes in the bond length Δr ($=r' - r$) and the bond angle $\Delta\alpha$ ($=\alpha' - \alpha$) of H_2O between the ionic and neutral ground state

	Δr	$\Delta \alpha$	Predicted sign	
			Δr	$\Delta \alpha$
<i>X³B₁ state</i>				
Observed value ^a	+0.0416 Å	+5.94°	+	+
Observed value ^b	+0.0528 Å	+4.28°		
($\nu_i - \nu'_i$)/ ν_i	+11%	+10%	+	+
($f_i - f'_i$)/ f_i	+21%	+18%	+	+
ΔP^c	0	0		
VSEPR theory ^d				+
ESF theory ^d				+
<i>A²A₁ state</i>				
Observed value ^e	+0.0398 Å	+75.48°	+	+
($\nu_i - \nu'_i$)/ ν_i	—	+27%		+
($f_i - f'_i$)/ f_i	—	+23%		+
ΔP^c	−0.0088	−0.0398	+	+
VSEPR theory ^d				+
ESF theory ^d				+
Walsh diagram ^d				+
Nodal repulsive forces model ^d				&

^aSee ref. 11. ^bSee ref. 10. ^cThe changes in overlap population for the OH bond and H...H atoms in the X^2B_1 state and the A^2A_1 state were based on the results of INDO calculation on the H_2O molecule [43]. ^dSee text. ^eSee ref. 10. ^fFor linear H_2O^+ , the calculation of the stretching force constant is similar to that for diatomic molecules by replacing the reduced mass by the $(G_s)_{22}$ matrix element of the ion.

ionization processes, Koopman's theorem [47] is assumed to be valid to account for the changes in bonding properties from a neutral molecule to the corresponding ion. From an INDO calculation [43], the highest occupied molecular orbital (HOMO) is found to be completely non-bonding. Thus, the changes in overlap population are zero for both Δr and $\Delta\alpha$ in the X^2B_1 state. However, in the A^2A_1 state, ΔP_{OH} has a value of -0.0088 . This implies an O—H bond weakening upon ionization, thus leading to an increase in bond length. Moreover, the sign of ΔP_{HH} is negative, in parallel with the nodal repulsive forces mentioned previously. Hence an angle widening is expected upon removal of an electron from the second HOMO.

The oxygen valence orbitals in H_2O may be considered to form four sp^3 hybrid orbitals in the valence bond theory. The H_2O molecule possesses two bond pairs and two lone pairs according to the bonding scheme. In accordance with VSEPR theory [45], the repulsive force between a bond pair and another bond pair is less than that between a bond pair and a lone pair. In turn, the latter force is weaker than that between a lone pair and another lone pair. This explains why the bond angle of H_2O is less than the tetrahedral angle 109.5° if all repulsive forces between electron pairs are equal for the four hybrid orbitals. Thus, removal of an electron from the HOMO results in two bond pairs but only one and a half lone pairs, thus leading to an angle widening. The same argument applies to the second HOMO since it is mainly of non-bonding character as indicated from an INDO calculation [43].

In the electrostatic force (ESF) theory, the molecular geometry and other chemical phenomena are explained by the force concept on the basis of the electrostatic theory of Hellmann and Feynman [48]. According to the theory, there exists two types of forces which affect molecular geometries. The atomic dipole (AD) forces represent the attraction between the central oxygen nucleus of H_2O and a weighted center of the polarized electron distribution belonging to the atomic orbitals of oxygen atom. These AD forces operate to make the molecule nonlinear. The AD forces increase with the number of lone pair electrons and are strongly dependent on the nature of the central atom. These AD forces are weak for the second-row elements and increase considerably for the higher-row elements.

Another type of force is the exchange (EC) forces which represent the electrostatic attractions between the oxygen nucleus and the electron distribution between oxygen and hydrogen atoms. These EC forces are the restoring forces to the linear H_2O . The resultant geometry is the balance of the AD and EC forces. The ESF theory explains why the bond angle of H_2S is smaller than that of H_2O owing to weaker AD forces in the later molecule. When an electron is removed from a lone pair of the H_2O molecule, the AD forces decrease and result in angle widening in the H_2O^+ ion. Thus the ESF theory predicts the signs of $\Delta\alpha$ are positive for both the X^2B_1 and the A^2A_1 states.

The various guidelines for the prediction of signs for Δr and $\Delta\alpha$ for H_2O

upon ionization were applied successfully to the H_2S molecule, but details are not presented here.

According to Badger's rule [49, 50], the stretching force constant of a molecule is related to the corresponding bond length r by

$$\log f = a - b \log r \quad (13)$$

Linear regression on $\log f_{\text{OH}}$ and $\log r_{\text{OH}}$ was performed on the OH molecule in various electronic states with f_{OH} derived from the corresponding vibrational frequencies [51]. A good linear relationship was obtained with a and b being 0.8071 and 2.9252, respectively.

By applying the experimental bond lengths in the X^1A_1 , X^2B_1 and C^1B_1 state [10, 36, 38], the stretching force constants are found to be 7.2889, 6.2294 and 6.4510 $\text{md } \text{\AA}^{-1}$, respectively from normal coordinate analyses (see Table 2). By applying the experimental force constants as given above, the calculated bond lengths of the X^1A_1 , X^2B_1 and C^1B_1 states are 0.9363, 1.019 and 1.037 \AA , respectively with relative deviations from experimental bond lengths [10, 36, 38] of -2, +1 and +4%.

Badger's rule has not been applied to the H_2S molecule owing to the limited number of experimental data available for the SH molecule in various electronic states.

Coon and Luz [41, 52] ascribed the difference in geometry of tetrachloroethylene in the neutral ground state and its lowest ionic state partly to the changes in electrostatic forces between carbon atoms. In the present work, the electrostatic force model is applied to the H_2O and H_2S molecules to estimate Δr in the A^2A_1 state. Assuming that the distribution of the positive charge in the H_2O^+ and H_2S^+ ions is in parallel with the square of the coefficients of the corresponding atomic orbitals and the validity of the point charge model, r_{OH} and r_{SH} in the A^2A_1 state are found to be respectively 0.982 and 1.373 \AA , in comparison with 0.997 and 1.375 \AA from experimental data [10, 23].

CONCLUSIONS

Various methods for Franck-Condon analysis were applied to determine the geometries of H_2O and H_2S in the X^2B_1 , A^2A_1 and C^1B_1 states. These methods include the generating function method [16], Coon et al.'s method [17], the Duschinsky matrix method [4] and two approximate methods for long vibrational progressions. The resultant ionic geometries agree favourably with experimental data [10, 11, 22, 23, 38].

L_s matrices from GVFF and SVFF in both the neutral ground and lowest ionic states as well as approximate L'_s matrices from the characteristic set method were incorporated into Coon et al.'s procedure. The geometries obtained for H_2O^+ and H_2S^+ ions are close to the observed values. This indicates that for molecular systems with small coupling effects between differ-

ent vibrational modes, the choice of L_s matrices in Franck—Condon analyses is not crucial.

Various guidelines for prediction of the signs for changes in bond lengths and bond angles were proposed and studied in the light of experimental evidence available. These guidelines include the changes in vibrational frequency, force constant and overlap population as well as the nodal repulsive forces model, the VSEPR theory, the Walsh diagram, and the electrostatic force theory. The validity and limitations of these criteria were discussed in detail.

ACKNOWLEDGEMENTS

The author wishes to thank Prof. K. Siegbahn and L. Karlsson of the Uppsala University in providing photoelectron spectra of H_2O and H_2S . Thanks are also due to the Staff Development Committee of the Hong Kong Polytechnic in providing a research grant for the author to work in Uppsala University, Sweden.

REFERENCES

- 1 G. L. Goodman and J. Berkowitz, in J. Berkowitz and K. O. Greenefeld (Eds.), *Molecular Ions*, Plenum Press, New York, 1983.
- 2 F. T. Chau, *J. Mol. Struct. (Theochem)*, 110 (1984) 97.
- 3 D. C. Frost, S. T. Lee and C. A. McDowell, *J. Chem. Phys.*, 59 (1973) 5484.
- 4 F. T. Chau, *J. Mol. Struct. (Theochem)*, 151 (1987) 157.
- 5 C. R. Brundle and D. W. Turner, *Proc. R. Soc. London, Ser. A*, 307 (1968) 27.
- 6 A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, 326 (1972) 181.
- 7 L. Karlsson, L. Mattsson, R. Jadrny, R. G. Albridge, S. Pinchas, T. Bergmark and K. Siegbahn, *J. Chem. Phys.*, 62 (1975) 4745.
- 8 R. N. Dixon, G. Duxbury, J. W. Rabalais and L. Asbrink, *Mol. Phys.*, 31 (1976) 423.
- 9 R. Botter and J. Carlier, *J. Electron Spectrosc. Relat. Phenom.*, 12 (1977) 55.
- 10 Ch. Jungen, K. E. J. Hallin and A. J. Merer, *Mol. Phys.*, 40 (1980) 25.
- 11 H. Lew, *Can. J. Phys.*, 54 (1976) 2028.
- 12 R. Botter and H. M. Rosenstock, *Adv. Mass Spectrom.*, 4 (1968) 579.
- 13 R. Botter and H. M. Rosenstock, *J. Res. Natl. Bur. Stand., Sect. A*, 73 (1969) 313.
- 14 P. M. Dehmer and J. L. Dehmer, *J. Chem. Phys.*, 73 (1980) 126.
- 15 J. H. Callomon and F. Creutzberg, *Philos. Trans. R. Soc. London, Ser. A*, 277 (1974) 157.
- 16 T. E. Sharp and H. M. Rosenstock, *J. Chem. Phys.*, 41 (1964) 3453.
- 17 J. B. Coon, R. E. DeWames and C. M. Loyd, *J. Mol. Spectrosc.*, 8 (1962) 235.
- 18 F. T. Chau, *J. Mol. Spectrosc.*, 103 (1984) 66.
- 19 D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley Interscience, London, 1970.
- 20 J. Delwiche, P. Natalis and J. E. Collin, *Int. J. Mass Spectrom. Ion Phys.*, 5 (1970) 443.
- 21 L. Karlsson, L. Mattson, R. Jadrny, T. Bergmark and K. Siegbahn, *Phys. Scr.*, 13 (1976) 229.
- 22 G. Duxbury, M. Horani and J. Rostas, *Proc. R. Soc. London, Ser. A*, 331 (1972) 109.
- 23 G. Duxbury, Ch. Jungen and J. Rostas, *Mol. Phys.*, 48 (1983) 719.
- 24 F. Duschinsky, *Acta Physicochim URSS*, 7 (1937) 551.

- 25 E. B. Wilson, Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
- 26 R. N. Dixon and C. R. Webster, *Mol. Phys.*, 41 (1980) 441.
- 27 J. Overend and J. R. Scherer, *J. Chem. Phys.*, 32 (1960) 1289.
- 28 J. Herranz and F. Castano, *Spectrochim. Acta*, 22 (1966) 1965.
- 29 W. Sawodny, *J. Mol. Spectrosc.*, 30 (1969) 56.
- 30 D. E. Freeman, *J. Mol. Spectrosc.*, 27 (1968) 27.
- 31 C. J. Peacock and A. Muller, *Z. Naturforsch. Teil A*, 23 (1968) 1029.
- 32 T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, NSRDS-NBS 39, Natl. Bur. Stand., Washington DC, 1972.
- 33 S. Bell, *J. Mol. Spectrosc.*, 16 (1965) 205.
- 34 A. Katrib, Ph.D. Thesis, The University of British Columbia, 1972.
- 35 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordinate Compounds*, Wiley-Interscience, New York, 1978.
- 36 G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1966.
- 37 W. S. Benedict, N. Gailai and E. K. Plyler, *J. Chem. Phys.*, 24 (1956) 1139.
- 38 J. W. C. Johns, *Can. J. Phys.*, 49 (1971) 944.
- 39 F. T. Chau, *Comput. Chem.*, 9 (1985) 19.
- 40 F. T. Chau, *J. Mol. Struct. (Theochem)*, 110 (1984) 97.
- 41 F. T. Chau, *Spectrochim. Acta Part A*, 40 (1984) 629.
- 42 E. Heilbronner, K. A. Muszkat and J. Schaublin, *Helv. Chim. Acta*, 54 (1971) 58.
- 43 J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
- 44 R. S. Berry, M. Tamres, C. J. Ballhausen and H. Johnson, *Acta Chem. Scand.*, 22 (1968) 231.
- 45 J. K. Burdett, *Molecular Shapes*, Wiley-Interscience, New York, 1980.
- 46 H. O. Desseyn, M. A. Herman and J. Mullens, *J. Chem. Educ.*, 62 (1985) 220.
- 47 T. Koopman, *Physica (The Hague)* 1 (1933) 104.
- 48 H. Nakatsuji, *J. Am. Chem. Soc.*, 95 (1973) 345, 354, 2084.
- 49 R. M. Badger, *J. Chem. Phys.*, 2 (1934) 128; *J. Chem. Phys.*, 3 (1934) 710.
- 50 D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 35 (1961) 458.
- 51 G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1950.
- 52 C. A. Coulson and Z. Luz, *Trans. Faraday Soc.*, 64 (1968) 2884.