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High-resolution spectroscopy of 4-fluorostyrene-rare gas van der Waals complexes: Results and comparison with theoretical calculations

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High-resolution laser excitation spectra of the $S_1 \leftarrow S_0 0_0^0$ bands of the 1:1 van der Waals complexes of 4-fluorostyrene with atoms of argon and neon are presented. The rotational structure of each is fully assigned using a rigid asymmetric rotor Hamiltonian. The rotational constants for the complexes are used to extract effective coordinates for the rare-gas atoms which contain both dynamic and geometric information. Semiempirical potentials for the clusters in the ground and excited states are determined by fitting to the rotational constants and vibrational frequencies from three-dimensional quantum calculations to the experimental data. The effective coordinates are interpreted by comparison with the results of these quantum calculations on the potential surfaces obtained. © 1998 American Institute of Physics. [S0021-9606(98)01405-6]

I. INTRODUCTION

The van der Waals (vdW) complexes formed between simple aromatic molecules and rare-gas atoms have been much studied because of the importance of these systems in developing an understanding of phenomena such as solvation, nucleated growth, and matrix shifts in vibrational and electronic spectra. In particular, rotationally resolved spectra for these complexes provide a window onto their geometry and internal dynamics. In a recent paper we presented the laser excitation spectra of the $S_1 \leftarrow S_0 \ 0_0^0$ bands of the 1:1 vdW complexes of aniline with atoms of argon and neon formed in a super-sonic molecular beam.¹ Effective coordinates determined for the rare-gas atoms were interpreted by comparison with quantum-mechanical calculations. The present paper describes the results of an equivalent study of the complexes of the 4-fluorostyrene (4FST) molecule. This represents a step up in complexity: The lack of symmetry of the complexes makes the interpretation of the effective coordinates more difficult and the low frequency of the torsional mode in the ground state of 4FST makes coupling with the vdW modes energetically more favorable.

Over the past thirty years there have been numerous spectroscopic studies of styrene (ST) and its derivatives

(Refs. 2 and 3 (and references therein). In a series of papers, Hollas and co-workers derived torsional potentials for ST and 4FST in their ground and excited states.⁴⁻⁶ Both molecules have been classed as quasi-planar in the ground state: The torsional barriers and first vibrational intervals were estimated to be around 348 and 44 cm⁻¹, respectively, for 4FST,⁴ so that the molecule is subject to a large amplitude zero-point torsional motion in the lowest vibrational level. In their excited states ST and 4FST are far more rigid: The torsional barrier and vibrational intervals have been estimated at about 5190 and 170 cm⁻¹, respectively, in 4FST.⁴ As a prelude to the present study, we recorded the laser excitation spectra of the $S_1 \leftarrow S_0 \ 0_0^0$ and $41_0^1 42_0^1$ bands of the bare 4FST molecule in a supersonic molecular beam.² Both bands were a/b-hybrids with the transition moment inclined at an angle of $\pm (35^{+4}_{-5})^{\circ}$ to the *a*-principal inertial axis. The rotational constants obtained for the different vibronic states were used to derive effective molecular geometries.

Several studies of complexes between ST derivatives and small molecules or rare-gas atoms have been performed using resonant two photon ionization (R2PI) processes in a supersonic molecular beam. The $S_1 \leftarrow S_0$ one color (1C)-R2PI spectra of ST-Ar and 4FST-Ar are shifted to the red of the corresponding spectra of the bare molecule by about 31 and 42 cm⁻¹, respectively.⁷ These shifts are of the magnitude expected for a mainly dispersive bonding interaction, which strengthens on excitation of the complexes to their S_1 states. The vibrational structures of these spectra are dominated by the "internal" modes of the aromatic molecule, with weaker satellite bands assigned to excitation of the vdW

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modes. The disappearance of band structure for vibrational excitation exceeding $0_0^0 + 410 \text{ cm}^{-1}$ for ST-Ar^{3,8,9} and $0_0^0 + 496 \text{ cm}^{-1}$ for 4FST-Ar⁷ has been taken as indication of dissociation of these complexes in their excited states. The vdW intervals and dissociation energies of these complexes were reasonably well reproduced by modeling the atomaromatic potential using a pairwise summation of atomatom potentials of the Lennard-Jones 6-12 type.^{3,10,11} The equilibrium position of the argon atom was calculated to be approximately above the center of the aromatic ring but subject to large amplitude vdW oscillations parallel to the ring. Analogous spectra were recorded for the 4FSTX (X=Ne, Kr, and Xe) complexes, where the spectral shift increases with the atoms polarizability as expected from the dispersive nature of bonding interaction.^{7,12}

In this paper, we describe the measurement of the $S_1 \leftarrow S_0 \ 0_0^0$ bands of the 4FST-X (X=Ar and Ne) vdW complexes (Sec. II) and the analysis of their rotational structure (Sec. III). Effective coordinates for the rare gas atom are extracted from the rotational constants in Sec. IV. In Sec. V rotational and vibrational eigenvalues are calculated from a parameterized form of the 4FST-X potential-energy surface and the potential is optimized by least-squares fitting to the experimental data. The role of the effective coordinates in judging the empirical potentials is also demonstrated. The results are then discussed (Sec. VI) in comparison with analogous molecular systems and finally the main points of the work are summarized (Sec. VII).

II. EXPERIMENT

The experimental apparatus has been described in great detail elsewhere¹³ and a brief description only will be given here. A molecular beam is formed by expanding the carrier gas, at a pressure of 400–500 kPa, through a conical nozzle (50 μ m diam) and skimmer (400 μ m diam) into the detection chamber. The gas flow is seeded by passing it over the sample, contained in a heated container, before it enters the nozzle. The nozzle assembly is stabilized to a temperature about 10–15 °C higher than that of the sample to prevent condensation at the nozzle throat. The laser radiation enters and exits the detection chamber through a well baffled path and crosses the molecular beam perpendicularly. The total undispersed laser-induced fluorescence (LIF) is focused onto a photomultiplier tube (EMI 9893Q/350) and the signal is processed by a photon counter (Stanford Research 400).

The UV laser radiation is generated by an intracavity doubled single-mode ring dye laser (Coherent Radiation 699-21) operating on Rhodamine 6G dye (Exciton) and pumped by an argon ion laser (Spectra-Physics mod. 2040-E). In this region, the frequency stability of the system is about ± 2 MHz, the laser power at the crossing point with the molecular beam is 1.5–2.5 mW and the instrumental line broadening is about 15 MHz, which is mainly due to residual Doppler broadening. Absolute frequency calibration to an accuracy of within ± 120 MHz is provided by simultaneously monitoring the absorption spectrum of iodine excited by the dye laser fundamental. Relative frequency shifts

FIG. 1. Comparison between the experimental (exp) and simulated spectra for *a*-type (*a*) and *c*-type (*c*) components of the $S_1 \leftarrow S_0 \ 0_0^0$ transition in 4FST-Ar. The simulated spectra were convoluted with a Lorenzian function of 33 MHz linewidth.

are determined by recording the trace from a 150 MHz free spectral range étalon.

Commercially available 4FST (Aldrich, purity 99%) was used without further purification. The sample was maintained at a temperature around 40 °C, which provides a convenient vapor pressure without significant thermal decomposition. The spectrum of 4FST-Ne was recorded using neon as the expansion gas and that of 4FST-Ar using a 5% mixture of argon in helium. The intensity ratio of the monomer spectrum to that of the complex was about 44:1 for 4FST-Ar, 6:1 for 4FST- 22 Ne and 23:1 for 4FST- 20 Ne.

III. DESCRIPTION OF SPECTRA AND ANALYSIS

The laser excitation spectra of the $S_1 \leftarrow S_0 \ 0_0^0$ vibronic bands of the 4FST-X vdW complexes with X=Ar and Ne are shown in the upper traces of Figs. 1 and 2 respectively. The corresponding spectra of 4FST² consists of ${}^{q}P$ and ${}^{q}R$ branches onto which are superimposed a few strong ${}^{q}Q$ lines. In contrast the spectra of the complexes contain strong Qbranches, consisting of many overlapping transitions.



FIG. 2. Comparison between the experimental (exp) and simulated spectra for *a*-type (a^{20} Ne and c^{20} Ne) and *c*-type (a^{22} Ne) components of the S₁ \leftarrow S₀ 0⁰₀ transition in 4FST-Ne. The simulated spectra were convoluted with a Lorenzian function of 33 MHz line width.





In this type of complex, the equilibrium position of the rare gas atom is normally about 3.5 Å above the center of the aromatic ring.^{1,3} Complexation is not expected to greatly alter the orientation of the transition moment and the principal inertial axes of the complex are primarily a translation of those of the bare molecule towards the rare-gas atom. A re-labeling of the inertial axes occurs: The a axis of the complex remains approximately parallel to that of the bare molecule but the labels of the other two axes are exchanged (i.e., $a \rightarrow a$, $b \rightarrow c$, $c \rightarrow b$). As a result, the a/b-hybrid bands of 4FST are expected to become a/c-hybrids in the complex; this is confirmed by the spectral assignments. The greater intensity of the Q branch in the spectra of the 4FST-X complexes compared to that for the bare molecule results from two effects. First, the ${}^{q}Q$ transitions, produced by the component of the transition moment along the *a* axis, is overlapped by ${}^{p}Q$ and ${}^{r}Q$ transitions produced by the component along the c axis. Second, the intensity and number of observable transitions is increased by a lowering of the ground state A rotational constant upon complexation, increasing the populations of the lowest K_a'' levels. The same effect was observed in the spectra of the equivalent aniline-X complexes.1

The spectra of both 4FST-X complexes are well reproduced by a rigid asymmetric rotor Hamiltonian; least-squares fitting and simulations were performed using a modified version of the ASYROT Fortran code written by Sears.¹⁴

For 4FST-Ar, initial assignments were obtained by simulating the spectrum using, for both states, the previous calculated ground-state rotational constants.¹⁰ The number of assignments was built-up iteratively by simulation and leastsquares fitting. The lines were weighted with the squared inverse of their uncertainty, which was taken as half of the experimental linewidth (33 MHz) for features with a single assignment, or a factor of \sqrt{n} less for a feature assigned to n transitions of approximately equal predicted intensity. The final fit contained 234 rovibronic assignments with $J \leq 15$ and $K_a \leq 10$, accounting for 97% of the total observed intensity. No consistent set of assignments to *b*-type transitions could be made. The band was estimated to be of 62^{+4}_{-3} % *a*-type and $38^{-4}_{+3}\%$ *c*-type, by averaging the value of $I_{\rm obs}/I_{\rm calc}$, where I is the intensity of a particular line, over the ten strongest unblended lines of each transition type. The results from the least-squares fit of the spectrum of 4FST-Ar are given in Table I. The lower two traces of Fig. 1 show simulations of the spectra produced by each component of the transition moment, assuming a Boltzmann distribution of rotational populations in the ground state (see Table I) and convoluting the transitions with a Lorenzian function.

The spectrum of the 4FST-Ne complex, shown in Fig. 2, is very similar to that expected for an asymmetric nearprolate top, as is the case for the analogous spectrum of aniline-Ne.¹ The aniline-Ne spectrum consists of superimposed signals assigned to the isotopomers resulting from complexation with ²⁰Ne and ²²Ne atoms, despite the fact that the experimental ratio ($\approx 3.5:1$) does not agree with the ratio of their natural isotopic abundances ($\approx 9.8:1$). It is clear from Fig. 2 that a similar phenomenon is observed in the spectrum

TABLE I. Results from the least-squares fit of the $S_1 \leftarrow S_0 \ 0_0^0$ band of 4FST-Ar. Here the symbols ν_0 , θ , and σ refer to the band origin, rotational temperature of the expansion (estimated by simulation of the spectrum assuming a Boltzmann distribution in the ground state) and the standard deviation of the fit respectively.

Variable	Unit	Value ^a
Α"	cm^{-1}	0.035 746(13)
B''	cm^{-1}	0.027 348 7(53)
C''	cm^{-1}	0.018 859 2(53)
A'	cm^{-1}	0.036 186(14)
B'	cm^{-1}	0.027 271 9(54)
C'	cm^{-1}	0.0191842(54)
ν_0	cm^{-1}	34 270.0892(12)
θ	K	2.0(5)
σ	MHz	8.2

^aNumbers in parentheses represent one standard deviation of the parameter in units of the last quoted decimal place.

of 4FST-Ne: The strong Q branch is accompanied by a similar feature of about one quarter the intensity, shifted to the red by ~0.1 cm⁻¹. These two features are assigned to the isotopomers 4FST-²⁰Ne and 4FST-²²Ne respectively.

Starting values for the rotational constants of the 4FST-²⁰Ne complex were estimated by assuming that the 4FST moiety has the same geometry as the bare molecule² and that the neon atom sits in the same equilibrium position calculated for the rare-gas atom in 4FST-Ar.¹⁰ Initial assignments for the much weaker lines produced by the 4FST-²²Ne isotopomer required more accurate starting estimates of the rotational constants for both states. These were calculated from the effective inertial tensor, given in Sec. IV, using the effective coordinates values obtained from the rotational constants of the 4FST-20Ne complex but with the appropriate effective mass term for the 4FST-²²Ne complex. The final least-squares fits contained 263 and 55 rovibronic assignments for 4FST-²⁰Ne and 4FST-²²Ne, respectively, with $J \leq 14$ and $K_a \leq 7$ and accounted for 97% of the total observed intensity. Again, no consistent set of assignments to *b*-type transitions could be made. For the more intense 4FST-²⁰Ne isotopomer, the percentages of the two components of the transition moment were estimated as 73^{+5}_{-4} % *a*-type and 27^{-5}_{+4} % *c*-type. For the less intense 4FST-²²Ne isotopomer, all of the observable lines were assigned as a-type transitions and the c-type transitions were simply too weak to be seen.

The intensity ratio for the two isotopomers ($\approx 3.5:1$) was estimated from the relative intensities of the *Q* branches. For aniline-Ne the increase in the relative intensity of transitions for the more massive complex was attributed to an increase in the efficiency of complex formation resulting from the slightly lower zero-point energy.¹ Brooks *et al.* reported a similar increase in the intensity of the strongest lines in the IR spectra of the ν_3 band of jet cooled ²²Ne-SiH₄ compared to ²⁰Ne-SiH₄.¹⁵ They explained this increase in terms of a quasi-equilibrium, maintained by binary collisions in the expansion, which interconverts the two isotopomers. Applying this model to 4FST-Ne, using the rotational temperature estimated from simulations of the band profiles (see Table II)

TABLE II. Results from the least-squares fits of the $S_1 \leftarrow S_0 0_0^0$ bands of 4FST-²⁰Ne and 4FST-²²Ne. The symbols ν_0 , θ , and σ have the definitions given in the heading to Table I.

		Value ^a			
Variable	Unit	4FST- ²⁰ Ne	4FST- ²² Ne		
<i>A</i> ″	cm^{-1}	0.056 539(11)	0.054 01(58)		
B''	cm^{-1}	0.027 329 1(44)	0.027341(16)		
C''	cm^{-1}	0.023 389 6(44)	0.022 860(16)		
A'	cm^{-1}	0.056 411 9(94)	0.053 96(58)		
B '	cm^{-1}	0.027 259 8(44)	0.027 265(15)		
C'	cm^{-1}	0.023 678 1(44)	0.023 152(15)		
ν_0^{b}	cm^{-1}	34 304.1211(32)	34 304.0756(32)		
$\hat{\theta}$	Κ	1.2(5)	1.2(5)		
σ	MHz	8.0	7.4		

^aNumbers in parentheses represent one standard deviation of the parameter in units of the last quoted decimal place.

^bThe error in the band origin is dominated by the uncertainty in line positions of the iodine spectrum caused by Doppler broadening in the static cell. The separation between the two isotopic bands is better determined: $\Delta \nu = 0.045 57(17) \text{ cm}^{-1}$; the accuracy in this case is limited by the uncertainty determined in the least-squares fit.

and zero-point energies from the vibrational eigenvalues calculated in Sec. V (see Tables XI and XIII), the relative populations of the lowest rovibronic levels of the two isomeric forms of the 4FST-Ne cluster should be about 5:1. Considering the approximate nature of this model (which neglects three body collisions) this value is in reasonable agreement with experiment.

The results from our least-squares fit of the spectra of 4FST-²⁰Ne and 4FST-²²Ne are given in Table II. Simulations of the spectra of both isotopomers using these constants are shown in the lower three traces of Fig. 2.

IV. d₀ STRUCTURE

The "loose" nature of the binding in the 4FST-X complexes makes it particularly difficult to extract unambiguous



FIG. 3. Principal axes (a_0, b_0) and molecular geometry of 4FST in its electronic ground state used for calculation in this paper $(c_0 \text{ axis is perpendicular to the page})$. The atoms are represented as follows: Solid circle for carbon, open circle for hydrogen, centered circle for fluorine.

structural information from the rotational constants. In the lowest vibrational levels of the complexes these constants depend upon the average of the instantaneous inverse inertial tensor over the zero-point oscillations of the atoms in the complex. The oscillations are particularly large and anharmonic for the vdW modes owing to the weak dispersive interaction between the rare-gas atom and the aromatic molecule.

As in our previous work on aniline-X complexes,¹ we have used the rotational constants to determine an effective inertial tensor for each electronic state. The tensor is set up in the body-fixed reference frame (BF) with its origin at the center of mass of the complex and with axes parallel to the principal axes (a_0 , b_0 , c_0) of the molecule. The principal axis system is shown in Fig. 3 for 4FST. The inertial tensor is given by

$$\begin{cases} k/A_0 + \mu(Y^2 + Z^2) & -\mu XY & -\mu XZ \\ -\mu XY & k/B_0 + \mu(Z^2 + X^2) & -\mu YZ \\ -\mu XZ & -\mu YZ & k/C_0 + \mu(X^2 + Y^2) \end{cases},$$
(1)

where μ is the reduced mass of the complex, *X*, *Y* and *Z* are the Cartesian coordinates of the rare-gas atom with respect to the principal axes of 4FST, the proportionality constant $k = h/8\pi^2 c$ and A_0 , B_0 , C_0 are the rotational constants of the bare 4FST molecule in the same electronic state.² The effective *X*, *Y*, and *Z* have been called the d₀ structure by Brooks and van Koeven.¹⁶

The d_0 approach makes the assumption that the aromatic molecule remains a rigid body which is unchanged by com-

plexation. In aromatic-rare gas complexes, this assumption is normally justified by the fact that the internal modes of the aromatic molecule are much higher in frequency than the vdW modes. The assumption is questionable for complexes involving 4FST, particularly in the S₀ state where the torsional internal mode, $v_{42}'' = 42 \text{ cm}^{-1}$,⁴ is very close in frequency to the calculated vdW vibrational modes (see Tables IX and XI). In the S₁ state, where the lowest vibrational mode is the out-of-plane motion of the vinyl group [41(1-0)]

TABLE III. Comparison between the d₀ coordinates for the argon atom in 4FST-Ar determined from experimental rotational constants (exp), and those obtained from rotational constants calculated variationally (var) and by perturbation theory (per). The calculations are numbered according to the parameter sets give in Table VII.

			Calc ^a					
		-	1	2		3		
(Å)	Exp ^a	per	var	per	var	var		
S ₀ state								
X	0.014(10)	0.216(5)	0.217(7)	0.050(27)	0.042(25)	0.037(22)		
Y	0.542(8)	0.069(46)	0.459(31)	0.086(55)	0.537(27)	0.484(28)		
Ζ	3.469(2)	3.476(2)	3.453(4)	3.493(2)	3.462(4)	3.491(3)		
S ₁ state								
X	0.019(3)	0.205(6)	0.204(11)	0.039(23)	0.039(24)	0.036(23)		
Y	0.501(13)	0.072(48)	0.428(45)	0.098(61)	0.522(32)	0.452(34)		
Ζ	3.423(3)	3.460(2)	3.441(5)	3.478(2)	3.450(5)	3.441(5)		
Z' - Z''^{b}	-0.046(5)	-0.016(4)	-0.012(9)	-0.015(4)	-0.012(9)	-0.050(8)		

^aNumbers in parentheses represent the range of solutions within the tolerance levels of the calculation in units of the last quoted decimal place.

^bDifference in the Z coordinates determined for S_1 and S_0 states.

at about 79 cm⁻¹, an adiabatic separation of the vibrational modes is more justifiable. This is further supported by the relatively small "solvation" effects of attaching an argon atom to the aromatic modes on the internal modes of ST and trans- β -methylstyrene (BMS) in their S₁ states: The frequencies of the in-plane vibrations generally change by less than 1% and the out-of-plane vibrations by only 3% - 4%.³ The treatment of the 4FST molecule as a rigid body is also more reasonable for the excited state where its inertial defect is less negative than in the ground state.²

Tables III and IV contain the effective coordinates of the rare-gas atom calculated from the experimental rotational constants for the 4FST-Ar and 4FST-Ne complexes, respectively. The inertial tensor is calculated using trial values for X, Y, and Z and then diagonalized to give values for the rotational constants. The trial coordinates are accepted if the calculated rotational constants reproduce the experimental ones to within certain tolerance limits. The effective parameters are then obtained by averaging over the set of acceptable parameter values. In the calculations for 4FST-Ar and 4FST-²⁰Ne tolerance limits of 2×10^{-5} and 3×10^{-5} cm⁻¹ were required to produce solutions from the ground-state and excited-state rotational constants, respectively. These limits are of the same order of magnitude as the experimentally

TABLE IV. Expectation values of the argon atom coordinates, $\langle X \rangle$, and RMS amplitudes of zero-point motion along these coordinates, ΔX , calculated for 4FST-Ar in the lowest vibrational levels. The calculations are numbered according to the parameter sets give in Table VII.

	1		2	2		3	
(Å)	S ₀	S_1	\mathbf{S}_0	S_1	\mathbf{S}_0	\mathbf{S}_1	
$\langle X \rangle$	-0.221	-0.212	0.065	0.045	0.054	0.019	
$\langle Y \rangle$	-0.053	-0.053	-0.064	-0.064	-0.071	-0.071	
$\langle Z \rangle$	3.475	3.460	3.492	3.477	3.515	3.462	
ΔX	0.265	0.259	0.316	0.305	0.276	0.257	
ΔY	0.319	0.310	0.352	0.342	0.314	0.294	
ΔZ	0.112	0.112	0.119	0.119	0.107	0.105	

determined standard deviation in the A rotational constant but about an order greater than the standard deviations in the Band C constants, reflecting the approximation made in determining the rotational constants from the inertial tensor (1). For 4FST-²²Ne the experimental rotational constants are not so well determined and the tolerance limits were set equal to their standard deviations.

Pratt and co-workers have pointed out that the d₀ coordinates should be regarded as root-mean-square displacements averaged over the vibrational wavefunction of the complex.¹⁷ This is re-enforced by the fact that the inertial tensor is invariant to sign changes in X, Y, or Z. These coordinates will contain both static contributions, reflecting the equilibrium position of the rare-gas atom with respect to the center of mass of the 4FST molecule in the lowest vibrational level, and dynamic contributions, reflecting the vibrational excursions due to the zero-point motion. In the case of the aniline-X vdW complexes, the rare-gas atoms have their equilibrium positions in the symmetry plane of the complex; the *static* contribution to the b_0 coordinate, perpendicular to this plane, is therefore necessarily zero and the effective Y-coordinate contains only dynamic information.^{1,14} In complexes of lower symmetry, such as 4FST-X, it is more difficult to predict a priori the exact extent to which the effective coordinates will depend upon either of these contributions and their interpretation is aided by comparison with calculated values.

V. QUANTUM CALCULATIONS ON VAN DER WAALS **STATES**

A. LCHOP method

We have used the linear combination of harmonic oscillator products (LCHOP) method of Brocks and van Koeven^{16,18} to calculate the rotational and vibrational energy levels of the 4FST-X complexes. This method has previously been used successfully to interpret the 1C-R2PI spectra of

TABLE V. Comparison between the d₀ coordinates for the neon atom in 4FST-Ne determined from experimental rotational constants (exp), and those obtained from rotational constants calculated variationally (var). The calculations are numbered according to the parameter sets given in Table VIII.

	4FST- ²⁰ Ne						4FST- ²² Ne	
(Å)	Exp ^a	1 Var ^a	2 Var ^a	3 Var ^a	4 Var ^a	Exp ^a	4 Var ^a	
S_0 state								
X	0.039(26)	0.223(19)	0.355(11)	0.040(26)	0.030(20)	0.139(84)	0.101(61)	
Y	0.414(11)	0.335(15)	0.416(15)	0.364(9)	0.432(7)	0.508(47)	0.497(30)	
Ζ	3.368(2)	3.166(2)	3.324(2)	3.168(1)	3.377(1)	3.338(18)	3.355(10)	
S_1 state								
X	0.035(23)	0.198(21)	0.306(19)	0.037(24)	0.019(13)	0.131(79)	0.096(57)	
Y	0.374(9)	0.301(14)	0.380(22)	0.328(7)	0.377(3)	0.467(39)	0.449(26)	
Ζ	3.334(1)	3.152(2)	3.311(2)	3.155(1)	3.344(1)	3.301(15)	3.320(8)	
Z' - Z''^{b}	-0.034(3)	-0.014(4)	-0.013(4)	-0.010(2)	-0.033(2)	-0.037(33)	-0.035(18)	

^aNumbers in parentheses represent the range of solutions within the tolerance levels of the calculation in units of the last quoted decimal place.

^bDifference in the Z coordinate determined for S₁ and S₀ states.

these complexes,^{10–12} as well as those of several related complexes (styrene-Ar,^{3,10} fluorene-Ar,¹⁶ aniline-Ar,^{1,19} aniline-Ne,¹ benzene-Ar^{18,20}).

Briefly, the Hamiltonian is constructed in the BF frame, described in Sec. IV. This choice enables the Cartesian coordinates of the noble gas atom to be used to describe the intermolecular vdW vibrations and the internal vibrations of the aromatic species to be described by their normal coordinates. The only approximation made in this derivation is the adiabatic separation of the internal modes and the vdW modes. The Hamiltonian for a given rovibronic state is averaged over the internal modes and the vdW eigenfunctions are then calculated by diagonalizing the matrix representation of the purely vibrational part of the Hamiltonian in a basis set of products of harmonic oscillator functions in x, y, and z. These oscillators are centered at the equilibrium position of the rare-gas atom, X_e , Y_e , Z_e , and their frequencies, ω_x , ω_{v} , ω_{z} , are scaling parameters which are optimized variationally. The matrix elements of the kinetic energy operator are obtained through the use of harmonic oscillator creation and annihilation operators.

The rovibrational energy levels are calculated from the rotation-vibration part of the Hamiltonian, including the overall rotation of the complex and the Coriolis coupling between this rotation and the internal motions. This Hamiltonian is used in full variational calculations for each given value of J. Rotational constants are then obtained for the ground vibrational level by fitting the levels computed for a series of J-values to a rigid asymmetric rotor Hamiltonian (in the same way as one usually deduces rotational constants from the measured frequencies of the rotational levels). In addition, we calculate the vibrationally averaged rotational constants of the complex from the vdW eigenfunctions computed for J=0 by means of first and second order perturbation theory, with the Coriolis coupling operator as the perturbation.

Apart from the validity of the adiabatic separation of vibrational frequencies, the accuracy of these calculations is mainly limited by the quality of the aromatic molecule-raregas interaction potential. Ab initio calculations for this type of complex have only been performed for benzene-Ar.^{20,21} In the absence of such calculations, we represent the potential, V(r), as a sum of pairwise atom-atom dispersive interaction terms of the Lennard-Jones 6-12 form

$$V(r) = \sum_{i,j} 4\varepsilon_{ij} (-(\sigma_{ij}/r)^6 + (\sigma_{ij}/r)^{12}), \qquad (2)$$

TABLE VI. Expectation values of the argon atom coordinates, $\langle X \rangle$, and RMS amplitudes of zero-point motion along these coordinates, ΔX , calculated for 4FST-Ne in the lowest vibrational levels of the S₀ and S₁ states. The calculations are numbered according to the parameter sets given in Table VIII.

	4FST- ²⁰ Ne								4FST	²⁻²² Ne
(Å)	1	1	2	2	2	3	4	4		4
State:	S_0	S_1	S_0	\mathbf{S}_1	S_0	S_1	S_0	\mathbf{S}_1	S_0	\mathbf{S}_1
$\langle X \rangle$	-0.256	-0.243	-0.372	-0.333	-0.076	-0.081	0.025	-0.002	0.021	-0.006
$\langle Y \rangle$	-0.051	-0.053	-0.042	-0.043	-0.070	-0.069	-0.069	-0.069	-0.069	-0.069
$\langle Z \rangle$	3.177	3.160	3.338	3.322	3.178	3.163	3.391	3.354	3.388	3.351
ΔX	0.351	0.342	0.386	0.379	0.368	0.358	0.385	0.361	0.377	0.354
ΔY	0.387	0.377	0.423	0.411	0.391	0.381	0.408	0.385	0.403	0.381
ΔZ	0.155	0.156	0.166	0.166	0.159	0.159	0.158	0.155	0.154	0.151

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where ε_{ij} is the well depth and σ_{ij} is the distance at the minimum of the interaction between atoms i and j (alternatively, they are referred to as the "energy" and "geometric" parameters, respectively²²). This model excludes the dipoleinduced dipole contribution to the vdW interaction, which has been evaluated as less than 3% of the total energy in complexes of aniline and fluorobenzene.²³ Interatomic separations are calculated using the effective molecular geometries for the relevant state of 4FST determined in our recent study.² The matrix elements of this potential are evaluated numerically using Gauss–Hermite quadrature in x, y, and z. One of the problems with this approach is the lack of knowledge of the potential parameters, ε_{ii} and σ_{ii} . Furthermore, the simplification is made that these parameters are identical for interactions between atoms of the same type regardless of their position in the molecule.

Previous attempts to model the vibrational energy levels of 4FST-Ar in this way made use of parameter values collected from various sources in the literature.^{10,11} In following section we test the ability of these parameter sets to reproduce the rotational constants of the 4FST-Ar and 4FST-Ne. We also test a parameter set calculated using the Scheraga model.^{7,24,25} The geometric parameter is calculated from the equilibrium distance, r_{ii}^{0} , for interactions between atoms of the same type

$$\sigma_{ij} = (1/2)^{1/7} (r_{ii}^{0} + r_{jj}^{0}), \qquad (3)$$

and the energy parameter is then determined from a modified version of the Slater and Kirkwood formula²⁴ for the vdW attraction between a generic group of atoms

$$4\varepsilon_{ij}\sigma_{ij}^{\ 6} = \frac{Z_c\alpha_i\alpha_j}{(\alpha_i/N_i)^{1/2} + (\alpha_i/N_i)^{1/2}}.$$
(4)

Here α_i is the polarizability and N_i is an "effective" number of electrons for atom i, and the Z_c is a constant. The values of r_{ii}^{0} , α_i , and N_i required for the calculation of the two parameters have been optimized by Scheraga to reproduce the molecular crystal structure of a large number of organic compounds. Finally, empirical parameterizations of the potentials for these complexes are obtained by fitting the calculations to the experimentally determined rotational constants and vdW vibrational intervals.

The parameter sets discussed in these sections are listed in Table VII for 4FST-Ar and Table VIII for 4FST-Ne. For the calculations on 4FST-Ar, the optimum scaling of the basis functions was achieved using $\omega_x = 5 \text{ cm}^{-1}$, $\omega_y = 6 \text{ cm}^{-1}$, and $\omega_z = 35 \text{ cm}^{-1}$ and for 4FST-Ne using $\omega_x = 6 \text{ cm}^{-1}$, $\omega_{v} = 5 \text{ cm}^{-1}$, and $\omega_{z} = 30 \text{ cm}^{-1}$. In both cases the calculations were converged with 10 harmonic oscillator functions in the x and y coordinates and 8 functions in the z coordinate. The interaction potential matrix elements were calculated over a grid of 24×24×24 integration points in the Gauss-Hermite quadrature.

B. 4FST-Ar

Tables IX and X compare the results of calculations using parameter sets taken from the literature (set 1),^{10,11} from

TABLE VII. Parameter values used in the atom-atom pair potentials of 4FST-Ar.

	1 ^a	2 ^b	3	c
State:	\mathbf{S}_0 and \mathbf{S}_1	\mathbf{S}_0 and \mathbf{S}_1	S ₀	\mathbf{S}_1
$\varepsilon_{C-Ar}(cm^{-1})$	53.63	44.71	70.87	77.45
$\varepsilon_{\rm H-Ar} (\rm cm^{-1})$	32.34	30.85	30.85	30.85
$\varepsilon_{\rm F-Ar} (\rm cm^{-1})$	81.0	38.49	38.49	38.49
$\sigma_{\mathrm{C-Ar}}(\mathrm{\AA})$	3.37	3.37	3.382	3.349
$\sigma_{\mathrm{H-Ar}}(\mathrm{\AA})$	3.03	2.98	2.98	2.98
$\sigma_{ m F-Ar}(m \AA)$	3.52	3.03	3.03	3.03

^aReference 10 and 11.

^bReference 7.

^cThis work.

the Scheraga model (set 2)^{7,24,25} and empirically optimized (set 3) for the S_0 and S_1 states of 4FST-Ar, respectively. The vdW modes in which the rare gas moves approximately parallel to the aromatic plane are referred to as "bending" modes, b_x , b_y , and that involving motion of the argon mostly perpendicular to this plane as a "stretching" mode, s_{z} . The characters of the calculated vibrational eigenstates were defined by the highest contributing functions of the harmonic basis set, labeled (n_x, n_y, n_z) where n_x is the harmonic quantum number in the x axis, etc. The frequencies of b_x , b_y , and s_z are then the eigenvalues of the states which contain the highest percentages of the (100), (010), and (001)basis functions, respectively. The rotational constants, A, B, C, given in the tables refer to the values obtained from a full variational treatment of the rotation vibration Hamiltonian for the lowest vibrational level. Both tables contain the equilibrium coordinates and well depth, V_{\min} . Table X also contains the dissociation energy from the lowest vibrational level of the excited state, D_0' , and the "solvent" shift, $\Delta v_{\rm solv}$.

1. Parameter sets 1 and 2

Parameter set 1 was recommended by Consalvo et al. on the basis of a good agreement between the separations of the main bands in the $S_1 \leftarrow S_0$ 1C-R2PI spectrum and the vdW eigenvalues calculated for the So state.¹⁰ The potential was subsequently used to extend the set of assignments to com-

TABLE VIII. Parameter values used in the atom-atom pair potentials of 4FST-Ne.

	1^{a}	2 ^b	3°	4	lq
State:	\boldsymbol{S}_0 and \boldsymbol{S}_1	\boldsymbol{S}_0 and \boldsymbol{S}_1	$S_0 \mbox{ and } S_1$	\mathbf{S}_0	S_1
$\varepsilon e_{C-Ne}(cm^1)$	21.48	20.01	25.28	28.91	31.06
$\varepsilon_{\rm H-Ne}(\rm cm^1)$	25.39	16.03	15.65	15.65	15.65
$\varepsilon_{\rm F-Ne}({\rm cm}^{-1})$	43.00	44.02	26.16	26.16	26.16
$\sigma_{ m C-Ne}(m \AA)$	3.109	3.22	3.06	3.239	3.220
$\sigma_{\mathrm{H-Ne}}(\mathrm{\AA})$	2.887	2.79	2.68	2.68	2.68
$\sigma_{ ext{F-Ne}}(ext{Å})$	3.204	3.18	2.72	2.72	2.72

^aReference 12.

^bReference 28.

^cReference 7.

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TABLE IX. Comparison between experimental data and the results of calculations for 4FST-Ar in its S_0 state. The calculations are numbered according to the parameter sets given in Table VII. The rotational constants were obtained in a full variational calculation.

	Exp^{a}		Calc ^b	
		1	2	3
$X_{e}(\text{\AA})$ $Y_{e}(\text{\AA})$ $Z_{e}(\text{\AA})$ $V_{\min}(\text{cm}^{-1})$ $A(\text{cm}^{-1})$ $B(\text{cm}^{-1})$ $C(\text{cm}^{-1})$	0.035 746(13) 0.027 348 7(53) 0.018 859 2(53)	-0.255 -0.060 3.433 502.2 0.036 457[1.99] 0.027 091 0[-0.94] 0.018 950 5[0.49]	-0.041 -0.075 3.445 387.0 0.035 892[0.41] 0.027 324 2[-0.09] 0.018 874 3[0.08]	-0.022 -0.078 3.477 566.9 0.035 559[-0.52] 0.027 298 6[-0.18] 0.018 799 0[-0.32]
$b_x^1(cm^{-1}) b_x^2(cm^{-1}) b_y^1(cm^{-1}) s_z^1(cm^{-1})$	11.5° 19.0 ^d	13.47 25.33 25.26 41.46	9.32 17.00 20.63 34.93	12.40 23.20 26.44 44.56

^aThis work. Numbers given in round parentheses are one standard deviation of the fitted constant in units of the last quoted decimal place. ^bNumbers given in square parentheses are the percentage deviation from the experimentally determined value of the rotational constant. ^cReference 11.

^dReference 7.

bination vdW bands by Piccirillo *et al.*¹¹ The expected Franck–Condon factors for these transitions were also used as a guide, so that two features at 28.2 and 31.1 cm⁻¹ to the blue of the 0_0^0 band were assigned as b_{x0}^2 and b_{y0}^1 , respectively, contrary to their calculated energy order. A weak feature at $0_0^0 + 3.5$ cm⁻¹ was assigned as the hot band b_{x1}^1 , giving a first vibrational interval of about 11.5 cm⁻¹ for this mode in the ground state.

In our calculations we first used parameter set 1 to represent the potential in both ground and excited states; the calculations differ only in the geometries of the 4FST moiety in these states. The agreement of the calculated vdW eigenstates for the excited state with experiment, obtained using a more accurate geometry for 4FST in this state, is an improvement on the results of Consalvo *et al.*: The b_x and s_z eigenvalues agree with the assigned intervals to within ± 1 cm⁻¹ and b_y is about 5 cm⁻¹ too low. Only the value of b_x changes appreciably in the ground-state calculation but the decrease of about 0.7 cm⁻¹ is much less than that expected from the hot band assignment.

The well depths obtained for these states can be judged by comparing the experimental solvent shift and dissociation energy for the S_1 state with the calculated values. To a first approximation

$$D_0' \approx -V_{v=0}(S_1),$$
 (5)

$$\Delta \nu_{\text{solv}} \approx V_{v=0}(S_1) - V_{v=0}(S_0), \tag{6}$$

TABLE X. Comparison between experimental data and the results of calculations for 4FST-Ar in its S_1 state. The calculations are numbered according to the parameter sets given in Table VII. The rotational constants were obtained in full variational calculation.

			Calc ^b	
	exp ^a	1	2	3
X_e (Å)		-0.243	-0.049	-0.044
Y_e (Å)		-0.060	-0.073	-0.076
Z_e (Å)		3.417	3.429	3.424
$V_{\rm min}({\rm cm}^{-1})$		505.2	388.9	616.8
$D_0' ({\rm cm}^{-1})$	350–581 ^c	460.4	350.7	567.2
$\Delta \nu_{\rm solv} ({\rm cm}^{-1})$	-42.017(5)	-2.5	-1.5	-46.8
$A(\mathrm{cm}^{-1})$	0.036 186(14)	0.036 286[0.28]	0.035 731[-1.25]	0.036 023[-0.45]
$B(\mathrm{cm}^{-1})$	0.027 271 9(54)	0.027 036 6[0.86]	0.027 256 1[-0.05]	0.027 225 3[0.17]
$C(\mathrm{cm}^{-1})$	0.019 184 2(54)	0.019 109 3[-0.13]	0.019 029 6[-0.81]	0.019 132 6[-0.27]
$b_x^1 ({\rm cm}^{-1})$	15.0 ^d	14.14	10.05	14.21
$b_{\rm r}^2 ({\rm cm}^{-1})$	28.2	26.59	18.37	26.70
$b_{y}^{\hat{1}}$ (cm ⁻¹)	31.1	25.48	20.98	28.42
b_{y}^{2} (cm ⁻¹)	56.0	53.01	46.33	57.96
$b_x^{i} b_y^{1}$ (cm ⁻¹)	40.5	38.23	34.72	40.77
$s_z^{1}(cm^{-1})$	41.0	41.69	35.43	47.18

^aThis work. Numbers given in round parentheses are one standard deviation of the fitted constant in units of the last quoted decimal place. ^bNumbers given in square parentheses are the percentage deviation from the experimentally determined value of the rotational constant. ^cReference 7.

^dvdW vibrational intervals obtained from Ref. 11.

where $V_{y=0}$ is the value of the potential function for the lowest vibrational level. The calculated value of Δv_{solv} =-2.5 cm⁻¹ using parameter set 1 compares poorly with the experimental shift of -42.017(5) cm⁻¹, indicating that different parameter values are needed to model the two states. It is difficult to judge the accuracy of the calculation for the dissociation energy in either state because of the large uncertainty in experimental measurements of this quantity (see Ref. 26 for a review of the experimental difficulties). Comparison of the 1C-R2PI spectra of 4FST and 4FST-Ar, reveals that the intensities of analogous vibronic bands are similar up until 0_0^0 +350 cm⁻¹ after which the intensity of the bands of the complexes drop off until there is no sign of a band corresponding to that of the bare molecule at 0_0^0 $+581 \text{ cm}^{-1.7}$ This reduction in intensity is attributed to the onset of predissociation and the dissociation energy of the complex in the excited state may then be put within the limits $360 < D_0' < 581 \text{ cm}^{-1}$. Haas and Kedler warn that one-color photo-ionization schemes may lead to excitation from levels above the dissociation limit of the complex and that the true dissociation energy will be lower than those determined here.²⁶ This is supported by recent LIF and lifetime measurements for ST-Ar by the same authors.²² The values of 460 cm⁻¹ for the dissociation energy in S₁ calculated using parameter set 1 is therefore probably on the high side. In the following sections we demonstrate that the well depth is the quantity most sensitive to the choice of parameters used in the atom-atom pair potentials.

Calculations using the same parameter set 2, obtained from the Scheraga model, were performed for both groundand excited-state geometries. The calculated vdW eigenstates consistently under-estimate the experimental values for both states. However, their energy order for the S₁ state reproduces that of the assignments in 1C-R2PI spectrum. The eigenstates labeled b_x^2 and b_y^1 are the third and fourth, respectively. Moreover, the eigenstates labeled b_x^{-1} , b_y^{-1} and, s_z^{1} are the sixth and eighth, separated by about 0.7 cm⁻¹, which is in good agreement with the experimental separation of about 0.5 cm⁻¹. A smaller dissociation energy for the S₁ state (350.7 cm^1) is obtained using this parameterization but, the use of the same parameters to represent the potential in both states, results in a calculated solvent shift (-1.5 cm^{-1}) which is again far too small.

Using parameter set 1, the rotational constants obtained in the full variational calculation agree with the experimental values to within about 2% for both states. Using parameter set 2, the level of agreement is about 0.5% for the ground state and 1% for the excited state. The rotational constants determined by treating the Coriolis term as a perturbation are $\sim 0.5\%$ worse in all of the calculations. It was found that the effective d₀ coordinates for the argon atom, obtained from the calculated rotational constants, are of much greater use in judging the two parameter sets than the constants themselves. Table III compares the effective coordinates obtained from both the perturbative (per) and variational (var) calculations with those determined from experiment. The tolerance limits applied to the calculated rotational constants were identical to those used for the corresponding experimental values.

It is immediately apparent that, for both parameter sets, the variationally determined coordinates are much closer to the experimental values. This is reflected best in the effective Y coordinate, for which a value close to 0.5 Å is determined experimentally for both states. For both parameter sets the variational calculations yield $Y \approx 0.4-0.5$ Å, whilst perturbation theory gives $Y \approx 0$ for both states of the complex. In addition, the Z coordinates obtained variationally were also closer to the experiment in all of the calculations than those obtained by perturbation theory. From this point on we shall concentrate solely on the results of the variational calculations.

The main difference in the effective coordinates obtained with the two parameter sets occurs in the values obtained for X. This coordinate is close to 0.2 Å for the set 1 calculations, while the negligibly small experimental values are well reproduced by the set 2 calculations. Parameter sets 1 and 2 differ most significantly in the value of the ε_{Ar-F} parameter used (81.0 cm⁻¹ in set 1 compared to 38.89 cm⁻¹ in set 2). Table IV contains the calculated values of the rootmean-square (RMS) amplitudes of the zero-point motion, ΔX , and average value of the coordinates, $\langle X \rangle$, for the argon atom in the lowest vibrational level of each state. The RMS amplitudes are similar for both states and both parameterizations; ΔX and ΔY are about 0.3 Å, indicating large freedom of motion parallel to the molecular plane, and ΔZ is about 0.1 Å, since the potential well is narrower in this coordinate. The vibrationally averaged coordinates are only slightly displaced from the equilibrium coordinates of the potential (given in Tables IX and X) but differ significantly in the two parameterizations. The larger value of ε_{F-Ar} in set 1 produces a stronger dispersive interaction between this atompair which shifts the potential towards the fluorine atom, $X_e \approx \langle X \rangle \approx -0.2$ Å. While using set 2 gives a potential minimum much closer to the center of mass of the 4FST molecule, $X_e \approx \langle X \rangle \approx 0.0$ Å. The effective coordinate, X, obtained with the two parameter sets reflects the difference in the position of the potential minimum. The effective Z coordinate reflects mainly the vibrationally average value of this coordinate, since $\langle Z \rangle \gg \Delta Z$. Neither parameter set reproduces the reduction in the value of this coordinate upon excitation, which results from the strengthening of the dispersive interaction. The interpretation of the effective coordinates will be discussed in more detail in Sec. VI.

It was concluded that parameter set 2 produces the more realistic description of 4FST-Ar in these states. Although set 1 produces a better approximation to the observed vdW frequencies in S_1 , this is achieved by using an artificially high parameter for the Ar-F atom-pair potential which shifts the potential towards the fluorine to an extent not suggested by the experimental d_0 coordinates. This highlights the danger of collecting parameter values from different literature sources. The parameters contained in set 2, while underestimating the vdW frequencies, were calculated in a consistent manner and more correctly reflect the balance of the dispersive interactions which determined the position of the argon



FIG. 4. Dependence of the (i) A, (ii) B, and (iii) C rotational constants calculated for the S₁ state of 4FST-Ar on the C-Ar atom pair parameters. The constants obtained are plotted against the geometric parameter, σ_{C-Ar} , using a different symbols for calculations using different values of the energy parameter, ε_{C-Ar} [30(\Box), 40(\bigcirc), 50(Δ), 60(∇), 70(\diamondsuit), 80(+) cm⁻¹]. The calculations treated the Coriolis term as a perturbative correction to the rotation-vibration Hamiltonian.

above the aromatic plane. There was, however, a need to produce a new set of parameters which better reproduce the vdW frequencies without adversely influencing the d₀ structure.

2. Parameter set 3

Ab initio calculations indicate that the $S_1 \leftarrow S_0$ transition in ST is dominated by two configurational changes, both involving promotion of one electron to an antibonding orbital located primarily on the aromatic ring.²⁷ Consequently, it might be expected that the potential parameters which change most significantly between the ground and excited states will be those which model the interaction of the argon atom with the carbon atoms of the aromatic ring. Clearly, a deficiency in the present model of the potential is that it does not differentiate between the carbon atoms of the aromatic ring and those of the vinylic group.

To quantify their effect, the LCHOP calculation was repeated over a grid of values for ε_{C-Ar} and σ_{C-Ar} , with the other parameters constrained to those of the ground state in set 2. The graphs given in Fig. 4 show the rotational constants calculated by perturbation theory and those in Fig. 5 the potential well depth (i) and the s_z^{-1} vdW vibrational intervals (*ii*) as functions of ε_{C-Ar} and σ_{C-Ar} . The other vdW vibrational eigenstates showed a dependence upon the parameters similar to that of s_z^{-1} . These calculations were performed with the S₁ geometry of 4FST-Ar since the vdW vibrational intervals are known for this state. The A and C rotational constants are largely independent of the energy parameter, ε_{C-Ar} , but are strongly dependent upon the geometric parameter, $\sigma_{
m C-Ar}$ (the calculated values change by less than 0.2% for a 20% change in ε_{C-Ar} but by about 20%



FIG. 5. Dependence of the (i) well depth, V_{\min} , and (ii) s_z^{-1} vdW vibrational eigenvalue calculated for the S1 state of 4FST-Ar on the C-Ar atom pair parameters. These quantities are plotted against the geometric parameter, σ_{C-Ar} , using different symbols for calculations using different values of the energy parameter, $\varepsilon_{C-Ar}[30(\Box), 40(\bigcirc), 50(\Delta), 60(\nabla), 70(\diamondsuit), 80(+) \text{ cm}^{-1}].$

for the same change in σ_{C-Ar}). The calculated *B* rotational constant is always an underestimate of the experimental value. It is a much weaker function of $\sigma_{ ext{C-Ar}}$ than the other two constants and may also be considered approximately independent of ε_{C-Ar} . The calculated vdW eigenstates are strongly dependent upon both parameters (the frequencies change by about 10% and 40% for 20% changes in ε_{C-Ar} and $\sigma_{\rm C-Ar}$, respectively) and the well depth is more sensitive to changes in ε_{C-Ar} (the corresponding changes are 18% and 4%).

The simple, near-linear dependence of these quantities upon the two parameters enabled estimates of each parameter to be determined by least-squares fitting to the experimentally determined rotational constants and vibrational intervals. The derivatives were determined analytically and the data were weighted as the inverse of their experimental uncertainties, taken as twice the standard deviation of the fitted rotational constants (see Table I) and $\pm 0.5~{\rm cm}^{-1}$ for the vibrational intervals measured by 1C-R2PI.11 The parameter values at convergence were $\epsilon_{C-Ar} = 77.5 \pm 1.2 \text{ cm}^{-1}$ and $\sigma_{\rm C-Ar}$ = 3.349 ± 0.001 Å (parameter set 3 in Table VII). The results of the calculation using parameter set 3 for the excited state are given in Table IX. The calculation reproduces the rotational constants to within about 0.5% and effective coordinates, determined from these constants (see Table III), are in agreement with the experimental values. The vdW vibrational eigenvalues for the levels involving only the bending vibrations $(b_{x0}^{-1}, b_{x0}^{-2}, b_{y0}^{-1}, b_{x0}^{-1}, b_{y0}^{-1}, and b_{y0}^{-3})$ reproduce the intervals obtained in the 1C-R2PI spectrum to within 0.2-2.7 cm⁻¹. The calculated vdW stretching eigenvalue is, however, about 6 cm^{-1} greater than the experimental value and the energy order of the eigenstates does not reproduce that deduced experimentally. In addition, the calculation gives a high value for the dissociation energy (567.2 cm^{-1}) for this state.

TABLE XI. Comparison between experimental data and the results of calculations for 4FST-²⁰Ne in its S₀ state. The calculations are numbered according to the parameter sets given in Table VIII. The rotational constants were obtained in a full variational calculation.

	$\operatorname{Calc}^{\mathfrak{b}}$						
	Exp ^a	1	2	3	4		
X_e (Å)		-0.308	-0.384	-0.181	-0.103		
Y_e (Å)		-0.063	-0.056	-0.079	-0.080		
Z_e (Å)		3.088	3.246	3.085	3.309		
$V_{\rm min}~({\rm cm}^{-1})$	149-251 ^c	233.7	187.7	203.8	224.1		
$A(\mathrm{cm}^{-1})$	0.056 411 9(94)	0.061 514 6[9.05]	0.057 764 9[1.21]	0.061 305 5[8.67]	0.056 287 6[-0.22]		
$B(\mathrm{cm}^{-1})$	0.027 259 8(44)	0.027 247 0[-0.05]	0.027 179 3[-0.55]	0.027 329 3[0.25]	0.027 344 1[0.31]		
$C(cm^{-1})$	0.023 678 1(44)	0.024 156 5[2.02]	0.023 466 8[0.33]	0.024 165 3[2.06]	0.023 343 5[-1.41]		
$b_x^{1}(\text{cm}^{-1})$		10.43	8.94	9.23	8.85		
b_{y}^{1} (cm ⁻¹)		17.67	15.71	23.33	17.20		
$s_z^{(1)}$ (cm ⁻¹)		42.69	36.68	41.04	41.97		

^aThis work. Numbers given in round parentheses are one standard deviation of the fitted constant in units of the last quoted decimal place.

^bNumbers given in square parentheses are the percentage deviation from the experimentally determined value of the rotational constant. ^cReference 7.

For the ground state, fitting to the experimentally determined rotational constants and a single vdW interval (which is determined from the position of the b_x hot band^{7,11}) gives $\varepsilon_{\text{C-Ar}} = 70.9 \pm 4.6 \text{ cm}^{-1}$ and $\sigma_{\text{C-Ar}} = 3.382 \pm 0.001 \text{ Å}$. Parameter set 3 predicts that the b_x^2 level should occur about 23 cm⁻¹ above the 0⁰ level, this supports the assignment of a weak feature at $0_0^0 + 9 \text{ cm}^{-1}$ in 1C-R2PI spectrum to the b_{x2}^{2} hot band.⁷ The solvent shift of -46.8 cm⁻¹ calculated using this parameterization compares well with the experimental one of -42.017(5) cm⁻¹. The effective coordinates obtained for the ground state agree well with experiment and, in addition, the reduction in the Z coordinate upon excitation is reproduced reasonably by this parameterization.

The high values calculated for the dissociation energy and s_z^{-1} eigenvalue in the S₁ state suggest that fitting the ε_{C-Ar} parameter to the anharmonicity of the bending vdW vibrations probably overestimates the interaction energy of the argon atom with the aromatic molecule. The good agreement in the solvent shift and reduction in the effective Z coordinate suggest, however, that the difference in this interaction energy is well reproduced. The calculations using parameter sets 1 and 2 show that the vdW vibrational eigenvalues were also affected by the parameterization of the F-Ar atom pair. Attempts were therefore made to simultaneously determine the ε_{C-Ar} and σ_{C-Ar} parameters but the fits were ill-conditioned and did not converge despite damping. Constraining the C-Ar parameters for the vinylic carbon atoms to the values calculated using the Scheraga model, while fitting the parameters for the aromatic ring, led to further increases in the calculated well depth. The parameter values of set 3 are therefore recommended for calculations of the vdW eigenstates and molecular geometries in clusters of this type.

C. 4FST-Ne

The parameter values used to represent the potential in 4FST-²⁰Ne are listed in Table VIII. Set 1 is a collection of values taken from the literature and used in a previous LCHOP calculation of the vdW vibrational eigenvalues of this complex.¹² Set 2 was kindly provided by Ph. Bréchignac;²⁸ they were obtained for the aniline-Ne complex by empirical optimization of the parameters of Ondrechen et al.²⁹ Set 3 contains values calculated using the Scheraga model⁷ and set 4 was obtained from this set by fitting the parameters for the C-Ne atom pairs, as was done in the previous section for 4FST-Ar. The results of these calculations are given in Tables XI and XII for the ground and excited states of the complex, respectively. The results of calculations for both states of 4FST-²²Ne using parameter set 4 are given in Table XIII.

1. Parameter sets 1-3

Only the vdW bending fundamentals, b_{x0} (0⁰₀+11.2 cm⁻¹) and b_{y0} (0⁰₀ +20.0 cm⁻¹), have been assigned with certainty in the 1C-R2PI spectra of the $S_1 \leftarrow S_0$ transition of 4FST-Ne. A band of similar intensity $(0_0^0 + 31.0 \text{ cm}^{-1})$ was tentatively assigned as sz_0^1 and a much weaker feature (0_0^0 +43.3 cm⁻¹) was unassigned.^{7,12} The first vibronic band observed for 4FST but absent in the corresponding spectrum of 4FST-Ne occurs at 0_0^0 +222 cm⁻¹, providing the upper limit for D_0' . The band at $0_0^0 + 120 \text{ cm}^{-1}$ is observed at comparable intensities in both spectra but it is more cautiously used as the lower limit on D_0' since bands resulting from 4FST-H₂0, present as an impurity, are expected in this region.

The vdW vibrational eigenvalues calculated for the S₁ state, given in Table XII, are very similar for all three parameter sets and are consistently about 2 to 3 cm⁻¹ less than the experimental separations of the b_{x0} and b_{y0} bands from the 0_0^0 band. The s_z^1 eigenvalue is calculated at 37–43 cm⁻¹, suggesting that the correct assignment of sz_0^1 is the feature at 0_0^0 +43.3 cm⁻¹. This is also in agreement with the values assigned for the s_z vdW stretching frequencies in the other 4FST-X complexes [41(1) cm⁻¹ for X=Ar, 37(1) cm⁻¹ for X = Kr, 38(1) cm⁻¹ for $X = Xe^{7}$]. The assignment of the band at $0_0^0 + 31.0 \text{ cm}^{-1}$ is less clear cut since a large number of levels are calculated with energies in this region. The bending eigenvalues are underestimated by about 20% in these

TABLE XII. Comparison between experimental data and the results of calculations for $4FST_{-}^{20}Ne$ in its S₁ state. The calculations are numbered according to the parameter sets given in Table VIII. The rotational constants were obtained in a full variational calculation.

		Calc ^b					
	Exp ^a	1	2	3	4		
X_e (Å)		-0.292	-0.354	-0.178	-0.111		
Y_e (A) Z_e (Å)		-0.063 3.069	-0.055 3.228	-0.076 3.067	-0.077 3.270		
$V_{\min} (\mathrm{cm}^{-1})$		235.0	189.6	204.8	240.8		
$D_0' ({\rm cm}^{-1})$	120–222 ^c	196.1	155.5	167.3	201.8		
$\Delta v_{\rm solv} ({\rm cm}^{-1})$) - 7.895(7)	-1.0	-1.6	-0.8	-14.6		
$A(\mathrm{cm}^{-1})$	0.056 411 9(94)	0.060 780 5[7.74]	0.057 079 0[1.18]	0.060 581 1[7.39]	0.056 188 1[-0.40]		
$B(\mathrm{cm}^{-1})$	0.027 259 8(44)	0.027 176 7[-0.30]	0.027 136 3[-0.45]	0.027 248 5[-0.04]	0.027 257 8[-0.007]		
$C(\mathrm{cm}^{-1})$	0.023 678 1(44)	0.024 367 5[2.91]	0.023 678 7[0.003]	0.024 370 2[2.92]	0.023 634 2[-0.19]		
$b_x^{1}(\text{cm}^{-1})$	11.2	11.00	9.28	9.82	10.07		
b_{y}^{1} (cm ⁻¹)	20.0	17.87	16.00	17.41	18.48		
$s_z^{(1)}$ (cm ⁻¹)	43.3	42.99	37.01	41.45	43.32		

^aThis work. Numbers given in round parentheses are one standard deviation of the fitted constant in units of the last quoted decimal place. ^bNumbers given in square parentheses are the percentage deviation from the experimentally determined value of the rotational constant. ^cReference 7.

calculations, indicating that the correct eigenstate should be obtained at about 25 cm⁻¹. The strongest candidates are the b_x^{3} and $b_x^{1}b_y^{1}$ levels, which are close to this value in all three parameterizations. Both might be expected to have good Franck–Condon factors for excitation from the lowest vdW level of the ground state, but the lack of observation of a band assignable to b_{x0}^{2} in the spectrum favors the assignment to the $b_{x0}^{0}b_{y0}^{1}$ combination band.

The dissociation energies for the S_1 state are acceptable in all three calculations but little more can be said because of the lack of precise knowledge of this quantity. The use of the same parameters in the ground state calculation gives a solvent shift of about -1 cm^{-1} in all three cases, which considerably underestimates the experimental value of $-7.895(7)\text{ cm}^{-1}$.

The rotational constants obtained in a full variational calculation again provide the most significant test of the three parameterizations. The values of these constants calculated using parameter sets 1 and 3 are very similar and in much poorer agreement with experiment than those obtained

with set 2. By analogy with 4FST-Ar, these constants are expected to be most sensitive to the choice of the geometric parameter, $\sigma_{\rm C-Ne}$. The larger value of this parameter in set 2 produces a better agreement with experiment than the similar values used in the other sets. The effective d₀ coordinates for the neon atom, derived from these calculated rotational constants, are given in Table V. The poor reproduction of the experimental rotational constants using sets 1 and 3 results because the effective Z coordinates obtained using these sets are about 0.1 Å less than the experimental values for both states. The values of this coordinate obtained with set 2 are much closer to the experimental ones. Table VI contains the RMS vibrational amplitudes and average coordinate values for the lowest vibrational level calculated using these parameter sets. The Z coordinates are dominated by the contribution from $\langle Z \rangle$, which is reduced by the use of a smaller value for σ_{C-Ne} . Although the effective Y coordinates are in reasonable agreement with the experimental values in all three calculations, the effective X coordinates again demonstrate the differences in the parameterizations. The negligibly small

TABLE XIII. Comparison between experimental data and the results of calculations for $4FST-^{22}Ne$ in its S_0 and S_1 states using the atom-atom pair potential represented by parameter set 4 in Table VIII. The rotational constants were obtained in a full variational calculation.

	S ₀		S ₁	
(cm^{-1})	Exp ^a	Calc ^b	Exp ^a	Calc ^b
A	0.054 01(58)	0.053 342[-1.54]	0.053 96(58)	0.053 308[-1.21]
В	0.027 341(16)	0.027 346 7[0.02]	0.027 265(15)	0.027 263 9[-0.004]
С	0.022 860(16)	0.022 817 5[-0.18]	0.023 152(15)	0.023 105 3[-0.20]
$D_0' ({\rm cm}^{-1})$	188.3		203.0	
b_x^{1}		8.69	9.88	
b_{y}^{1}		17.07	18.30	
s_z^{1}	40.26		42.44	

^aNumbers given in round parentheses are one standard deviation of the fitted constant in units of the last quoted decimal place.

^bNumbers in square parentheses represent the percentage deviation from the experimentally determined value of the constant given in Table II.

values obtained from the experimental rotational constants are reproduced using parameter set 3 only. Similar to the 4FST-Ar calculations, parameter sets 1 and 2 differ from set 3 in the use of much larger values for the energy parameter, in this case ε_{F-Ne} . The minima of the potentials calculated using sets 1 and 2 are shifted towards the fluorine atom compared to that obtained with set 3 by the larger interaction energy for the F–Ne atom pair. Since the a_0 axis is inclined at only about 6° to the C–F bond in both states of 4FST, this difference in the position of the minimum is mostly reflected in the values of $\langle X \rangle$, given in Table VI, and in the effective values for the *X* coordinate of the neon atom. The effective *Y* coordinates of the neon are in reasonably good agreement with experiment for calculations with all three parameter sets.

It was concluded that the most realistic description of the $4FST^{-20}Ne$ complex in the S₀ and S₁ states using a potential constructed from an atom–atom summation was again provided by the Scheraga model (set 3), but that the parameters were in need of refinement in order to produce more accurate predictions of the vdW vibrational eigenstates and the molecular geometries in these states.

2. Parameter set 4

Following the same procedure as described in Sec. V A 2. for the 4FST-Ar complex, the geometric and energy parameters for the C-Ne atom pairs in the S1 states were least-squares fitted to the vdW vibrational intervals determined from the 1C-R2PI spectrum^{7,12} and the rotational constants obtained in this study. The values of the other parameters were constrained to those calculated by the Scheraga model for the S₀ state. Uncertainties of $\pm 1 \text{ cm}^{-1}$ were used to weight the vdW intervals because of the lower signal-tonoise in the 1C-R2PI spectra of 4FST-Ne compared to that for 4FST-Ar. The fit converged to give $\sigma_{C-Ne} = 3.220 \pm 0.001$ Å and $\varepsilon_{C-Ne} = 31.1 \pm 1.5 \text{ cm}^{-1}$. The calculation using these parameter values (set 4 in Table VIII) is given in Table XI. The vdW vibrational intervals are reproduced to within 1.5 cm⁻¹ for all three modes and the $b_x^{\ 1}b_y^{\ 1}$ eigenstate is calculated at 30.99 cm⁻¹, further supporting the assignment of 0_0^0 $+31.0 \text{ cm}^{-1}$ as the combination band. The calculated rotational constants differ from the experimental ones by less than 0.4% and all three of the effective coordinates for the neon atom, given in Table V, are now in good agreement with those determined from experiment.

No vdW vibrational intervals have been measured for 4FST-²⁰Ne in its ground state. To enable a determination of the energy parameter for the C–Ne atom pairs we fitted to $V_{v=0}(S_0)$, which was determined from the corresponding value calculated for the excited state and the experimental solvent shift using Eq. (6). This gave $D_0' \approx V_{v=0}(S_0) = 194 \pm 10 \text{ cm}^{-1}$, where the error bar is inherited from the uncertainty in the ε_{C-Ne} parameter value for the excited state calculation. The parameter fit converged to give $\sigma_{C-Ne} = 3.239 \pm 0.001 \text{ Å}$ and $\varepsilon_{C-Ne} = 28.9 \pm 1.6 \text{ cm}^{-1}$. The calculated solvent shift of -14.6 cm^{-1} is subject to an error of about $\pm 10 \text{ cm}^{-1}$, due to the uncertainties of the C–Ne en-

TABLE XIV. Comparison between the d_0 coordinates for the argon atom in FB-Ar, 4FST-Ar and 2FN-Ar in their S₀ states.

(Å)	FB-Ar ^{a,b}	4FST-Ar ^{a,c}	2FN-Ar ^{a,d}
X	0.420(5)	0.014(10)	0.232(11)
Y	0.372(19)	0.542(8)	0.513(15)
Z	3.540(3)	3.469(2)	3.456(4)

^aNumbers in parentheses represent estimated errors in coordinate values. ^bDetermined using rotational constants from Ref. 30. ^cThis work.

^dReference 17.

ergy parameters for ground- and excited-state calculations. The rotational constants obtained using these parameters, given in Table XI, and the effective coordinates determined from them, given in Table V, are both in good agreement with the experimental values. Furthermore the reduction in the effective *Z* coordinate on excitation of the complex is very well reproduced by the calculation. Good agreement with experiment was also obtained for the rotational constants (Table VIII) and effective coordinates for the neon atom in the 4FST-²²Ne complex (Table V) calculated using parameter set 4.

VI. DISCUSSION

The orientation of the $S_1 \leftarrow S_0$ transition moment for the 4FST-X complexes with respect to their *a* inertial axes, θ , may be calculated using

$$\tan^2 \theta = I(c)/I(a),\tag{7}$$

where I(a) and I(c) are the percentages of *a*- and *c*-type character in a band, respectively. The resulting values of $\pm (38\pm 2)^{\circ}$ for 4FST-Ar and $\pm (31\pm 3)^{\circ}$ for 4FST²⁰Ne are both within the experimental error of the value of $\pm (35^{+4}_{-5})^{\circ}$ for the angle between the S₁ \leftarrow S₀ transition moment and *a* inertial axes in 4FST.² The principal axes of the complexes are mainly a translation of those of the 4FST molecule, suggesting that the S₁ \leftarrow S₀ transition moment in 4FST is not greatly affected by the complexation.

In the previous section the effective coordinates of the rare-gas atom in the 4FST-X complexes were used as an indirect guide to the position of the potential minima. The accuracy of the calculated average coordinate values and RMS amplitudes in the lowest vibronic levels was assessed by the ability of the calculation to reproduce the experimental values of the effective coordinates. This represents a different approach from that adopted in previous publications,^{1,17} where the values of the effective coordinates were used to estimate the expectation values and RMS amplitudes in complexes of this type. A simple correspondence of this type can be made in complexes involving mono-substituted benzene derivatives but they do not apply in lower symmetry complexes such as 4FST-X. This is demonstrated in Table XIV which compares the effective coordinates for the argon atom in the ground state of 4FST-Ar with those derived from the rotational constants of the corresponding vdW complexes with fluorobenzene $(FB)^{30}$ and 1/2-fluoronapthalene (1/2FN).¹⁷

The signs of the effective coordinates are not obvious in vdW complexes (as they are when the Kraitchmann equations are applied to covalently bound molecules) and eight possible sets of solutions are possible. The four pairs corresponding to opposite signs of Z correspond to stereoisomers, which cannot be distinguished experimentally. As previously mentioned, the effective Z coordinate is generally in good agreement with the calculated vibrational average, $\langle Z \rangle$, since the RMS amplitude is a much smaller quantity $(\Delta Z \approx 0.1 \text{ Å})$. The reduction in the value of Z in the ground state in going from FB to 4FST to 2FN reflects the increase in π -electron density in the complexed aromatic. In FB-Ar, the C_{2v} symmetry of the aromatic molecule leads to the requirement that $\langle Y \rangle = 0$ and the effective Y coordinate reflects only the contribution to the inertial tensor from the zero-point vibrational oscillation with respect to the b_0 axis. The value of Y=0.37 Å for the ground state of FB-Ar is reasonable as a measure of the vibrational amplitude by comparison with the values calculated for the corresponding complexes of benzene¹⁸ and aniline.¹ Calculations indicate a displacement of the argon atom towards the fluorine in FB-Ar giving $\langle X \rangle \approx 0.18$ Å.³⁰ Therefore both the average value and the RMS vibrational amplitude with respect to this coordinate are of the same magnitude and the effective Xcoordinate is not directly related to one or the other.

The replacement of a hydrogen by a vinylic group to give 4FST produces a rotation of the principal axes of about 7° about the *c* axis and translates the center of mass towards the new group. The calculations of the previous section indicate that the potential minima in both S₀ and S₁ states of 4FST-Ar are located almost directly above the center of mass of the 4FST moiety. Therefore both $\langle X \rangle$ and $\langle Y \rangle$ are expected to be small. Nevertheless no simple correspondence can be made between the effective values of these coordinate, $X \approx 0.0$ Å, $Y \approx 0.5$ Å, and their RMS vibrational amplitudes, calculated to be $\Delta X \approx 0.26$ Å, $\Delta Y \approx 0.30$ Å. This suggests that the effective coordinates of the rare-gas atom should be interpreted with caution in systems where symmetry does not impose a zero value for one or more of the equilibrium coordinates.

This possibly explains the difficulty in interpreting the effective coordinates for 1FN-Ar and 2FN-Ar vdW complexes. In terms of principal axes and potential-energy surfaces these molecules are similar to 4FST. The change from 4FST to 2FN produces a further shift of the center of mass towards the C_1-C_6 bond and further rotation of the principal axes by about 14° about the c axis. The "second" binding site, previously associated with the vinylic group, is now another aromatic ring of almost equal energy. A clear interpretation of the effective coordinates for the 1/2FN-Ar complexes was not possible, even by comparison with threedimensional quantum calculations performed on napthalene-Ar.31

VII. CONCLUSION

In conclusion, the $S_1 \leftarrow S_0 0_0^0$ bands of 4FST-X (X=Ar and Ne) have been recorded at rotational resolution for the first time. Rotational constants obtained from the analysis of the spectra were used to obtain effective coordinates for the rare gas atoms in the complex. The rare gas-aromatic potentials were represented as a pairwise sum of atom-atom terms. These potentials were judged by their ability to reproduce the effective coordinates, vibrational intervals, dissociation energies, and solvent shifts of the complexes. The potentials were optimized by least-squares fitting the parameters of the C-X atom pair to the experimental data. The fitted parameters produce good agreement with the rotational constants and in-plane bending vdW frequencies, but overestimate the dissociation energies and vdW stretching frequency. We believe that a better description of the potential surface can only be achieved with a more sophisticated model than simple atom-atom pair interaction. Future work includes the use of these parameters to predict the structure and vibrational frequencies in the clusters of ST with one or more attached rare-gas atoms.

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