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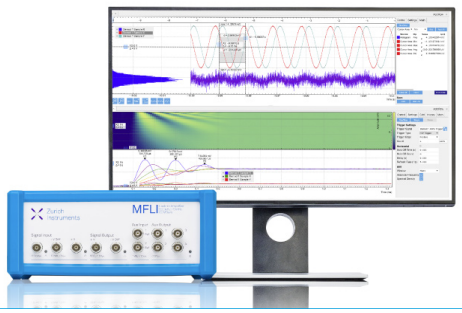

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A contribution to the understanding of the structure of xenon hexafluoride

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Three stationary points of symmetry C_{3v}, C_{2v}, and O_h on the potential energy surface of XeF_6 have been located and characterized at the self-consistent field level of theory with a large basis set. At this level of theory, and contrary to results given earlier in the literature, two of these stationary points (C_{2v} and O_h) are determined to be transition states, with harmonic vibrational frequencies leading to the third stationary point (C_{3v}). In addition, second-order Møller–Plesset perturbation theory, configuration interaction, and coupled-cluster energies have been determined at each of these optimized geometries. The C_{3v} structure is predicted to lie lowest, followed by the C_{2v} and then the O_h structure. © *1995 American Institute of Physics.*

INTRODUCTION

Shortly following its synthesis in 1962,[1] the electronic structure of XeF_6 became the subject of a long-standing scientific debate.[2–13] Many interesting interpretations of the molecule's very complicated ir and Raman spectra[2,4,9,10] led to the conclusion that an octahedral structure could not be the lowest in energy.[13,15–17] Indeed, the simple VSEPR model[14,15] predicted that the ''extra'' electron pair should be stereochemically active and distort the molecule to any of a number of lower symmetries. If the electron pair were localized on one face or in the ''belt'' of the octahedron, for example, C_{3v} and C_{2v} structures would result, respectively.

Past theoretical studies of the electronic structure of XeF_6 included the pioneering self-consistent field (SCF) study of the XeF_n series with a relatively small basis by Basch, Moskowitz, Hollister, and Hankin,[8] an excellent crystal field study by Wang and Lohr[16] which examined the energetics of the geometric divergence from the O_h structure, and a pseudopotential SCF-MO study by Rothman, Bartell, Ewig, and Van Wazer,[17] which predicted a large deformation from the O_h structure. Most recently, theoretical work by Klobukowski, Huzinaga, Seijo, and Barandiaran[18] provided information concerning the O_h, C_{2v}, and C_{3v} structures. They determined optimized geometries for XeF_6 at the SCF level of theory using a medium-sized basis set.

Recent experimental work by Cutler, Bancroft, Bozek, Tan, and Schrobilgen[19] used high-resolution photoelectron spectroscopy to resolve the ligand-field splittings for XeF_6, and reported bond angles for the C_{3v} structure which agreed well with the results of Klobukowski *et al.*[18] But they report no experimental data for the bond lengths. In addition, they concurred with the earlier results[5,13,18] that the dipole moment of the molecule is exceedingly small, on the order of a few tenths of a debye. However, both of these recent works[18,19] referred to the C_{2v} structure as a local minimum, though no theoretical vibrational frequency analysis has been presented in the literature to support this conclusion.

In this work, the O_h, C_{3v}, and C_{2v} structures for XeF_6 are studied with a significantly larger basis set and higher levels of theory. In addition, harmonic vibrational frequencies for each structure have been determined and analyzed. At the SCF level of theory, the C_{2v} stationary point has been shown not to be a minimum, but, in fact, to be a transition state whose imaginary vibrational frequency leads to the C_{3v} structure.

THEORETICAL METHODS

Three stationary points on the potential energy surface of XeF_6 have been determined and characterized using the restricted Hartree–Fock (SCF) method. At each of these stationary points, second-order Møller–Plesset perturbation theory (MP2), configuration interaction including all single- and double-excitations (CISD), and Davidson-corrected CISD (CISD+Q) energies were determined. At the O_h and C_{2v} stationary points coupled-cluster including all single- and double-excitations (CCSD) single-point energies have also been determined. All results were obtained using the PSI[20] and CADPAC[21] suites of quantum chemistry codes.

The basis set used for Xe was provided by Harry Partridge[22] in its uncontracted form. This basis set was contracted via an iterative scheme by using the molecular orbital coefficients from isolated-atom SCF calculations on Xe as the contraction coefficients. The uncontracted basis was determined to have a Hartree–Fock energy of −7 232.138 101 h, while that for the contracted basis was −7 231.724 437 h. This contraction represents an energy difference of less than 0.006% from the Hartree–Fock limit of −7232.153 h.[23] This differs by an order of magnitude from the basis set used for Xe in previous work,[18] which reported a 5 h difference from the Hartree–Fock limit. In addition, one extra set of d-type orbitals and one set of f-type orbitals were added to the basis. The exponent of the d-type orbitals (α_d=0.160 871) resulted from an even-tempered extrapolation from the previous two lower d-type orbital sets. The exponent on the f-type orbitals (α_f=0.503 94) was obtained by determining the energy of the XeF_6 molecule at a fixed geometry near that of the O_h minimum with three different f-orbital exponents and finding the minimum of the parabola fitting the three points. The final contraction scheme may be designated

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TABLE I. The contracted gaussian $(24s19p14d1f/12s11p8d1f)$ basis set used for Xe in this study. The atomic basis set was supplied by Partridge.

Function	Exponent	Contraction coefficient
s	71 082 420.0	0.000 001 6
	10 642 320.0	0.000 012 7
	2 421 851.0	0.000 067 1
	686 010.2	0.000 283 3
	223 823.9	0.001 032 5
	80 813.37	0.003 365 7
	31 524.33	0.010 008 8
	13 078.18	0.027 302 4
	5 706.402	0.067 683 9
	2 596.865	0.147 551 1
s	1 224.248	0.263 723 4
	594.200 7	0.335 767 0
	293.798 7	0.236 041 1
	141.975 1	0.055 175 7
s	141.975 1	0.004 481 4
	73.973 28	0.611 024 1
s	38.188 05	1.0
s	18.786 29	1.0
s	10.342 10	1.0
s	5.487 182	1.0
s	2.636 719	1.0
s	1.306 924	1.0
s	0.469 391	1.0
s	0.236 422	1.0
s	0.103 898	1.0
p	110 104.5	0.000 025 3
	26 056.61	0.000 226 2
	8 463.323	0.001 318 0
	3 240.730	0.005 944 3
	1 378.596	0.021 920 4
	631.526 1	0.066 787 1
p	305.729 1	0.162 716 1
	154.056 7	0.295 767 1
	80.026 0	0.351 416 5
	42.255 03	0.219 139 9
p	42.255 03	0.037 770 8
	22.171 42	0.333 872 0
p	11.873 60	1.0
p	6.356 799	1.0
p	3.321 110	1.0
p	1.703 667	1.0
p	0.844 142	1.0
p	0.397 700	1.0
p	0.175 363	1.0
p	0.073 773	1.0
d	3 605.356	0.000 135 4
	1 091.745	0.001 338 7
	426.853	0.008 001 2
	190.431	0.033 371 4
	91.699 560	0.101 518 5
	46.452 430	0.223 666 1
	24.154 870	0.341 553 7
d	12.792 640	1.0
d	6.792 993	1.0
d	3.542 693	1.0
d	1.800 995	1.0
d	0.878 397	1.0
d	0.375 917	1.0
d	0.160 871	1.0
f	0.503 940	1.0

as $(24s19p14d1f/12s11p8d1f)$. This basis set is summarized in Table I. The basis set used for the F atoms was the standard Huzinaga–Dunning double-zeta $(9s5p/4s2p)$ basis[24] with an extra set of *d*-type orbitals added with exponent $\alpha_d=1.2$. All *d*- and *f*-type orbitals used in this work were the six- and ten-component Cartesian Gaussian functions, respectively. There were a total of 199 contracted Gaussian functions used in this basis.

TABLE II. Geometrical parameters (bond lengths in Å) as determined at the SCF level of theory for the O_h, C_{2v}, and C_{3v} structures of XeF_6. Total energy (hartrees) as determined at the SCF level of theory. Definitions of geometrical parameters may be found in Figs. 1–3.

Structure	Bond lengths	Bond angles	Total energy
O_h	**r**=1.902		−7828.1061
C_{2v}	**a**=1.960	**j**=139.7°	−7828.1743
	b=1.826	**k**=79.9°	
	c=1.805	**l**=74.8°	
C_{3v}	**a**=1.927	**j**=80.8°	−7828.1799
	b=1.796	**k**=115.1°	

The three stationary points were determined using analytic gradients of SCF energies. Calculations on the O_h structure were carried out in the D_{2h} subgroup of O_h, and those on the C_{3v} structure were carried out in the C_s subgroup of C_{3v}. All structures were optimized until all Cartesian components of the analytic gradients were less than 10^{-6}.

The harmonic vibrational frequencies at each stationary point were determined using finite differences of analytic gradients along cartesian coordinates. In addition, MP2 single-point energies at the SCF stationary points were determined using a standard MP2 algorithm. CISD single-point energies at these same stationary points were determined using algorithms based on the shape-driven graphical unitary group approach.[25] For the CISD single-point energy calculations, the F 1*s* and Xe 1*s*, 2*s*, 3*s*, 4*s*, 2*p*, 3*p*, 4*p*, and 3*d* core orbitals were frozen. In addition, the virtual orbitals corresponding to the F 1*s* and the Xe 1*s*, 2*s*, 3*s*, 4*s*, 2*p*, 3*p*, and 4*p* orbitals were deleted. This resulted in a total of 1 255 360 configurations state functions (CSFs) for the O_h calculation (carried out in D_{2h} symmetry), 2 449 121 CSFs for the C_{2v} calculation (carried out in C_{2v} symmetry), and 4 831 192 CSFs for the C_{3v} calculation (carried out in C_s symmetry). In addition, the Davidson correction to the CISD energies was determined to account for the size-extensivity error of the truncated CI.[26] Finally, CCSD single-point energies for the O_h and C_{2v} structures were also obtained.[27,28]

RESULTS

Table II summarizes the geometrical parameters, as defined in Figs. 1–3, and total SCF energy for the three stationary points. The definitions of the geometric parameters given in the figures are based on those of the work by Klobukowski *et al.*[18] As is evident from the table, bond lengths and angles in the C_{3v} and C_{2v} structures diverge significantly from those of O_h structure. Such deviations are expected, based not only on the early models of Pitzer and Bernstein[13] and Wang and Lohr,[16] but also, on the more recent results of Klobukowski *et al.*[18] and Cutler *et al.*[19]

There are several quantitative deviations from the previous theoretical results in the geometric data. For example, Klobukowski *et al.* report the single geometric parameter for the O_h structure to be **r**=1.951 Å, while that reported in

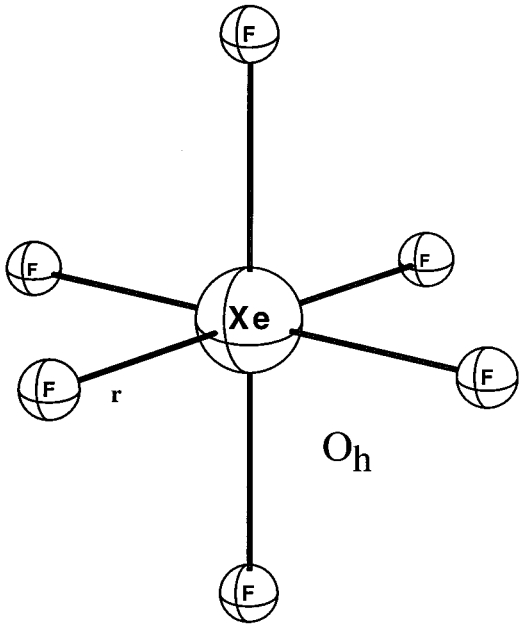

FIG. 1. Structural parameters for O_h symmetry.

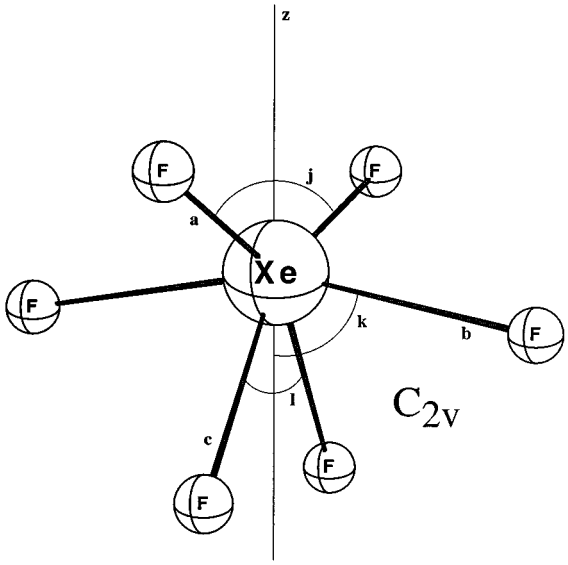

FIG. 2. Structural parameters for C_{2v} symmetry. In this figure, the two fluorines with bond length (a) and the two fluorines with bond length (c) lie in the $\sigma_v(xz)$ plane, while the two fluorines with bond length (b) lie in the $\sigma_v'(yz)$ plane. The C_2 axis coincides with the z axis shown.

Table II is much shorter, namely, $\mathbf{r}=1.902$ Å. The average difference between the bond lengths reported here and those reported by Klobukowski *et al.* is 0.056 Å. Agreement among the reported bond angles is excellent. The differences in bond lengths are most likely due to the significantly smaller basis set used in the previous work, as well as to the fact that analytic gradients were converged to only 10^{-3}. See the previous section for a complete description of the basis set and convergence criteria used in this work.

Table III summarizes the total and relative energies for the three stationary points for the MP2, CISD, and CISD+Q levels of theory. The SCF relative energies reported here are much larger than those reported previously. Klobukowski *et al.* report that the C_{2v} structure lies 23.0 kcal/mol lower in energy than the O_h structure, and that the C_{3v} structure is only 1.0 kcal/mol lower than the C_{2v} structure. While this works agrees with the ordering of these relative energies, we report that the difference between the O_h and C_{2v} structures has increased to 42.8 kcal/mol, and that of the C_{3v} and C_{2v} structures to 3.5 kcal/mol. These discrepancies are also explained by differences in basis set and convergence criteria.

In addition, we report MP2, CISD, and CISD+Q single-point energies determined at each of the three SCF optimized geometries. The relative energies of the three structures including the MP2, CISD, and CISD+Q corrections are included in Table III. Surprisingly, the MP2 results alter the order of the structures, most notably by shifting the O_h structure 4 kcal/mol lower than the C_{3v} structure. The ordering of the C_{3v} and C_{2v} structures relative to each other is unchanged, though the energy separation is reduced by 2.1 kcal/mol. On the other hand, the CISD and CISD+Q energies correct this shift, placing the C_{2v} structure 28.0 and 20.9 kcal/mol, respectively, below the O_h structure, and the C_{3v} structure 2.4 and 1.9 kcal/mol, respectively, below the C_{2v}. For the O_h and C_{2v} structures, CCSD single-point energies were found to be -7829.7205 and -7829.7420 hartree, respectively. This gives an energy difference of 13.5 kcal/mol between the two symmetries, in qualitative agreement with the CISD and CISD+Q results. It is our opinion that in this case, the MP2 single-point energies alone are not sufficient to draw definitive conclusions about the effect of correlation energy on the geometry and energetics of the XeF_6 system, and that the CISD, CISD+Q, and CCSD energies present a more reliable picture of the relative energetic ordering of these three structures. However, it is clear that correlation is most important for the octahedral structure. While the Davidson correction is inaccurate for systems with large numbers

TABLE III. Total energies (hartrees) and relative energies (kcal/mol) as determined at the SCF, MP2, CISD, and CISD+Q levels of theory at the SCF optimized geometries.

	Total energy				Relative energy			
Structure	SCF	MP2	CISD	CISD+Q	SCF	MP2	CISD	CISD+Q
O_h	−7828.1061	−7830.3058	−7829.3779	−7829.5996	0.0	0.0	0.0	0.0
C_{2v}	−7828.1743	−7830.2960	−7829.4226	−7829.6329	−42.8	+6.1	−28.0	−20.9
C_{3v}	−7828.1799	−7830.2983	−7829.4264	−7829.6360	−46.3	+4.7	−30.4	−22.8

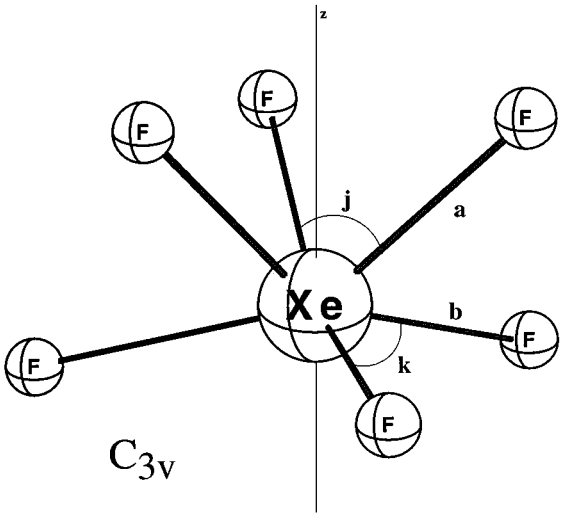

FIG. 3. Structural parameters for C_{3v} symmetry. In this figure, the three fluorines with bond length (a) lie above the xy plane, and those with bond length (b) lie below the xy plane. The C_3 axis coincides with the z axis shown.

TABLE IV. Harmonic vibrational frequencies (in cm^{-1}) for XeF_6 in O_h, C_{2v}, and C_{3v} symmetries determined at the SCF level of theory. Infrared intensities for the C_{3v} minimum are shown in parentheses (in km/mol) beside the associated vibrational frequency.

O_h		C_{2v}		C_{3v}	
Mode	Frequency	Mode	Frequency	Mode	Frequency
a_{1g}	699	a_1	786	a_1	798(82)
e_g	560	b_1	732	e	759(165)
		b_2	729		
t_{1u}	558	a_1	690	a_1	617(20)
		a_1	592	e	547(271)
		a_1	528		
t_{2g}	212	b_1	501	e	479(29)
		b_1	447		
		b_2	439	a_1	449(47)
t_{2u}	150	a_1	365	a_2	353(0)
		a_2	361	e	342(0)
		a_1	236		
t_{1u}	$342i$	b_1	212	a_1	324(46)
		a_2	88	e	46(0)
		b_2	$132i$		

of electrons, the CISD+Q and CCSD energies reported here suggest that the size-extensivity error does not alter the relative ordering of the three structures.

Table IV summarizes the calculated harmonic vibrational frequencies for all three structures at the SCF level of theory, including assignment of each to the appropriate irreducible representation. To our knowledge, this is the first report of theoretically determined harmonic vibrational frequencies for this molecular system. In addition, Table IV includes the theoretical infrared intensities (in km/mol) for the C_{3v} structure.

Of particular interest in Table IV are the imaginary t_{1u} bending mode for the O_h structure and the imaginary b_2 bending mode for the C_{2v} structure. Each of these modes were followed, and each led to the C_{3v} structure, thus interconnecting this small region of the potential energy surface for XeF_6. It is very important to note here, that the C_{2v} structure is not predicted to be a minimum at this level of theory, contrary to statements in the literature.[18,19]

Group theoretical analysis determines that all of the vibrational modes for the C_{3v} structure are both Raman and infrared active except for the single a_2 bending mode at 353 cm^{-1}, which is inactive in both. The calculated intensities provided in Table IV for the C_{3v} vibrational frequencies suggest that there should be perhaps five observable fundamental bands in the vibrational spectrum. Comparison of these results to the low-temperature matrix-isolation infrared and Raman spectra of Claassen, Goodman, and Kim[10] show fair agreement. Their spectra show five strong absorptions at 630, 624, 506, 302, and 252 cm^{-1} and five weaker absorptions at 557, 384, 365, 352, and 326 cm^{-1}. The infrared and Raman spectra show almost complete coincidence in the stretching region of 500–700 cm^{-1}. If the values presented in Table IV are scaled by a factor of 9% to account for electron correlation and anharmonicity, quantitative agreement with these experimental results is obtained for only three of the vibrational frequencies. In particular, the a_1 stretch at 617 cm^{-1} scales to 561 cm^{-1} and compares to the peak at 557 cm^{-1}; the e stretch at 547 cm^{-1} scales to 498 cm^{-1} and compares to the peak at 506 cm^{-1}; and the a_1 bend at 324 cm^{-1} scales to 294 cm^{-1} and compares to the peak at 302 cm^{-1}. None of the experimentally observed absorptions corresponds to the higher-frequency stretches at 798 and 759 cm^{-1} (726 and 691 cm^{-1} after reduction by 9%), both of which are predicted here to be of relatively high intensity. Pitzer and Bernstein[13] report an analysis and preliminary assignment of the matrix-isolation infrared and Raman spectra of Claassen, Goodman, and Kim[10] based on symmetry correlation of frequencies from an O_h structure to a C_{3v} structure. Their assignment predicts two a_1 stretches at 630 and 624 cm^{-1}, an a_1 bend at 302 cm^{-1}, two e stretches at 557 and 506 cm^{-1}, and an e bend at 252 cm^{-1}. Again, only three of these assignments correspond well to the frequencies presented in Table IV, namely, the a_1 stretch at 617 cm^{-1} (which Pitzer and Bernstein assign to an e stretching mode) the e stretch at 547 cm^{-1} and the a_1 bend at 324 cm^{-1}, as described above.

Electric dipole moments were also predicted for the three structures. The C_{3v} structure was determined to have a dipole moment of 0.46 D, twice that predicted by Klobukowski *et al.*,[18] but certainly within the range determined by Falconer *et al.* ($\approx$0.3 D)[5] and by Pitzer and Bernstein (0.1–0.6 D).[13] The dipole moment determined for the C_{2v} structure was 0.23 D, in agreement with that of Klobukowski *et al.* (0.22 D).[18]

CONCLUSIONS

We have presented geometric parameters, relative energies, dipole moments, and harmonic vibrational frequencies for three stationary points on the potential energy surface of XeF_6 as determined by *ab initio* SCF energy and analytic gradient calculations with a large basis. These results indicate that the C_{3v} structure is a minimum and that the O_h and C_{2v} structures are transition states with imaginary vibrational

frequencies leading to the C_{3v} structure. The geometric parameters and vibrational frequencies, as well as the electric dipole moment all agree well with past experimental results, though some disagreement is found with earlier theoretical reports. In addition, MP2, CISD, CISD+Q, and CCSD single-point energies have been presented. While the MP2 results alter the order of the relative energies, CISD, CISD+Q, and CCSD maintain them as compared to the SCF results.

Before any final conclusions may be drawn about this region of the XeF_6 potential energy surface, other effects should be included in the theoretical model. In particular, improved inclusion of electron correlation effects may have a significant influence on the calculated harmonic vibrational frequencies and relative energies. If experience is a guide, the MP2 method overestimates the effects of correlation, and the ultimate theoretical treatment will somewhat disfavor the octahedral structure with respect to MP2; the reported CISD, CISD+Q, and CCSD results support this prediction. Although the CISD+Q predictions are the most reliable to date, coupled-cluster [CCSD and CCSD(T)] methods will probably nudge $\Delta E(C_{3v}-O_h)$ to a lower absolute value. A reasonable estimate is that the C_{3v} structure lies below the O_h structure by about 5 kcal/mol. In addition, for a molecule containing a heavy atom such as Xe, relativistic effects will be very important in absolute terms, although probably not so for the relative energies of our three structures.

Note added in proof. Dr. Timothy J. Lee has informed the authors of new data resulting from his own CCSD and CCSD(T) calculations on the XeF_6 system. His calculations indicate that the CCSD energy for the C_{3v} structure is -7829.7445 hartree, that is, 15.1 kcal/mol lower than the O_h structure and 1.6 kcal/mol lower than the C_{2v} structure. In addition, the CCSD(T) energies for the O_h, C_{2v}, and C_{3v} structures were determined to be -7829.7808, -7829.7881, and -7829.7902 hartree, respectively. Thus, at this level of theory, the C_{3v} structure lies below the O_h structure by 5.9 kcal/mol and below the C_{2v} structure by 1.3 kcal/mol. These data completely support the authors' conclusions that the relative ordering of energies would be retained on greater inclusion of correlation effects. We gratefully acknowledge Dr. Lee's contribution to this work.

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