J. Phys. Chem. A **1997,** *101,* 1455−1459

Ab Initio and Resonance Raman Studies of Hexafluoro-1,3-butadiene

Mary S. C. Foley, Dale A. Braden, and Bruce S. Hudson*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Marek Z. Zgierski

Steacie Institute for Molecular Science, National Research Council of Canada, Ottawa K1A 0R6, Canada

Received: August 23, 1996; In Final Form: December 10, 1996[⊗]

Fluorine substitution can have a major effect on the electronic spectra and sometimes on the ground electronic state conformations of organic compounds. In this work we investigate the effect of perfluorination on the resonance Raman spectra of the simple diene hexafluoro-1,3-butadiene (HFBD) where the preferred ground state geometry is believed to be skew s-cis. *Ab initio* calculations at the 6-31+G* level (which includes diffuse functions (+) and polarization functions (*) on both C and F atoms) together with MP2, BLYP-DFT, and hybrid B3LYP-DFT/HF treatments of electron correlation were performed. The most stable conformer of HFBD is confirmed to be the skew s-cis form ($\phi \approx 58°$) with a fundamental vibrational C−C torsional mode at 44 cm^{-1}. *Ab initio* calculations of the gradient of the potential energy surface of the resonant excited singlet state provide a prediction of the relative resonance Raman intensities. A detailed comparison of theory with experiment is possible, and excellent agreement is observed. Activity in the fundamental transition of the torsional mode confirms the low frequency of this mode and the nonplanar nature of the ground state.

I. Introduction

Resonance Raman spectroscopy can be a useful way to investigate the nature of geometry changes associated with electronic excitations. In some cases new information is revealed about the ground electronic state in resonance Raman experiments because vibrations that are not observed off-resonance become strongly enhanced. In some cases this includes highly excited overtone transitions. There have been numerous applications of resonance Raman spectroscopy in the ultraviolet region to a variety of hydrocarbons and other systems.[1] In the present investigation we explore the effect of fluorine substitution on conformational states and electronic excitations. We also explore the extent to which quantum chemical methods can be applied to such systems. The comparison of calculated and observed resonance Raman spectra is a test of the validity of the description of both the ground and excited electronic state surfaces and the form of the ground state normal modes.

The effect of replacement of hydrogen by fluorine on the electronic structure of an unsaturated hydrocarbon may be summarized by noting that the increased electronegativity and the involvement of fluorine π orbitals results in a reduction of the C−C π interaction and the introduction of greater steric interactions due to the larger van der Waals radius of fluorine (1.47 vs 1.2 Å for H).[2] A more detailed examination of the literature in this field reveals considerable controversy over the years in terms of the origin of the effect of fluorine substitution.[2] In particular, for substitution of unsaturated carbon the effect has been described in terms of a rehybridization[3] from sp^2 to sp^3 and the effects of electronegativity[4] and also in terms of the involvement of the fluorine lone pairs.[5]

The preferred geometry of buta-1,3-diene is well-known to be trans planar (C_{2h}).[6] By contrast, the perfluorinated analogue, hexafluoro-1,3-butadiene, C_4F_6 (hereafter referred to as HFBD) is nonplanar (C_2).[7−9] On the basis of both theoretical and experimental studies, the preferred geometry is believed to be s-cis skewed with a torsional angle, ϕ, of ca. 45−60°. Figure 1 illustrates the s-cis skewed geometry of HFBD. The experimental evidence for this geometry comes from the electronic absorption spectrum of HFBD vapor[7] and electron diffraction results[8] which are consistent with a torsional angle of 47.4 ± 2.4° away from the planar s-cis geometry. Theoretical *ab initio* calculations of the ground state geometry and normal modes of vibration of HFBD have been presented by Dixon.[9] These calculations were based on a Hartree-Fock[9a] or MP-2[9b] level treatment with a 6-31G*(C) basis set in which the d-type polarization orbitals are only on the C atoms. In view of the increased electronegativity and involvement of fluorine π orbitals, we have extended these calculations to a larger (6-31+G*) basis set that includes polarization and diffuse functions on both C and F atoms in conjunction with the MP2 and DFT treatments of electron correlation.

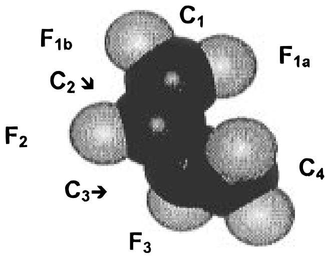

Figure 1. Hexafluoro-1,3-butadiene. The numbering scheme used in Table 2 is shown.

The primary motivation of the present study is to evaluate modern large basis *ab initio* methods for the treatment of a fluorine-substituted unsaturated hydrocarbon to see if there is good agreement with experiment. In particular, the treatment of electronic excitations by such methods is new. The ultimate objective of such studies is to see if a simple and unambiguous description of the effect of H to F replacement can be established.

---

* Author to whom correspondence should be directed at Department of Chemistry, 1-014 Center for Science & Technology, Syracuse University, Syracuse, New York 13244-4100.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S1089-5639(96)02611-4 CCC: $14.00

II. Computational and Experimental Methods

Computational Methods. *Ab initio* calculations were performed using Gaussian 92 and 94.[10] Ground state molecular geometries were fully optimized and the normal modes of vibrations of HFBD were determined at the HF, MP2, BLYP, and B3LYP levels[11,12] using the 6-31+G* basis set.

The excited electronic states were calculated at the CIS (configuration interaction singles) level with the HF/6-31+G* basis set. The CIS method has recently been discussed in detail.[13] The reliability of this method in the context of excited state geometry calculations has been demonstrated in a series of recent papers.[14]

In order to calculate resonance Raman intensities, the gradient of the potential is calculated at the optimized ground state geometry. For large molecules with diffuse absorption spectra, rapid dephasing implies that only very early time dynamics is important to the Raman process.[15] The short-time dynamics is, in turn, largely determined by the gradient of the potential in the Condon region. The minimum of the potential of the excited state can be estimated from this gradient if a harmonic model is invoked and the same force constants as those of the ground state are assumed.

Experimental Methods. The experimental methods used to obtain resonance Raman spectra in the ultraviolet region have been described elsewhere.[16] Briefly, excitation wavelengths from 200 to 239 nm were obtained by anti-Stokes stimulated Raman shifting of the 532, 355, and 266 nm harmonics of the output of a Nd:YAG laser in hydrogen gas. The excitation source was incident on free-flowing hexafluoro-1,3-butadiene (PCR Inc.) diluted in nitrogen. The Raman scattered light was collected in a backscattering geometry at *f*/1 and dispersed by a 1 m McPherson GCA 225 monochromator in scanning mode. The dispersed radiation was detected by a Hamamatsu R166H solar blind photomultiplier tube. In the very low frequency region of the resonance Raman spectrum, scattered light becomes a serious problem and an accurate determination of the fundamental intensities proved to be unsuccessful. Methods to rectify this problem are currently being investigated.

III. Results and Discussion

Absorption Spectra. The electronic absorption spectrum of HFBD vapor (Figure 2) exhibits two low-energy, broad transitions with similar intensities.[7] This spectrum has been interpreted[7] in terms of an exciton model. The two transitions in this model are due to the in-phase and out-of-phase excitation of the two ethylenic units. The relative intensity of the two transitions depends on the angle between the ethylenic units. This type of analysis results in excellent agreement between the implied torsional angle, ϕ, away from the planar cis geometry and that determined by electron diffraction data. It assumes that both observed transitions are $\pi\pi^*$ in nature; a $\pi\sigma^*$ assignment for the higher energy transition is also possible, in principle. The excitonic model is also only approximate, and other low-energy $\pi\pi^*$ transitions may occur in this energy region. This calculation confirms the $\pi\pi^*$ nature of these excitations.

Ab initio 6-31+G* level calculations of the electronic excitations of HFBD at the CIS level give the following results for the optimized s-cis, skew geometry:

ΔE (eV)	**7.53**	7.67	8.32	8.57	9.11	**9.55**	9.59	9.91
f	**0.47**	0.03	0.00	0.19	0.10	**0.37**	0.08	0.12
type	$\pi\pi^*$	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\sigma^*$	$\pi\pi^*$	$\pi\pi^*$	$\pi\pi^*$	$\pi\sigma^*$

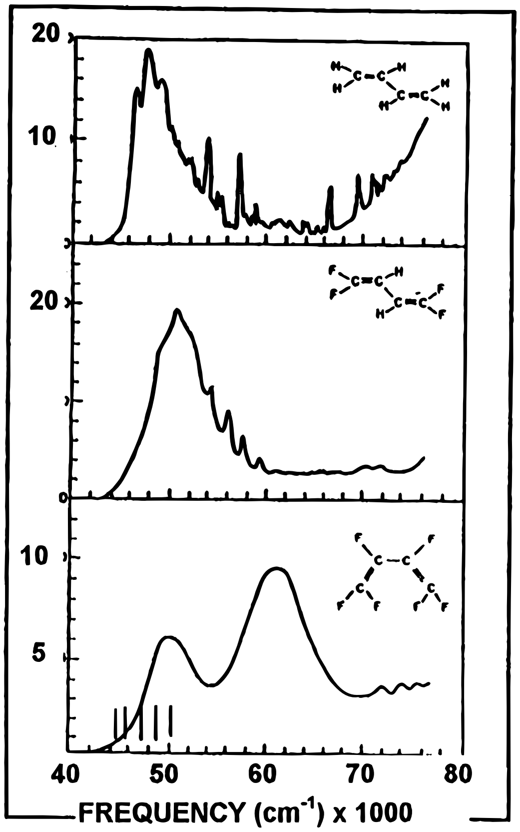

Figure 2. Absorption spectra of butadiene and fluorinated butadienes, modified from ref 7. The lines in the hexafluorobutadiene spectrum indicate the excitation wavelengths used for the resonance Raman experiments.

The two transitions indicated in bold clearly correspond to the two observed strong bands. The lower energy of these transitions is described as a HOMO → LUMO (π)−HOMO → LUMO + 1 (π) mixture. The transition with a positive relative phase for these configurations is at 9.11 eV. The more intense transition at higher energy is due to the HOMO − 1 → LUMO (π)−HOMO − 1 → LUMO + 1 (π) combination.

The low lying $\pi\sigma^*$ excitations in this molecule are seen as discrete spectral features in other unsaturated fluorine-substituted molecules such as hexafluorobenzene.[17] These transitions are, however, very weak. The two lower energy $\pi\sigma^*$ excitations of HFBD at 7.67 and 8.32 eV are indeed also very weak, but the higher energy transitions of this type are considerably stronger. These transitions as well as the $\pi\pi^*$ transition at 9.11 eV may contribute to the intensity of the second transition. This is consistent with the observation that the calculated intensities for the first two highlighted $\pi\pi^*$ transitions give 25% more intensity to the one at lower energy while the observed intensity pattern has more overall intensity in the higher energy band. It should be noted that the inclusion of doubly excited configurations would move a $\pi\pi^*$ state of this character into the low-energy region.[6]

A similar calculation for 1,1,4,4-tetrafluoro-1,3-butadiene shows that this molecule prefers an s-trans C_{2h} planar geometry which is in agreement with the experimental observations.[7,18,19] This calculation requires a large basis set and inclusion of electron correlation. The observation of only one strong transition for tetrafluoro-1,3-butadiene (Figure 2) is consistent with a planar s-trans conformation within the context of the exciton model.[7] A vibrational analysis[18] involving both Raman and IR data is also consistent with C_{2h} symmetry. The absence of an observed microwave spectrum supports this centrosymmetric structure.[19] Large basis set calculations also show that

TABLE 1: Comparison of Calculated and Observed Bond Lengths (Å) for Hexafluorobutadiene

	C=C	C−C	C−F (ave)
6-31G*(C)/HF[9]	1.308	1.459	1.308
6-31+G*/HF	1.311	1.459	1.307
6-31+G*/MP2	1.340	1.446	1.338
6-31+G*/BLYP	1.350	1.453	1.352
6-31+G*/B3LYP	1.336	1.450	1.333
experimental[8]	1.336 ± 0.018	1.488 ± 0.018	1.323 ± 0.006

TABLE 2: Calculated Ground State Geometry[a]

	HF	MP2	BLYP-DFT	B3LYP-DFT
C_1C_2 (Å)	1.3109	1.3391	1.3495	1.3357
C_2C_3 (Å)	1.4585	1.4460	1.4530	1.4503
$F_{1a}C_1$ (Å)	1.2974	1.3287	1.3406	1.3234
$F_{1b}C_1$ (Å)	1.2931	1.3234	1.3360	1.3190
F_2C_2 (Å)	1.3307	1.3623	1.3798	1.3581
$C_1C_2C_3$	125.81	124.82	126.25	125.78
$F_{1a}C_1C_2$	124.05	123.45	124.05	123.91
$F_{1b}C_1C_2$	124.23	124.20	124.03	124.06
$C_1C_2F_2$	118.57	118.23	117.38	117.92
$F_2C_2C_3$	115.62	116.96	116.36	116.29
$C_1C_2C_3C_4$	58.37	58.88	60.27	56.41
$F_{1a}C_1C_2C_3$	0.67	1.39	1.90	1.84
$F_{1b}C_1C_2C_3$	−178.4	−177.3	−176.8	−176.9
$F_2C_2C_3F_3$	56.81	58.75	58.86	55.83
energy (au)	−748.02	−749.56	−751.34	−751.41

[a] Bond lengths in angstroms; angles in degrees.

TABLE 3: Calculated and Observed Vibrational Frequencies (cm^{-1}) of Hexafluorobutadiene in the Optimized Skew s-cis Geometry[a]

	HF[9]	HF	MP2	BLYP	B3LYP	exptl[21]	
x	0.9	0.9	0.95	1.00	1.00		
a	1841	1835	1758	1745	1833	1796	
	1380	1377	1348	1299	1377	1379	
	1328	1331	1278	1238	1323	1379	
	1129	1129	1084	1061	1132	1128	933
	703	703	673	675	710	702	
	675	679	596	602	646	660	616
	535	535	501	500	526	529	
	468	466	443	442	465	408	
	368	366	358	360	374	375	329
	252	254	240	249	258		
	184	184	173	168	180	181	
	95	94	89	89	94	94	
	38	44	44	46	46	[52]	
b	1818	1810	1724	1704	1800	1765	
	1346	1342	1273	1237	1322	1329	
	1187	1185	1137	1098	1181	1189	
	963	966	923	922	974	972	
	639	646	584	588	617	633	
	614	614	565	570	609	547	
	554	554	520	516	549	520	
	418	417	396	401	415	422	
	288	289	274	279	291	292	259
	204	204	194	194	204	204	
	107	107	98	91	103		
RMSΔ		26.8	40.3	54.8	25.6		
*M*Δ		9.7	−28.2	−37.4	5.1		
M%|Δ|		3.2%	5.3%	5.9%	2.8%		

[a] The results in the first column are from Dixon[9] using a slightly different basis set. The experimental values used are given in the next to last column. The last column gives additional experimental values reported in ref 21. The top row gives the factor by which the ab initio frequencies have been multiplied. The root-mean-square deviation between the calculated and experimental values is given as RMSΔ (cm^{-1}). *M*Δ (cm^{-1}) is the mean deviation; *M*%|Δ| is the mean percentage absolute deviation.

the s-trans planar C_{2h} geometry is also the lowest energy for 2,3-difluoro-1,3-butadiene. This is consistent with the results of a combined NMR, IR, and Raman study.[20] The s-trans planar geometries of the 1,1,4,4-tetrafluoro- and 2,3-difluoro-butadiene species, in contrast to that of HFBD, are consistent with the simple idea that it it is 2−4 and 1−3 F−F nonbonded interactions that destabilize the s-trans planar structure. Attractive interactions between the fluorine atoms in the skew s-cis geometry,[5] if they exist, would be expected to stabilize the skew s-cis geometry of 1,1,4,4-tetrafluorobutadiene. On the other hand, it is not clear why a skew s-trans geometry with reduced 2−4 and 1−3 F−F interactions would not be similarly stable unless the s-cis geometry is preferred on the basis of π stabilization.[5] Dixon has argued that the skew s-cis geometry is favored by minimization of the dipolar interaction of the polar C−F bonds.[9] Our own calculations, however, indicate that both steric and simple electrostatic interactions favor a slightly skew s-trans geometry with $\phi \approx 110°$. This point concerning the relative s-cis vs s-trans energy is discussed further below.

Bond Lengths and Geometries. Using a larger basis set that includes polarization and diffuse functions on both C and F together with MP-2 and DFT treatments of electron correlation yields some significant differences in the bond lengths and bond angles compared with those determined either theoretically using a smaller 6-31G*(C) basis set or experimentally from electron diffraction data. The bond lengths of HFBD calculated at various levels and experimental determinations are listed in Table 1. While the computed C−F and C=C bond lengths and those deduced from the electron diffraction data are in reasonably good agreement, the C−C bond length calculated at the 6-31G*(C) level is appreciably too short. Table 2 shows a more detailed comparison of the calculated results. The post-Hartree−Fock methods give considerably longer C−F bond lengths than the Hartree−Fock value. This may be important in terms of the interaction of the nonbonded F atoms. All methods give a considerably longer C−F bond for the 2 (and 3) positions than the terminal C−F bonds which are very similar to each other. It should be noted that the analysis of the electron diffraction data assumed that all C−F bonds have the same length. The post-Hartree−Fock methods give quite different C=C and somewhat different C−C bond lengths than the Hartree−Fock result. The bond length difference between the C−C and C=C is 50% smaller for the post-Hartree−Fock methods. The bond angles do not appear to depend much on the method used. The FCF terminal bond angle is about 112° in each case.

Vibrational Frequencies and Resonance Raman Intensities. The calculated and experimental vibrational frequencies are compared in Table 3. The HF values are, as expected, very similar to those of Dixon. As is usual, these are higher than the observed values. (The numbers given have been multiplied by a uniform factor of 0.9.) The root-mean-square, mean, and mean percentage absolute deviations for all four methods used indicate that the hybrid B3LYP method is the most reliable.

The calculated frequencies are in excellent agreement with the most recent analysis of the vibrational spectrum[21] performed by Durig *et al.* with the exception that their analysis assigns the torsional vibration fundamental frequency to a value of 94 cm^{-1}. However, ab initio calculations show that while there is indeed a vibration at ca. 94 cm^{-1}, it is not the torsional mode. This is expected to be found in the 40−50 cm^{-1} range. This conclusion is in agreement with that of Dixon.[9] Our MP-2 and DFT calculations (see also 9b) confirm that this is not limited to the HF treatment.

The gradient of the potential energy for the resonant singlet excited state at the ground state geometry has been calculated at the CIS level. This can be used to estimate the relative Raman intensities[15] and the equilibrium excited state geometry on the

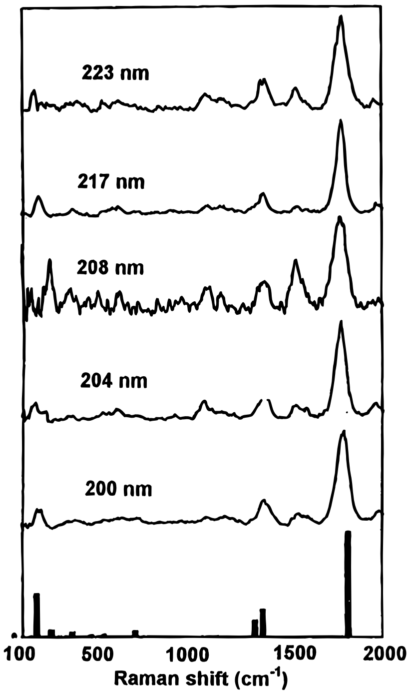

Figure 3. Resonance Raman spectra of hexafluorobutadiene vapor: spectra obtained at several excitation wavelengths (top); relative intensities calculated on the basis of predicted excited state geometry changes (bottom).

TABLE 4: Calculated Frequencies, Displacements and Raman Intensities for the $S_0 \rightarrow S_1$ Transition

frequency (cm^{-1})	displacement (Δ)	Raman intensity
1835	1.00	1.00
1377	0.67	0.25
1331	0.54	0.15
1129	0.12	0.01
703	0.59	0.05
679	0.01	0.00
535	0.37	0.01
466	0.41	0.01
366	0.97	0.04
254	1.80	0.06
184	6.32	0.40
44	9.45	0.05

basis of the assumption of a harmonic surface and the same force constants as the ground state. The calculated normalized displacements (Δ) associated with excitation to the first excited electronic state are given in Table 4. The approximate relative resonance Raman intensities calculated from the gradient of the excited state potential are also given.

Resonance Raman experiments have been conducted on hexafluorobutadiene vapor with excitation throughout the first absorption band (Figure 3). The fact that these spectra are largely independent of excitation wavelength (to a first approximation) is consistent with the idea that the nuclear motion on the excited state surface is largely damped before recurrences occur. This is, in turn, consistent with the observed absorption spectra. This is in contrast to the case for butadiene[22] where excitation throughout the absorption band results in continuous enhancement of strong overtone transitions which are not seen at lower excitation energies. This difference is presumably related to the low frequency and anharmonicity of the torsional potential of hexafluorobutadiene. In any case, the behavior of the Raman spectra of hexafluorobutadiene as a function of excitation wavelength justifies the computation of the relative Raman intensities on the basis of the gradient of the excited state potential surface.

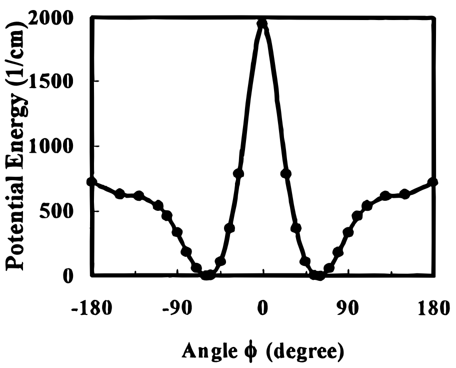

Figure 4. Torsional potential of hexafluorobutadiene calculated with the 6-31+G* basis set at the Hartree−Fock level.

The bottom panel of Figure 3 shows the computed relative Raman intensities based on this short time approximation (Table 4). The agreement is generally good. The band near 1550 cm^{-1} is an overlapped pair of combination bands (1377 + 184 and 1331 + 184). The observed intensity is approximately that expected (0.10 and 0.06, respectively). This agreement between the observed and computed relative resonance Raman intensities indicates that the simple CIS method provides the correct orientation of the slope of the excited state potential energy surface in terms of its projection onto the ground state normal modes of vibration. It also indicates that the normal mode description is substantially correct even at the HF level.

The Torsional Potential. Figure 4 shows the entire torsional potential calculated with optimization of all geometric parameters at each torsional angle. The minimum of the torsional angle is at 57−59°, and the torsional vibrational frequency is 45 cm^{-1}, both in very good agreement with the results of Dixon.[9] The barrier height is calculated to be 720 cm^{-1}.[23]

The torsional equilibrium for the excited state geometry can be estimated from the gradient and the harmonic approximation. With this approximate method the resonant excited state is found to be more nearly planar with a torsional angle of only 24°. Since this is very different from the ground state value, $\phi \approx 58°$, we expect a very large Franck−Condon factor for this transition and strong activity in the resonance Raman spectrum. The expectation of resonance Raman activity in the fundamental of transitions involving the torsional mode is analogous to the situation for *cis*-stilbene as investigated by Myers and Mathies.[24] Such activity depends on the cis, skew geometry of the ground electronic state. For a planar geometry the torsional motion is inactive by symmetry.

Figure 5 shows the ultralow-frequency region of the resonance Raman spectrum following excitation at 218 nm. The observation of intensity in the fundamental vibration of the mode at ca. 50 cm^{-1} confirms that the torsional vibration is at this low frequency as predicted and that this molecule has a nonplanar geometry. The complex intensity pattern in the region of the overtone transitions for this mode is expected given the low frequency and the highly anharmonic potential. Scans of the same spectral region for butadiene do not show any features of this type.

IV. Conclusions

The results presented here are the first studies of fluorine-containing compounds using resonance Raman spectroscopy. The results show significant differences from the corresponding hydrocarbons. In the case of hexafluorobutadiene the resonance Raman spectra confirm the electron diffraction, vibrational

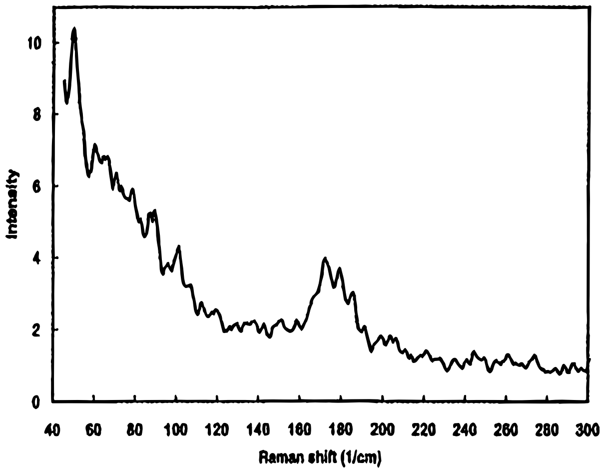

Figure 5. Resonance Raman spectrum in the low-frequency region. The peak at 52 cm^{-1} is the torsional mode.

analysis, and theoretical conclusions that this molecule has a skew s-cis geometry in the ground electronic state. The results of *ab initio* calculations of the excited electronic states at the CIS level are in good agreement with the observed electronic absorption spectra and correctly predict the relative intensities of the resonance Raman transitions.

We return now to the question of the preference of the skew s-cis geometry to the skew s-trans geometry that is equally effective at reducing the steric interaction between large substituents at the 1 and 3 or 2 and 4 positions. It has been assumed that the remarkable conformation of HFBD is due to fluorine substitution.[7-9] However, note that (*Z*,*Z*)-3,4-dimethyl-2,4-hexadiene, which may be regarded as a 1,2,3,4-tetramethylbutadiene, also adopts a skew s-cis geometry, as determined by electron diffraction ($\phi = 67°$).[25] If these two very different substituents cause the same conformation for the same reason, then the basis for this preference has nothing to do with electronegativity or bond dipoles. Other halo- and alkyl-substituted butadienes are also known to exist in a non-s-transoid geometry.[26] On the other hand, (*E*,*E*)-3,4-dimethyl-2,4-hexadiene adopts a skew s-trans geometry about the central C−C single bond ($\phi = 117°$).[25] It has been argued that the π interactions of conjugated double bonds, by themselves, favor an s-cis geometry, while the σ interactions prefer an s-trans configuration.[27] This argument was applied to glyoxal and N_2O_2, and involved an energy decomposition scheme in which the $\sigma-\pi$ mixing component was evenly distributed between the σ and π divisions.[27] A similar argument may perhaps be made for substituted butadienes, although the geometries in these cases are nonplanar, so that the π bonds should be more localized. In any case, the energetics responsible for the skew cis conformations are complex and will require further study. On the basis of this comparison of the effects of methyl and fluoro substitution, it appears, however, that in this case the effect of fluorine on the conformational equilibrium is equivalent to a steric perturbation.

Acknowledgment. This research was supported by a grant from the National Science Foundation, CHE-9503629.

References and Notes

(1) Hudson, B.; Sension, R. J. In *Vibrational Spectra and Structure*; Bist, H. D., Durig, J. R., Sullivan, J. F., Eds.; Elsevier: Amsterdam, 1989; Vol. 17A, pp 363−390. Hudson, B. In *Recent Trends in Raman Spectroscopy*; Jha, S. S., Banerjee, S. B., Eds.; World Scientific Press: Singapore, 1989; pp 368−385. Brudzynski, R. J.; Hudson, B. *J. Am. Chem. Soc.* **1990**, *112*, 4963. Mayne, L. C.; Hudson, B. *J. Phys. Chem.* **1991**, *95*, 2962. Chadwick R. R.; Strahan, G. D.; Zgierski, M. Z.; Hudson, B. *J. Chem. Phys.* **1991**, *95*, 7204. Shang, Q-y.; Hudson, B. S. *Chem. Phys. Lett.* **1991**, *183*, 63. Berryhill, J.; Pramanick, S.; Zgierski, M. Z.; Zerbetto, F.; Hudson, B. S. *Chem. Phys. Lett.* **1993**, *205*, 39. Strahan, G. D.; Hudson, B. S. *J. Chem. Phys.* **1993**, *99*, 5780. Foley, M. S. C; Hudson, B. S. *J. Mol. Struct.*, in preparation (invited review article).

(2) Smart, B. E. Fluorocarbons. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1983; pp 603−655. Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; pp 141−191.

(3) Bernett, W. E. *J. Org. Chem.* **1969**, *34*, 1772.

(4) Kollman, P. *J. Am. Chem. Soc.* **1974**, *96*, 4363.

(5) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1−242. Bernardi, F.; Bottini, A.; Epiotis, N. D.; Guerra, M. *J. Am. Chem. Soc.* **1978**, *100*, 6018.

(6) Hudson, B.; Kohler, B. E.; Schulten, K. *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; pp 1−95.

(7) Brundle, C. R; Robin, M. B. *J. Am. Chem. Soc.* **1970**, *92*, 5550−5555.

(8) Chang, C. H.; Andreassen, A. L.; Bauer, S. H. *J. Org. Chem.* **1971**, *36*, 920.

(9) (a) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 2038−2043. (b) Dixon, D. A., Smart, B. E. In *Selective Fluorination in Organic and Bioorganic Chemistry*; Welch, J. T., Ed.; ACS Symposium Series 456; American Chemical Society: Washington, DC, 1991.

(10) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart J. J. P; Pople, J. A. *GAUSSIAN 92, Rev. C*; Gaussian, Inc.: Pittsburgh PA, 1992.

(11) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(12) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(13) Foresman, J. B.; Schlegel, H. B. *NATO ASI Ser., Ser. C* **1993**, *406*, 11−26. Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135-49.

(14) Negri, F.; Orlandi, G.; Zerbetto, F.; Zgierski, M. Z. *J. Chem. Phys.* **1995**, *103*, 5911. Markham, L. M.; Mayne, L. C.; Hudson, B. S.; Zgierski, M. Z. *J. Phys. Chem.* **1993**, *97*, 10319. Zgierski, M. Z.; Zerbetto, F. *J. Chem. Phys.* **1993**, *99*, 3721. Zerbetto, F.; Zgierski, M. Z. *J. Chem. Phys.* **1993**, *98*, 4822.

(15) Lee, S.-Y; Heller, E. J. *J. Chem. Phys.* **1979**, *71*, 4777. Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822.

(16) Sension, R. J.; Hudson, B. *J. Chem. Phys.* **1989,** *90*, 1377.

(17) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: Orlando, FL, 1985; Vol. III, p 362 ff.

(18) Miller, F. A.; Elbert, W. F.; Pingitore, W. *J. Mol. Struct.* **1977**, *41*, 19.

(19) Beaudet, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 1390.

(20) Toth, J. P.; Koster, D. F. *Spectrochim. Acta, Part A* **1975**, *31A*, 1891−900.

(21) Wurrey, C. J.; Bucy, W. E.; Durig, J. R. *J. Chem. Phys.* **1977**, *67*, 2765.

(22) Chadwick, R. R.; Strahan, G. D.; Zgierski, M. Z.; Hudson, B. *J. Chem. Phys.* **1991**, *95*, 7204−7211.

(23) In ref 9b the SCF barrier height is given as 1.8 kcal/mol (630 cm^{-1}) and the MP-2 barrier height is 2.5 kcal/mol (980 cm^{-1}). It is stated that this MP-2 value is in good agreement with the “experimental” value of the barrier (2.85 kcal/mol = 986 cm^{-1}). However, this “experimental” value comes from an analysis of the Raman and infrared spectra[20] which uses an assignment of the fundametal torsional frequency (94 cm^{-1}) that differs from that deduced on the basis of all *ab initio* calculations (ca 45−50 cm^{-1}). This agreement must, therefore, be coincidental.

(24) Myers, A. B.; Mathies, R. A. *J. Chem. Phys.* **1984**, *81*, 1552.

(25) Traetteberg, M. *Acta Scand.* **1970**, *24*, 2295. Note that the author refers to this compound as the trans, trans isomer and that he defines the torsion angle about the single bond as being zero when the double bonds are s-trans planar.

(26) Bothner-By, A. A.; Jung, D. *J. Am. Chem. Soc.* **1968**, *90*, 2342.

(27) Mo, Y.; Zhang, Q. *Int. J. Quantum Chem.* **1995**, *56*, 19.