

Pseudopotential SCF-MO studies of hypervalent compounds. IV. Structure, vibrational assignments, and intramolecular forces in IF₇

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Ewig's pseudopotential procedure, applied with a small basis set, yielded a minimum energy structure with D_{5h} symmetry instead of the deformed pseudorotating structure proposed to account for electron diffraction and electric beam deflection experiments. Nevertheless, calculated restoring forces for e_2' displacements were so feeble that a higher quality calculation making the postulated e_2' deformation spontaneous is not at all precluded. Otherwise, calculated molecular characteristics of IF₇ closely resembled those deduced from the diffraction and beam experiments, from extended Hückel calculations, and from the simple valence shell electron pair repulsion theory in a repelling points-on-a-sphere (POS) variant. Axial bonds were shorter by 0.05 Å than equatorial bonds, and calculated mean bond lengths exceeded observed ones by only 0.03 Å. Furthermore, the calculated anharmonic coupling of e_1' polar displacements with large-amplitude e_2' puckering vibrations closely reproduced the coupling inferred from experiment. This favorable correspondence between theory and interpretation of experiment was found not to extend to vibrational assignments, however. Instead, the pseudopotential calculations were in surprisingly close agreement with the simple POS and EHT models predicting that equatorial in-plane bends are far stiffer, due to the close lateral contacts, than the other bending modes. None of the six published vibrational assignments had been interpreted on this basis. An alternative assignment was found which is reasonably consistent with both the calculated force field and the observed infrared and Raman spectra. A similar assignment seems appropriate for ReF₇. Calculations with and without d orbitals on iodine furnished evidence that the role of d orbitals in hypervalent compounds is less important than it is often considered to be. Neither the second-order Jahn-Teller softening of the e_2' force constants nor the covalent binding of seven fluorines to iodine was found to depend crucially upon valence d orbitals.

I. INTRODUCTION

Iodine heptafluoride is an interesting quasispherical molecule that has only grudgingly revealed its internal structure. Drawing its neon-like sheath of fluorines tightly around itself, it is highly volatile, though heavy (subliming at 4 °C),¹ much more inert to hydrolysis than other hypervalent halogen fluorides,² and difficult to characterize by standard physical procedures. Because of its shape and comparatively weak cohesive forces, it disorders easily when crystallizing, thereby hampering x-ray structure determinations. The several crystal structure analyses performed upon it led to somewhat contradictory results.³⁻⁸ Yet, as one of only two known seven-coordinate binary compounds stable in the vapor phase, (the other being ReF₇) the molecule is of potentially far greater value than most others as an illustration of how covalent bonds interact with each other. To show this, it is helpful to introduce one of the simplest and most widely used pictures to account for directed valence, the Sidgwick-Powell-Gillespie-Nyholm "valence-shell-electron-pair-repulsion" (VSEPR) theory.^{9,10} It makes definite and, for the most part, surprisingly satisfactory predictions of the structures^{9,10} and force field characteristics¹¹⁻¹³ of molecules consisting of a central atom (in the main group) with six or fewer electron pairs in its valence shell. In the case of seven pairs (e.g., XeF₆ or IF₇), however, purely geometric considerations of "electron repulsion" are no longer sufficient and predicted structures range from D_{5h}

through a series of intermediate configurations on to C_{3v} for "hard repulsions."^{14,15} Therefore, an accurate structure determination would presumably yield not merely another example that bonds tend to avoid each other, but it would also reveal the "force law" associated with this avoidance. If this seems an excessively naive and simplistic hope, we point out that the present investigation strongly reinforces the virtue and utility of this mode of interpretation.

The best structural information available indicates that IF₇ spends most of its time distorted by a weakly polar ($e_2'' + e_1'$) deformation from a D_{5h} configuration.^{16,17} The molecule is believed to be undergoing a dynamic ring-puckering pseudorotation. Structural inferences were drawn mainly from subtle features of a vapor-phase electron diffraction study,¹⁶ and the polar character was corroborated by a molecular beam investigation.¹⁸ Although the main features deduced by electron diffraction analysis are almost certainly correct, analyses were impeded somewhat by intramolecular multiple scattering¹⁹ of incident electrons by the heavy iodine atom. At the time of analysis, no satisfactory theory for this phenomenon had yet been worked out. Despite its weak polarity, the molecule has displayed no pure rotational spectrum. It has continued to resist attempts to establish its symmetry and force field by vibrational spectroscopy.²⁰⁻²⁹ Until the electron diffraction study, vibrational spectra had been interpreted in terms of a simple D_{5h} structure.²⁰⁻²⁵ Even though subsequent infrared and Raman analyses²⁶⁻²⁸ have been considered to be compatible with the distorted structure suggested by the diffraction experiment, the vibrational

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assignments are far from resolved. Each new study has suggested a different assignment. Furthermore, evidence, which we shall develop in the following, suggests that all of the published assignments are incorrect.

For the above reasons it seemed worthwhile to bring to bear an alternative method in an attempt to find the key to this interesting but elusive molecule. One promising approach is an *ab initio* pseudopotential SCF-MO method developed by Ewig and Van Wazer.³⁰ In previous papers in this series,³¹⁻³⁴ it was applied in single determinant form, to nonrelativistic calculations of the structures and force fields of the molecules F_4 , XeF_2 , XeF_4 , XeF_5^+ , XeF_6 , Te_4^{2+} , I_2 , IF , IF_3 , and IF_5 . Results, where comparisons could be made, were comparable to those of all-electron SCF calculations with similar basis sets. Although calculated bond lengths, bond angles, and force constants deviated from experimental values in systematic ways, the pattern of calculated molecular properties proved of value in interpreting existing observations. In the case of IF_7 , it was unrealistic to expect to be able to compute the structure and vibrational frequencies with sufficient absolute accuracy to give direct answers to the unresolved problems. On the other hand, it was likely that useful clues would be found which would clarify the situation considerably when prior experience with related molecules was taken into account. Adding to our optimism that the properties of IF_7 were decipherable were strong hints about the force field provided by previous computations based on two very simple models, the VSEPR concept of repelling points-on-a-sphere (POS)¹¹⁻¹⁶ and extended Hückel theory (EHT).^{11,35} How these contribute to the analysis will be described briefly in the following section.

II. PROCEDURE

A. Pseudopotential calculations

The computational method adopted in the present research is described in detail in Refs. 30-32. It is *ab initio* in its entirety. Basis sets for fluorine³² and iodine³⁴ were constructed from multizeta valence, single-zeta core orbitals of Clementi *et al.*^{36,37} and contracted to a minimal basis set superior to single zeta STO's. Force constants were computed as outlined in previous papers in this set.³¹⁻³³ Because a gradient procedure had not been incorporated into the computer code to facilitate energy minimization with respect to structure parameters, the minimum energy D_{5h} structures and a'_i force constants were found as follows.

The experimental¹⁶ mean bond lengths $r_{ax}^0 = 1.858 \text{ \AA}$ and $r_{ax}^0 = 1.786$ were adopted as reference values. Total molecular energies for this structure and other D_{5h} structures with bond lengths $(r_{ax}^0 + u, r_{ax}^0 + v)$ were calculated at displacements (u, v) in \AA of $(-0.1, 0)$, $(0.1, 0)$, $(0, 0.08)$, $(0, 0.16)$, and $(0.1323, 0.1323)$. For displacements of this magnitude the Morse anharmonicity is not negligible. In order to allow for it without going to the appreciable expense of additional pseudopotential computations, we adopted the Morse parameter $a \approx 1.6 \text{ \AA}^{-1}$ found in related computations on xenon fluorides²³ and fitted the above points exactly with the polynomial

$$2V(u, v) = 2V_0 + k_{ax}[u - u_0]^2 - a(u - u_0)^3 \\ + k_{ax}[v - v_0]^2 - a(v - v_0)^3 + 2k_{ax}uv.$$

From this polynomial can be found u_m , v_m , the displacement coordinates at minimum energy as well as the symmetry force constants F_{11} , F_{22} , and F_{12} at either the experimental or theoretical structures.

B. Points-on-a-sphere force constants

For reasons that will become apparent, it is useful to be able to calculate the profile of bending force constants corresponding to the simple model of seven repelling points on a sphere, the POS model. In the VSEPR model of Gillespie¹⁰ these repulsions are envisioned as acting, presumably by the operation of the exclusion principle, between electron pairs in the IF bonds of IF_7 . In a Urey-Bradley model they would, alternatively, be considered to be atom-atom nonbonded repulsions. Whatever the source of repulsion, we shall assume for this section that the repulsions correspond to pairwise additive potential energy terms $V(r_{ij})$ acting between points i and j separated by r_{ij} and constrained to move on a surface of radius R . A reference structure of D_{5h} symmetry is adopted. In prior work the potential terms $V(r_{ij})$ have often been expressed in explicit form such as Kr_{ij}^{-n} or, less often, as $C \exp(-\alpha r_{ij})$. For the present we leave them general. By expanding the potential function into a Taylor series we derive the following relations for quadratic bending force constants relative to a D_{5h} reference structure:

$$F_{44}(a_2'') = \mathcal{F}(90^\circ) - \frac{1}{2}R \sin 36^\circ (\partial V / \partial r)_{72^\circ} - \\ - \frac{1}{2}R \sin 72^\circ (\partial V / \partial r)_{144^\circ}, \\ F_{66}(e_1') = \mathcal{F}(72^\circ) + \frac{1}{4}R^2 (\partial^2 V / \partial r^2)_{144^\circ} \\ - 2R \cos^2 144^\circ \sin 72^\circ (\partial V / \partial r)_{144^\circ}, \\ F_{67}(e_1') = (R/2 \sin 36^\circ) (\partial V / \partial r)_{90^\circ}, \\ F_{77}(e_1') = \mathcal{F}(90^\circ) - 0.4R (\partial V / \partial r)_{180^\circ}, \\ F_{99}(e_2') = \mathcal{F}(72^\circ) + \frac{R^2 \cos^2 72^\circ}{4 \cos^2 144^\circ} \left(\frac{\partial V}{\partial r} \right)_{144^\circ} \\ + \frac{1}{4}R \tan 144^\circ (\partial V / \partial r)_{144^\circ}, \\ F_{10,10}(e_1'') = \mathcal{F}(90^\circ), \\ F_{11,11}(e_2'') = \mathcal{F}(90^\circ) + R \sin 72^\circ (\partial V / \partial r)_{72^\circ} \\ - R \sin 144^\circ (\partial V / \partial r)_{144^\circ},$$

where

$$\mathcal{F}(\theta) = R^2 \cos^2(\theta/2) (\partial^2 V / \partial r^2)_\theta - \frac{1}{2}R \sin(\theta/2) (\partial V / \partial r)_\theta,$$

in which θ represents one of the interbond angles in a pentagonal bipyramid.

C. Points-on-a-sphere normal coordinate calculations

The intended use of the equations in the preceding section is to permit a direct comparison between the force field implied by the simple POS model and calculated fields with a more conspicuous quantum origin. As a rough guide to assignments, however, we carried out normal coordinate calculations³⁸ using an al-

TABLE I. Preliminary points-on-a-sphere potential function for normal coordinate analysis of IF_7 .^a Relaxed sphere radius 1.858 Å.

Bond stretching: $V(r) = \frac{1}{2} R(r - r^0)^2$		
Bond	k	r^0
Axial	4.2	1.584
Equatorial	3.4	1.471

Atom-atom repulsion: $V(r) = 4.66/r^{3.5}$

^aEnergies in mdyne Å, distances in Å; for calculating bending frequencies alone, K can be made enormous and r^0 set at 1.858 Å.

ternative representation of a modified POS field. This field, in which valence force constants were never explicitly calculated, was formulated in order to cope with the following problem. As can be seen from the expression for $F_{11,11}$ above, the force constant for e_2'' ring puckering deformations becomes *negative* when the POS repulsions exceed a certain hardness (e.g., when n exceeds 2 for $V_{ij} = K/r_{ij}^n$). Under such a condition an e_2'' deformation becomes spontaneous and it, in turn, induces an e_1' axial bend via a cubic potential constant coupling the modes. Not only is such a possibility mathematically possible but it seems to be encountered in reality in the IF_7 molecule, according to evidence mentioned in the Introduction. In the case of such a fluxional, freely pseudorotating molecule it is not a trivial matter to express the structure and force field on a valence force constant basis. On the other hand, it is comparatively simple to invoke an atom-atom

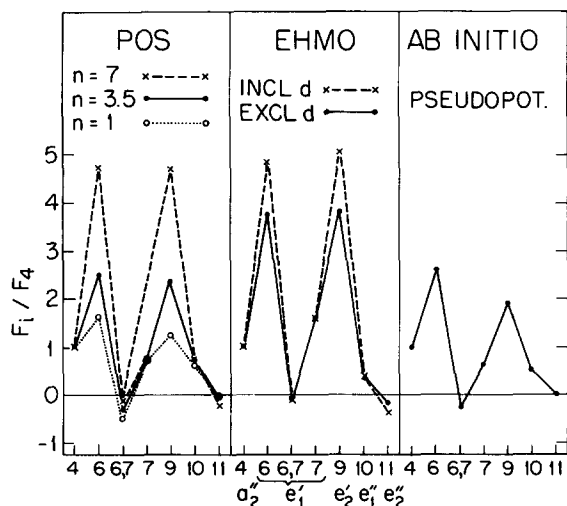


FIG. 1. Bending quadratic force constant profile calculated for IF_7 as a function of mode number by various approaches. Interaction constant $F_{\delta,7}$ is designated as 6, 7. (a) Repelling points-on-a-sphere results for three values of repulsion hardness parameter n . A value of 3.5 accounted for observed structure characteristics, Ref. 10. (b) Extended Hückel results including and excluding d orbitals. (c) Effective-potential results described in text.

(or bond-bond) repulsion of the desired magnitude and hardness to fit, approximately, both the observed structural deformation from D_{5h} and the bending frequencies. In addition, the bonds can be given Hookean force constants so that the stretch modes can be calculated, as well. If one had constructed such a field with identical reference bond lengths, the equatorial bonds would have stretched further under the atom-atom repulsions than the axial, much as implied by experiment. We chose arbitrarily instead, however, to assign different reference lengths to axial and equatorial bonds so that the final, relaxed structure gave equal (1.858 Å) bond lengths with atoms residing on the POS surface. This was for sake of comparison with prior calculations carried out with the POS model.^{14,16,39} Had unequal bond lengths been retained, the hardness parameter " n " to give the observed angle deformations would have been different. Parameters for the potential function, chosen for the present purposes with no attempt to optimize them, are listed in Table I.

One virtue of such a normal coordinate calculation based on a deformed structure is that it indicates the extent to which the modes depart in form from those expected for a D_{5h} structure. Such allowed mixing of modes is of concern in the plausibility of a revised assignment.

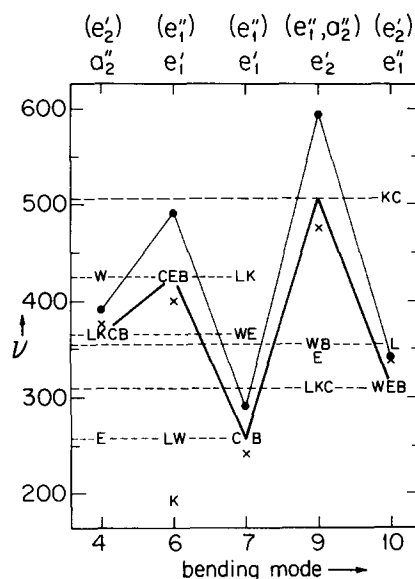


FIG. 2. Bending frequency assignments by various authors (capital letters, see below). Assignments suggested by present calculations are connected by the heavy line. Frequencies calculated by the pseudopotential method are connected by the light line. Dashed horizontal lines correspond to reported experimental frequencies. Crosses correspond to frequencies calculated by the POS force field of Table I. Symmetry designations above the figure represent dominant displacements (not in parentheses) and important secondary vibrational displacements (in parentheses) induced by the large amplitude e_2'' deformation according to the POS normal coordinate treatment. All of these secondary displacements are symmetry-allowed as are others which appeared with smaller amplitudes. Previous assignments: L, Ref. 20; K, Ref. 22; C, Ref. 24; W, Ref. 26; E, Ref. 27; B, Ref. 29.

TABLE II. Orbital energies (hartree) for IF₇ with and without *d* polarization functions. Two different conformations are included.

<i>C_s</i> ^a with <i>d</i> ^b	<i>D_{5h}</i> ^c with <i>d</i>	<i>D_{5h}</i> ^c without <i>d</i>	<i>C_s</i> ^a without <i>d</i>
<i>a'</i> -1.718 8	-1.719 2 <i>a'</i> ₁	-1.704 1 <i>a'</i> ₁	-1.703 8 <i>a'</i>
<i>a'</i> -1.700 8	-1.701 2 <i>a''</i> ₂	-1.677 866 5 <i>a''</i> ₂	-1.677 33 <i>a'</i>
<i>a'</i> -1.647 3	-1.647 5 <i>a'</i> ₁	-1.619 935 <i>a'</i> ₁	-1.619 7 <i>a'</i>
<i>a''</i> -1.621 361 9 } <i>a'</i> -1.621 361 0 }	-1.621 25 <i>e'</i> ₁	-1.598 847 <i>e'</i> ₁	{ -1.599 029 6 <i>a''</i> -1.599 029 1 <i>a'</i>
<i>a'</i> -1.592 4	-1.592 08 <i>e'</i> ₂	-1.558 928 4 <i>e'</i> ₂	{ -1.559 4 <i>a'</i> -1.559 1 <i>a''</i>
<i>a''</i> -1.592 3			
<i>a'</i> -1.054 6	-1.054 6 <i>a'</i> ₁	-1.096 70 <i>a'</i> ₁	-1.096 7 <i>a'</i>
<i>a'</i> -0.874 7	-0.874 89 <i>a''</i> ₂	-0.868 198 7 <i>a''</i> ₂	-0.867 9 <i>a'</i>
<i>a''</i> -0.853 950 5 } <i>a'</i> -0.853 950 4 }	-0.853 896 3 <i>e'</i> ₁	-0.848 184 7 <i>e'</i> ₁	{ -0.848 148 3 <i>a''</i> -0.848 148 1 <i>a'</i>
<i>a'</i> -0.798 305 8 } <i>a''</i> -0.798 303 1 }	-0.798 252 6 <i>e''</i> ₁	-0.736 188 8 <i>e''</i> ₁	{ -0.736 117 <i>a'</i> -0.736 113 <i>a''</i>
<i>a'</i> -0.769 5 } <i>a''</i> -0.768 9 }	-0.769 565 6 <i>e'</i> ₂	-0.714 187 6 <i>e'</i> ₂	{ -0.714 1 <i>a'</i> -0.713 6 <i>a''</i>
<i>a'</i> -0.724 0	-0.723 94 <i>a'</i> ₁	-0.694 11 <i>e'</i> ₁	-0.694 075 5 <i>a'</i>
<i>a''</i> -0.715 601 3 } <i>a'</i> -0.715 592 6 }	-0.715 684 8 <i>e'</i> ₁	-0.645 097 7 <i>a''</i> ₂	-0.694 072 3 <i>a''</i>
<i>a'</i> -0.670 1 } <i>a''</i> -0.670 0 }	-0.670 470 5 <i>e''</i> ₁	-0.640 803 9 <i>e''</i> ₁	-0.644 8 <i>a'</i>
<i>a'</i> -0.666 9	-0.667 16 <i>a''</i> ₂	-0.630 889 2 <i>e''</i> ₂	{ -0.640 369 9 <i>a''</i> -0.640 362 4 <i>a'</i>
<i>a'</i> -0.652 405 3 } <i>a''</i> -0.652 373 5 }	-0.652 190 2 <i>e''</i> ₂	-0.622 139 <i>a'</i> ₁	{ -0.632 5 <i>a'</i> -0.631 0 <i>a''</i>
<i>a'</i> -0.627 295 4 } <i>a''</i> -0.627 294 8 }	-0.627 193 7 <i>e'</i> ₁	-0.620 687 <i>a'</i>	-0.620 687 <i>a'</i>
<i>a'</i> -0.601 8 } <i>a''</i> -0.610 7 }	-0.627 193 7 <i>e'</i> ₁	-0.596 985 1 <i>e'</i> ₁	{ -0.597 267 1 <i>a''</i> -0.597 263 1 <i>a'</i>
<i>a''</i> -0.599 8 ^d	-0.610 670 6 <i>e'</i> ₂	-0.564 746 7 <i>a'</i> ₂	-0.565 648 <i>a''</i>
<i>a'</i> 0.076 2 ^e	-0.599 02 ^d <i>a'</i> ₂	-0.550 773 5 ^d <i>e'</i> ₂	{ -0.551 1 <i>a'</i> -0.550 9 ^d <i>a''</i>
<i>a'</i> 0.207 2	0.076 29 ^e <i>a'</i> ₁	0.041 719 6 ^e <i>a'</i> ₁	0.041 6 ^e <i>a'</i>
<i>a'</i> 0.243 8 } <i>a''</i> 0.243 9 }	0.207 045 9 <i>a''</i> ₂	0.152 126 0 <i>a''</i> ₂	0.153 0 <i>a'</i>
<i>a'</i> 0.357 567 8 } <i>a''</i> 0.357 568 8 }	0.246 561 6 <i>e'</i> ₁	0.190 248 7 <i>e'</i> ₁	{ 0.189 611 8 <i>a'</i> 0.189 611 9 <i>a''</i>
<i>a'</i> 0.648 0 } <i>a''</i> 0.648 3 }	0.354 642 2 <i>e''</i> ₁		
<i>a'</i> 1.036 321 9	0.647 809 6 <i>e'</i> ₂		
	1.038 863 9 <i>a'</i> ₁		

^a*e''*₂ deformation from *D_{5h}*, puckering amplitude of 3° (see Ref. 16), with experimental bond lengths (*I-F_{ax}*) = 1.786 Å, *r(I-F_{eq})* = 1.858 Å.

^bGaussian primitive with exponent 0.25.

^cPentagonal bipyramid, bond lengths as in footnote a.

^dHOMO.

^eLUMO.

D. Extended Hückel force constants

Extended Hückel computations of bending force constants were carried out with several different parametrizations, with and without *d* orbitals on iodine, in order to assess the sensitivity of results to parameters. Parameters were shifted from neutral atom values^{36,40} to make allowance for the displacement of charge. Representative parameters were -20.94, -15.61, -4.42, -35.15, and -14.68 eV for valence-orbital ionization potentials (VOIP) of 5*s*, 5*p*, 5*d*, 2*s*, and 2*p* Slater orbitals, respectively, whose orbital exponents were taken as 2.8, 2.44, 1.05, 2.53, and 2.52.

Although absolute values of force constants were dependent upon the parameters, the pattern of bending force constants of interest here was not, as verified by calculations with different sets of orbital exponents and VOIP values.

III. RESULTS

In Table II are listed orbital energies for IF₇, as calculated at *D_{5h}* and *C_s* symmetries by our pseudopotential approach. For the benefit of those concerned with *d*-orbital involvement or with orbital mixings encountered in second-order Jahn-Teller interactions,⁴¹⁻⁴³ tabulations include results incorporating and excluding Gaussian *d* orbitals on iodine. Force constants and bond lengths derived excluding *d* orbitals are given in Table III. Bending force constants, as calculated by Hückel and VSEPR-POS calculations are demonstrated in Fig. 1 to be in semiquantitative agreement with the *ab initio* force constants. Vibrational frequencies calculated from the pseudopotential force constants are tabulated in Table IV along with various spectroscopic results. Bending frequencies so calculated can be compared with observed frequencies^{24,27} according to prior published assignments²⁰⁻²⁹ and to our proposed assignment in Fig. 2.

TABLE III. Calculated symmetry force constants (mdyn/Å),^a cubic coupling constant (mdyn/Å²), and bond lengths (Å) for IF₇ in *D*_{5h} configuration.

Pseudopotential ^b		Pseudopotential ^b		POS ^c
Stretch		Bend		
$F_{11}(a_1'_{\text{eq}})$	5.678	$F_4(a_2'')$	0.573	(0.573)
$F_{12}(a_1')$	-0.700	$F_8(e_1'_{\text{eq}})$	1.489	1.443
$F_{22}(a_1'_{\text{ax}})$	7.434	$F_{6,7}(e_1')$	-0.156	-0.178
$F_{88}(e_2')$	5.734	$F_7(e_1'_{\text{ax}})$	0.385	0.423
		$F_9(e_2')$	1.093	1.357
Couple				
$F_{11,11,7}$	-0.13	$F_{10}(e_1'')$	0.298	0.442
		$F_{11}(e_2'')$	0.019	-0.018
$r(I-F_{\text{eq}})$	1.882 (1.858 obs)			
$r(I-F_{\text{ax}})$	1.832 (1.786 obs)			

^aNumbering convention of Khanna, Ref. 22. (1 mdyn Å = 10⁻¹⁸ J).

^bTaylor expansion about reference structure with experimental bond lengths, Ref. 16.

^cPoints-on-a-sphere model of Sec. II B using repulsion energy Kr^{-3.5} to reproduce observed ring pucker, Ref. 16, with constant *K* adjusted to make *F*₄ fit the pseudopotential value.

Frequencies and mode-mixing implied by the POS field of Table I are also included in Fig. 2.

IV. DISCUSSION

A. Structure and anharmonic coupling of modes

By all odds the most comprehensive analysis of IF₇ has been carried out by Bernstein and Pitzer²⁹ who took into account all of the evidence accumulated about structure, force field, and coupling with external fields prior to 1974 and fashioned a model to reproduce observations. This model, formally embodying a second-order Jahn-Teller distortion^{41,42} considered to be induced by *e*₁'(*F*_{2p}), *e*₁''(I_{5d}) orbital mixing, was based on a molecular behavior closely patterned after that proposed to account for the electron diffraction intensities of IF₇,¹⁶ and ReF₇.⁴⁴

Experimental evidence¹⁶ indicates that IF₇ in the vapor phase is a pentagonal bipyramid whose mean structure is distorted from *D*_{5h} symmetry by an *e*₂'' ring-puckering displacement of about 7.5°. Ring puckering, in turn, appears to induce a polar *e*₁' axial bend of perhaps 4.5° via a cubic coupling constant *F*_{11,11,7}. Equatorial bond lengths, averaging 1.858 Å, are 0.072 Å longer than axial. All of the above features are easily understood in terms of the VSEPR theory¹⁰ according to which equatorial bonds, wedged into a much more congested environment than the axial bonds, tend to squeeze each other out-of-plane and expand. Note that the points-on-a-sphere (POS) force constant *F*_{11,11}(*e*₂'') of Sec. II B becomes *negative* when repulsions are sufficiently hard (*n* > 2 if *V*_{*ij*} ∝ *r*_{*ij*}^{-*n*}). A negative *e*₂'' force constant corresponds to a spontaneous ring-puckering displacement. The POS model even yields a coupling constant of the right magnitude to account for the observed correlation between *e*₂'' and *e*₁' deformations.^{16,29}

A very similar picture of IF₇ emerges from the pseudopotential calculations. These make the mole-

cule a pentagonal bipyramid with equatorial bonds 0.05 Å longer than axial. Calculated bond lengths average 0.03 Å longer than experimental, a systematic defect noted in the other fluorides of iodine and xenon treated in the present series of computations. Since *all* calculated quadratic force constants for displacement from *D*_{5h} symmetry turned out to be positive, the equilibrium structure implied is *D*_{5h}, not a deformed bipyramid. It must be noted, however, that the calculated restoring force for *e*₂'' puckering is extremely weak, as shown in Table II. To appreciate how weak, it is instructive to consider the potential functions that would correspond to a simple diagonal valence force field.⁴⁵ For this field the *e*₂'' force constant would be identical to the *e*₁'', *e*₁' (axial bend) and *a*₂'' constants. Therefore, it is apparent from Table II that the bond-bond interactions intrinsic in the present pseudopotential calculations cut down the *e*₂'' constant to a value 20-fold below the level of others. That the calculation stopped just short of making the puckering constant negative is perhaps an accident of basis set or other factor of little significance. For that matter, not even experiment¹⁶ yielded a perfectly unequivocal conclusion about the *equilibrium* (minimum energy) structure. What is observed is the thermal distribution of structures. A molecule with a positive but very feeble restoring force would be seen as strongly puckered most of the time. Theory and experiment are in substantial agreement about the coupling between axial bend and pucker. Let us define the cubic constant *F*_{11,11,7} by the equation

$$V(e_2'', e_1'')_{\text{cubic}} = F_{11,11,7}[(S_{11b}^2 - S_{11a}^2)S_{7a} + 2S_{11a}S_{11b}S_{7b}],$$

adopting the symmetry coordinates of Fig. 3 of Ref. 44 and correcting the sign in Eq. (11), Chap. V, Ref. 29. Then the cubic constant calculated by the present pseudopotential method is -0.13 mdyn/Å², whereas the constant adjusted to fit the observed correlated displacements incorporated into the empirical field of Bernstein²⁹ is -0.19 ± 0.07 mdyn/Å².

If the combination bands assigned by vibrational spectroscopists²⁰⁻²⁹ in terms of *e*₂'' contributions of about 200 cm⁻¹ have been correctly interpreted, then the equilibrium structure *must* be distorted from *D*_{5h}. Only the "pseudoradial" vibrational component of a puckered pseudorotating molecule could have any chance of possessing that high a frequency for a nominally *e*₂'' mode, according to the present calculations. On the other hand, because existing assignments of combination bands are highly speculative, this argument has little force. The POS force field (Table I) suggests a pseudoradial *e*₂'' frequency well under 100 cm⁻¹.

B. Quadratic force field and assignments

It is pleasing to find that *ab initio* theory and experiment are in substantial agreement on structural aspects of IF₇ and moreover, that both can be understood in terms of simple conceptual model (VSEPR) previously found to have wide validity in chemistry.^{9,10} No such agreement between experiment and conceptual model was apparent in the published *force fields*²⁰⁻²⁴ of IF₇, however, when the structure was determined. The present work strongly suggests that the lack of agreement is not

to be attributed to a failure of the conceptual model but rather to errors in the spectroscopic assignments. A somewhat analogous situation also arose for trigonal bipyramids. For a long period of time, spectroscopists found it plausible to assign higher bending force constants to shorter bonds. In this case, too, the error in assignments was detected when assignments were seen to be inconsistent with VSEPR theory.¹³

The profile of bending force constants implied by the VSEPR theory in its points-on-a-sphere representation is illustrated in Fig. 1(a) for various degrees of hardness of repulsion. Simple Coulomb potentials ($n=1$) were never believed to be the source of the interactions and it is clear that they are too soft. An intermediate hardness, with n assigned the magnitude needed to account for the electron diffraction structure, is in surprising conformity with the *ab initio* molecular orbital results in Fig. 1(c), as shown in Table III. Computations carried out by extended Hückel theory, of course, are utterly devoid of explicit Coulomb interactions, yet they also simulate the profile constructed from *ab initio* theory. Despite the popular belief that *s* and *p* orbitals in a valence shell can support only four covalent bonds so that *d* orbitals must be called into play to account for the seven bonds in IF_7 , it can be seen in Fig. 1(b) that *d* orbitals play a minor role in the force field characteristics. This conclusion is in harmony with the *ab initio* calculations comparing D_{5h} and e_2'' deformed structures, including and excluding *d* orbitals (Table II), and the reasonable force field calculated without *d* orbitals.

The weight of theoretical evidence as portrayed in Fig. 1, then, strongly implies that the stiff bending modes are the equatorial in-plane bends ν_6 and ν_9 for which lateral atomic motions are strongly impeded by the close in-plane contacts. This physical argument appears not to have guided the half-dozen published assignments^{20,22,24,26,27,29} by spectroscopists, none of whom assigned what seems to be the highest frequency bend to an in-plane mode (see Fig. 2). Frequencies calculated by the present method are not expected to be quantitatively accurate but calculated bending frequencies for the similar molecules XeF_2 and XeF_4 were mostly within about 10% of the observed values. If it can be assumed that the present pseudopotential results are not off by much more than this and that their relative values are approximately correct, there is only one bending assignment which looks plausible, namely that indicated in Fig. 2. It agrees with the assignment of Bernstein and Pitzer²⁹ in all but one bending mode, the highly congested e_2' mode, but disagrees considerably from the others, all of which disagree with each other.

There is one troublesome feature of the present suggested assignment. It disregards as a separate mode the feature reported to be at 352 cm^{-1} by Claassen *et al.*²⁴ This not very sharp band of modest intensity could easily be taken to have a somewhat higher frequency, especially in curve B of Claassen's Fig. 1, depending upon the assumed slope of the background due to the broad 310 cm^{-1} band. If our suggested assignment is correct it is necessary to ascribe this band to the $363-$

365 cm^{-1} mode of nominally a_2'' symmetry. Our normal coordinate calculations (POS) with a $C_s(e_2'' + e_1')$ structure indicated a significant mixing in of an e_2' contribution (notation based on D_{5h} point group) and, hence, a possibly significant Raman activity. Analogously, as can be seen in Fig. 2, there is a contribution of an infrared-active component in the 510 cm^{-1} Raman mode. Claassen's published infrared spectrum exhibits a feature possibly ascribable to this mixing.

If the 352 cm^{-1} feature is accounted for this way and the 510 cm^{-1} band is assigned as a bend, only four recognized bands remain, two in the infrared and two in the Raman spectra, to be distributed among the five stretching frequencies expected. There seems to be no doubt that Eysel's a_1' assignments²⁷ [$\nu_1(\text{eq}) \approx 630\text{ cm}^{-1}$, $\nu_2(\text{ax}) \approx 675\text{ cm}^{-1}$] are correct for the two strong Raman-active modes, because our relative pseudopotential axial and equatorial stretching force constants are not only nicely consistent with their assignments but also with Badger's rule^{16,46} and the observed bond lengths. The latter, in turn, with $r_{\text{ax}} < r_{\text{eq}}$, are in accord with the simple VSEPR-POS picture. No new information about the infrared stretches was generated in the present study but there seems no reason to alter the more recent assignments.²⁴⁻²⁹

What should be done with the remaining e_2' Raman-active stretch ν_8 can only be conjectured. Stretching frequencies calculated by the present pseudopotential method are systematically too high by perhaps 20% and relatively less reliable than bending frequencies. Our computations suggest that the e_2' stretch is not greatly different in frequency from the a_1' equatorial stretch. It is possible, then, that ν_8 is either the weak 598 cm^{-1} feature in the foot of the 635 cm^{-1} band depicted by Claassen *et al.*²⁴ in their Fig. 1, but not identified, or that it is buried under the 635 cm^{-1} band itself. In either case, it would have to be a very weak band. Whether this is reasonable is not answered by the present calculations.

Combination bands offer little guide in the resolution of assignments. Each of the six different assignments referred to in Table IV was considered to offer a satisfactory account of combination bands. Our assignments closely resemble those of Bernstein and Pitzer,²⁹ differing principally in reassigning the 510 cm^{-1} band from an e_2' stretch to an e_2' bend. Accordingly, symmetry assignments are unchanged as are selection rules for combination bands. Some relaxation of D_{5h} selection rules can be expected anyway, because of the large amplitude e_2'' , e_1' vibrations.

C. Nature of POS interactions

Whether the "repulsions" in the successful POS calculation of bending force constants are better thought of as due to atom-atom nonbonded interactions or valence-shell-electron-pair interactions mediated by the spoiling of, say, optimum covalent binding by deformations, can be answered plausibly. Quite reasonable atom-atom interaction energies to be expected for $\text{F} \cdots \text{F}$ pairs were derived in paper I of this series.³² Bending force constants computed with the assumption that

TABLE IV. Vibrational assignments and frequencies (cm^{-1}) for IF_7 .

Mode	Activity	Type	LLSS ^a	Kh ^b	CGS ^c	WM ^d	ES ^e	BP ^f	Proposed ^g	MO calc. ^h
$\nu_1 (a_1')$	R	str-eq	678	678	676	676	629	676	635	696(650)
$\nu_2 (a_1')$	R	str-ax	635	635	635	635	675	635	676	828(758)
$\nu_8 (e_2')$	R	str-eq	511	360	352	510	509	510	598-635?	716
$\nu_3 (a_2'')$	IR	str-ax	670	670	670	746	672	670	670	...
$\nu_5 (e_1')$	IR	str-eq	547	670	746	670	746	746	746	...
$\nu_9 (e_1')$	R	bend-eq	313	313	310	352	342	352	510	594
$\nu_{10} (e_1'')$	R	bend _{eq} ^{ax}	360	511	510	310	308	310	310	340
$\nu_4 (a_2'')$	IR	bend-eq	368	368	365	425	257	365	365	390
$\nu_6 (e_1')$	IR	bend-eq	(250)	(190)	425	257	425	425	425	492
$\nu_7 (e_1')$	IR	bend-ax	426	426	257	365	363	257	257	290
$\nu_{11} (e_2'')$...	bend-eq	(350)	(340)	174	174	(200)	(200)	< 200	...

^aLord, Lynch, Schumb, and Slowinski, Ref. 20.^bKhanna, Ref. 22.^cClaassen, Gasner, and Selig, Ref. 24.^dWendling and Mahmoudi, Ref. 26^eEysel and Seppelt, Ref. 27.^fBernstein and Pitzer, Ref. 29.^gThis work. Calculated frequencies used F_{ij} computed at experimental bond lengths and (in parentheses) at calculated energy minimum; G matrix of Khanna as corrected by Claassen and Kim.

atom-atom interactions are solely responsible for the deformation energies had the correct profile (like those in Fig. 1) but numerical values were severalfold too low.

D. Comments on second-order Jahn-Teller effects

In simple cases, the hierarchy of interactions implied by the Jahn-Teller expansion^{41,47} can offer insights into the structure or dynamics of molecules.^{41-43,47} A dozen years ago⁴² connections were pointed out between second-order Jahn-Teller effects (then more commonly called pseudo-Jahn-Teller effects)⁴⁸ and the valence-shell-electron-pair-repulsion (VSEPR) theory found to work so admirably in the present case of IF_7 . In fact, the second-order Jahn-Teller effect was early invoked^{49,50} to account for the structure and dynamics of XeF_8 which, in VSEPR theory, is formally similar to IF_7 in that both possess seven stereochemically active valence-shell electron pairs. Second-order Jahn-Teller theory is helpful when the energetics of deformation from a symmetric molecular configuration is dominated by the mixing of a single high-lying filled MO with an empty low-lying orbital. Many cases, including XeF_8 , have been examined in which this dominance appears to hold. In the present case, EHT calculations made the e_2'' deformation from D_{5h} symmetry spontaneous while the *ab initio* pseudopotential calculations, instead, made the e_2'' deformations extremely soft, but not spontaneous. In neither set of calculations were the energetics of deformation dominated by a single orbital interaction; instead, contributions came from many symmetry-allowed interactions including some from rather low-lying valence orbitals. Therefore, there is little enlightenment to be derived from application of the second-order Jahn-Teller formalism in the present considerations.

As mentioned in the foregoing, Bernstein and Pitzer²⁹ based their analysis of existing observations of IF_7 upon an e_2'' spontaneous deformation formally assumed to result from $e_1'(F_{2p})$, $e_1''(I_{5d})$ mixing. Our calculations show that this interpretation grossly exaggerates such

mixing, for the lion's share of the softening of the e_2'' force constants is reproduced by calculations deleting I_{5d} orbitals. Moreover, the inclusion of $5d$ orbitals in one set of computations did not lead to an increased softening. We wish to emphasize, however, that although our conclusion about the minor importance of the F_{2p} , I_{5d} interactions conflicts with the formal basis of the Bernstein-Pitzer model, it only slightly impairs the practical utility of the molecular parameters derived by Bernstein. Only the magnitudes of the e_2'' potential constants are expected to be influenced appreciably.

E. Remarks about the assignments of ReF_7

According to electron diffraction evidence^{16,44} the molecular structure and intramolecular motions of ReF_7 closely resemble those IF_7 , except that the amplitudes of vibration in ReF_7 are larger. It is reasonable to expect the pattern of bending force constants to resemble that of IF_7 , although there is some indication that bonds of transition metals, with a substantial involvement of d orbitals, are less likely to be well-modeled by the POS approach than those of main-group elements.¹¹ It is reasonable to re-examine the spectral assignments for ReF_7 by Claassen *et al.*²⁴ with a view to trying to satisfy the POS implications. Presumably, we should expect the in-plane bending frequencies, topped by e_2' , to be the highest. In the case of ReF_7 , indeed, these expectations are met by Claassen's assignments, even if they were not for IF_7 . We can find nothing to question in his ReF_7 assignments except, perhaps, for his low-frequency Raman bands. The 352 cm^{-1} band, tentatively assigned to $\nu_{10}(e_1'')$, may possibly be ν_4 (nominally a_2'' rendered Raman active by $e_2'' + e_1'$ distortions, cf. the 352 cm^{-1} observed ν_4 infrared frequency); the actual ν_{10} band may be in the low-frequency tail of this spectral feature, perhaps at the 281 cm^{-1} position labeled with a question mark by Claassen *et al.* If the present reassignments for IF_7 are correct, the spectra of IF_7 and ReF_7 , which were considered to be "strikingly different" by Claassen *et al.*, can be seen to be less dissimilar than they originally appeared to be.

V. CONCLUDING REMARKS

The present pseudopotential computations proved to be of value in several respects, even if the quantitative accuracy achieved was modest. They showed the feasibility of exploring many facets of the potential surface of a rather complex molecule with a large number of electrons in a case where a comparable all-electron treatment would have been prohibitive. Prior computations³⁰⁻³⁴ with simpler, better understood molecules had delineated what systematic inaccuracies could be expected. The present results corresponded so closely to an interpretation of molecular behavior of IF₇ deduced somewhat speculatively from electron diffraction data and reinforced by an analysis by Bernstein and Ptizer²⁹ that there now seems to be little doubt about the principal features of the molecule. Despite the limited quantitative accuracy of the potential constants derived, the results compellingly suggested errors in all of the half-dozen published assignments of vibrations, and pointed to an alternative assignment. The computations leading to these conclusions revealed an appealingly simple molecular physics governing molecular motions. Force constants deduced followed surprisingly closely the patterns characteristic of a model of repelling points-on-a-sphere. It would appear advantageous in future studies of force fields to take greater advantage of this hint about molecular properties. Whether such a close correspondence between molecular orbital and points-on-a-sphere potential surfaces will survive in relativistic, multiconfiguration calculations remains to be seen.

Finally, the present results show that hypervalent compounds such as IF₇ can be understood quite well without invoking valence *d* orbitals on the central atom. These outer *d* orbitals are neither the preponderant source of second-order Jahn-Teller softening of the ring-puckering force constant nor the *sine qua non* of covalent binding of seven ligands by a central atom with but four valence *s* and *p* orbitals.

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