An *ab initio* study of the structure and vibrational spectra of allyl and 1,4-pentadienyl radicals

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MCSCF and MR-ACPF calculations on the structure and vibrational frequencies of allyl (2-propenyl) and 1,4-pentadienyl radicals are presented. Using different levels of theory the instability problem in allyl has been investigated in great detail. Based on these conclusions fully optimized structures and force constants were calculated at the three-orbital CAS-MCSCF and at the MR-ACPF level for allyl. To correct for systematic errors, an empirical scaling was also applied on the MCSCF force field. The scaled MCSCF and the unadjusted MR-ACPF force constants were used to calculate the vibrational frequencies. A reassignation of the experimental infrared spectrum is also given. Using the scale factors optimized for allyl the scaled MCSCF force field and vibrational frequencies of pentadienyl were also calculated.

I. INTRODUCTION

Conjugated π radicals form a special class of polyene compounds which have been investigated both theoretically and experimentally. Such conjugated π systems are of general importance not only in chemistry but also in solid state physics, where they are often used as model compounds for the investigation of the propagation of bond alternation defects along an otherwise unperturbed polyene chain (see e.g., Ref. 1). In this context too, detailed knowledge of the structure and vibrational spectra of these compounds is important, but very few experimental results are available, due to severe difficulties in the measurements. Thus, theoretical calculations play a special role in this field, although the latter are also complicated by the fact that conjugated π radicals, in particular the allyl (2-propenyl) radical, is subject to Hartree–Fock instabilities (see Refs. 2 to 11 and other references therein).

In the case of allyl the well known doublet instability of the restricted Hartree–Fock method has been studied in great detail by Paldus and Čížek[2-5] and an extensive survey of *ab initio* results has been given by Paldus and Veillard.[7] How to construct qualitatively correct wave functions for allyl has been shown by Kikuchi[10] on the basis of semiempirical MCSCF calculations. These results have been applied by Takada and Dupuis[11] in more detailed *ab initio* MCSCF/3-21G calculations. They concluded that a three-π-orbital/three-electron CAS wave function is suitable for the determination of the structure and vibrational frequencies of allyl. Very recently, Cometta–Moroni *et al.*[12] performed UMP2/6-31G* calculations on the structure and vibrational frequencies of allyl and compared them with UHF and MCSCF results. According to the model investigation of Čížek and Paldus[5] no Hartree–Fock instability exists for the 1,4-pentadienyl radical. To our knowledge, no *ab initio* investigations have been reported yet for checking the latter conclusion.

For allyl some experimental results are available, while no experimental investigation on the structure or the vibra-

tional frequencies of the 1,4-pentadienyl radical is known to us. The gas-phase molecular structure of allyl has been determined from high-temperature electron diffraction (ED) experiments by Vajda *et al.*[13] Their most striking result is that the measured r_g-type C–C bond distance is significantly longer than the bond length calculated previously by Takada and Dupuis at the MCSCF level.[11] The infrared spectrum of allyl has been measured in cryogenic matrices by Maier *et al*,[14] by Maltsev *et al.*[15] and very recently by Holzhauer and Oth.[16] No Raman study has been reported yet.

In this paper the geometry, force constants and vibrational spectra will be calculated for allyl and pentadienyl. Apart from some test calculations, basically two levels of theory will be applied: the MCSCF method and—to include dynamic electron correlation—a recent version of coupled pair theories, the averaged coupled pair functional (ACPF) method of Gdanitz and Ahlrichs.[17]

The MCSCF model is considered as a minimum to provide reasonable, semiquantitatively correct results for open-shell systems like the present radicals, while the ACPF results may come closer to the exact values. The latter high level calculations are, however, not feasible for larger systems. With this in mind, a combined theoretical-experimental approach will also be used: at the MCSCF level, empirical corrections ("scaling") will be applied on the force constants by fitting them through a few scale factors to the experimental frequencies. This is in the spirit of the scaled quantum mechanical (SQM) force fields which have been used with great success by Pulay and co-workers[18] on SCF results for closed-shell molecules. It is, of course, questionable but nevertheless of interest to investigate whether such a simple scheme to correct for deficiencies of the theoretical calculations is satisfactory in the present case. We will check this on allyl, for which both types of calculations will be applied, i.e., the ACPF force field will also be determined. For pentadienyl only the MCSCF calculations were carried out which were then scaled based on experience on allyl. In the light of the present results the available infrared spectro-

scopic data on allyl will be discussed and a predicted spectrum for pentadienyl will be given.

II. COMPUTATIONAL DETAILS

The COLUMBUS program system[19-21] together with the MCSCF program developed by Shepard[22] was used in all of our calculations. For the SCF calculations the open-shell restricted Hartree–Fock–Roothaan method was applied.[23] In order to eliminate the instability of the HF wave function the CAS-MCSCF method was used. The actual choice of the active orbitals is explained later. Based on the SCF and MCSCF wave functions single-reference (SR) and multireference (MR) CI calculations were performed where the CI space included all single and double excitations from the valence orbitals to all virtual orbitals, applying the interacting space restriction.[24] The MR-CI reference space contained all configurations defined by the CAS in C_{2v} symmetry for allyl and the six most important ones for pentadienyl. The latter were selected using a threshold of 0.05 for the coefficients of the MCSCF configurations. The size extensivity effects were treated by the ACPF method.[17] Geometry optimization was performed at several levels of theory. Both at the SCF and MCSCF levels analytic gradients and the GDIIS method of Császár and Pulay[25] were used for complete geometry optimizations. In the CI calculations pointwise geometry optimizations had to be carried out in an iterative fashion. In all calculations the MIDI3* basis of Huzinaga[26] was employed.

In the MCSCF calculations, the harmonic force constants were determined using analytic first derivatives and numerical second differentiation following the procedure proposed by Pulay *et al.*[27] The ACPF force field (calculated for allyl only) was obtained by purely numerical differentiation from energy points. In each case, force constants were evaluated around the equilibrium geometry of the respective theoretical level.

Both the geometry optimization and the force constants were treated in terms of internal coordinates. These were selected in accordance with the recommendation of Ref. 27, and for allyl they are defined in Table I. Geometries and
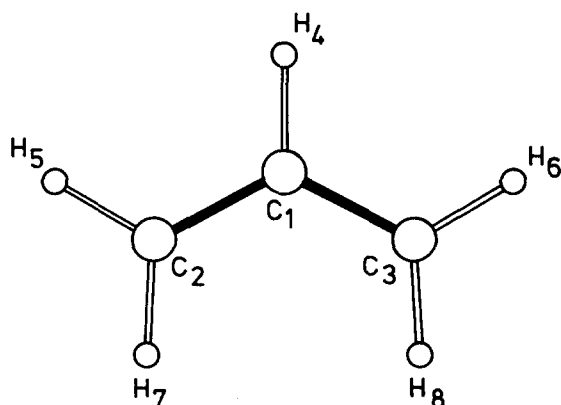
TABLE I. Definition of the internal coordinates for allyl.[a]

No.	Type	Definition[b]
1	C–C stretching	$r_{1,2}$
2	C–C stretching	$r_{1,3}$
3	C–H stretching	$r_{1,4}$
4	C–H stretching	$r_{2,5}$
5	C–H stretching	$r_{2,7}$
6	C–H stretching	$r_{3,6}$
7	C–H stretching	$r_{3,8}$
8	CCC bending	$\beta_{2,3,1}$
9	CH rocking	$\beta_{2,4,1} - \beta_{3,4,1}$
10	CH_2 scissoring	$2\beta_{5,7,2} - \beta_{1,5,2} - \beta_{1,7,2}$
11	CH_2 rocking	$\beta_{1,5,2} - \beta_{1,7,2}$
12	CH_2 scissoring	$2\beta_{6,8,3} - \beta_{1,6,3} - \beta_{1,8,3}$
13	CH_2 rocking	$\beta_{1,6,3} - \beta_{1,8,3}$
14	CH wagging	$\gamma_{4,2,3,1}$
15	CH_2 wagging	$\gamma_{1,6,8,3}$
16	CH_2 wagging	$\gamma_{1,5,7,2}$
17	CH_2 twisting	$\tau_{4,1,2,5} + \tau_{4,1,2,7} + \tau_{3,1,2,5} + \tau_{3,1,2,7}$
18	CH_2 twisting	$\tau_{4,1,3,6} + \tau_{4,1,3,8} + \tau_{2,1,3,6} + \tau_{2,1,3,8}$

[a] See Fig. 1 for the numbering scheme.
[b] r_{ij}: ij bond distance; $\beta_{i,j,k}$: angle between bonds ik and jk; $\gamma_{i,j,k,l}$: angle of bond il with plane jkl, positive if atom i is on the same side of the plane as the vector cross product $lj \times lk$; $\tau_{i,j,k,l}$: angle of planes ijk and jkl. Both torsional (τ) and out-of-plane (γ) coordinates are used as defined in E. B. Wilson Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw Hill, New York, 1955), p. 60. All composite coordinates were normalized, normalization constants are omitted.

atomic numbering schemes for allyl and 1,4-pentadienyl are defined in Figs. 1 and 2.

As noted in the introduction, an empirical scaling was applied on the MCSCF force fields. This was done following the standard scheme of Pulay *et al.*[18]: the internal coordinates are grouped according to their types and for each group a factor c_i is assigned. Diagonal constants are scaled by c_i, off-diagonal constants by $\sqrt{c_i c_j}$. The scale factors were optimized by fitting the calculated harmonic frequencies to the experimental ones. In addition to the standard scaling scheme we also used an extra scale factor for the CC/CC stretching coupling force constant (for more details see the Discussion).

Infrared intensities were calculated from theoretical, unadjusted dipole moment derivatives obtained numerically, with the form of normal vibrations taken from the scaled force field results. The determination of scale factors, scaled force fields and the calculation of vibrational frequencies and IR intensities were performed using the SCALE2 program of Pongor.[18]
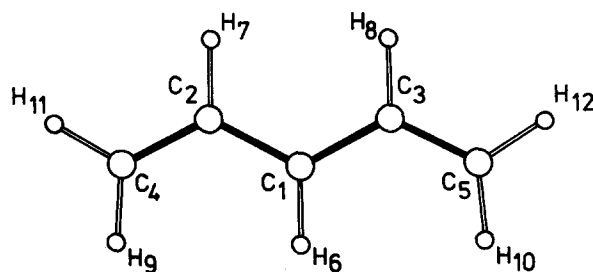

FIG. 1. Geometry and numbering scheme for the allyl radical.

FIG. 2. Geometry and numbering scheme for the pentadienyl radical.

III. RESULTS AND DISCUSSION

A. Geometries

1. Allyl radical

The doublet instability of the allyl radical has attracted considerable attention.[2-11] The analysis of this instability can be performed in at least two ways. First, for a fixed C_{2v} geometry the stability equation can be evaluated and symmetry breaking solutions can be discussed.[2-5,6,8] An alternative treatment is to remove some symmetry constraints and look for the optimized structures in a lower symmetry.[7,10] In the case of allyl, the symmetry broken solution is manifested by a 2-propenyl-type equilibrium structure at the SCF level with one C–C bond longer than the other. In order to obtain physically reasonable structural predictions (corresponding to C_{2v} symmetry) multideterminantal wave functions must be used.[10] As a minimum requirement MCSCF calculations have to be performed in a three-electron/three-orbital space.[10,11] To our knowledge no MR-CI calculations have been carried out so far for the allyl radical. In this section we intend to investigate the effect of a systematic extension of the orbital space for CAS-MCSCF wave function and to monitor the effect of CI depending on various choices of reference sets.

Based on chemical intuition and experience on other molecules with π electronic structure[28] we restricted the CAS treatment to the π space. The three-orbital CAS calculations included the conventional π and π^* orbitals (two b_1 and one a_2 orbitals referring to a C_{2v} molecular symmetry). To this set one a_2 orbital (four-orbital CAS), and in the next step a further b_1 orbital (five-orbital CAS) was added. Only planar structures were considered in this methodological part of our investigations. The optimized geometries resulting from our calculations are compiled in Table II.

The geometry optimization at the SCF level using the C_s symmetry restriction only resulted in the well known artificial splitting of the two C–C bond distances.[7,10] To a minor degree, splitting was also found for other geometry parameters which would be equivalent using the C_{2v} symmetry constraint. In agreement with Ref. 11, the three-orbital CAS-MCSCF calculation gives the C_{2v} structure as the lowest in energy. This was tested by starting the geometry optimization process with an appropriately distorted structure. Moreover, the complete force field has been calculated (see below), which shows no sign of instability. In the four-orbital case, however, a breaking of the symmetry can again be observed, although the effects are quite small. By adding a pair of orbitals (five-orbital CAS) one gets again the C_{2v} structure as the most stable one. Analyzing the Hamiltonian matrix we noted that the orbital excitations $1a_2 \rightarrow 2a_2$ and $1b_1 \rightarrow 3b_1$ are very close in energy, i.e., all configurations differing in these excitations only have almost the same diagonal matrix elements. Thus, in order to obtain a balanced description both orbitals ($2a_2$ and $3b_1$) have to be included in an extended CAS calculation. We also checked the six-orbital CAS (three b_1 and three a_2 orbitals, not shown in Table II) for which we suspected that symmetry breaking would again show up. The expected effects are very small, however. Hence it was difficult to decide whether the observed violation of C_{2v} symmetry was due to numerical errors arising from the geometry optimization procedure or a true instability was encountered. The geometries obtained with the three-orbital to six-orbital CAS-MCSCF calculations show very little variation. They also agree quite well

TABLE II. SCF and MCSCF geometries and total energies for allyl.[a]

| | SCF | | MCSCF | | | | |
| | | | Three-orb. | Four-orb. | | Five-orb. | Three-orb. (Ref. 11) |
	C_{2v}	C_s		C_{2v}	C_s		
C_1C_2	1.370	1.329	1.388	1.387	1.385	1.386	1.388
C_1C_3		1.435			1.389		
C_1H_4	1.087	1.087	1.087	1.087	1.087	1.087	1.075
C_2H_5	1.083	1.084	1.082	1.082	1.082	1.082	1.072
C_3H_6		1.081			1.082		
C_2H_7	1.084	1.086	1.084	1.084	1.085	1.085	1.073
C_3H_8		1.083			1.084		
$\angle C_2C_1C_3$	124.7	124.8	124.9	125.0	125.0	125.0	124.4
$\angle H_4C_1C_2$	(117.7)	118.6	(117.5)	(117.5)	117.6	(117.5)	
$\angle H_4C_1C_3$		(116.5)			(117.5)		
$\angle H_5C_2C_1$	121.7	121.7	121.4	121.4	121.5	121.5	121.4
$\angle H_6C_3C_1$		121.3			121.5		
$\angle H_5C_2C_7$	(117.2)	116.7	(117.4)	(117.4)	117.3	(117.3)	
$\angle H_6C_3H_8$		118.1			117.4		
$\angle H_7C_2C_1$	121.1	121.6	121.2	121.2	121.2	121.2	121.2
$\angle H_8C_3C_1$		120.6			121.2		
E^b	-0.23807	-0.24101	-0.27796	-0.27923	-0.27959	-0.28126	

[a] Bond distances in Å, bond angles in degree. For numbering scheme of atoms see Fig. 1; redundant parameters are in parentheses.
[b] Total energy + 116 hartree.

TABLE III. Variation of the CC bond distance with several CI approaches for allyl.[a]

Orb. basis	SR-CI (SCF/C_{2v})	SR-CI (SCF/C_s)	SR-CI (MCSCF/3)[b]	MR-CI (MCSCF/3)	SR-ACPF (MCSCF/3)	MR-ACPF (MCSCF/3)
CC	1.381	1.376	1.380	1.390	1.394	1.395
E[c]	− 0.600 64	− 0.600 15	− 0.600 51	− 0.616 08	− 0.652 83	− 0.656 03

[a] Bond distances in Å.
[b] Three-orbital/three-electron CAS.
[c] Total energy + 116 hartree.

with the MCSCF results of Takada and Dupuis[11] using the 3-21G basis set (see last column of Table II). The fact that their CH distances are significantly shorter is due to the absence of d functions on the carbon atoms.

Although the stability problem can be already resolved at the MCSCF level, it is still of interest to perform CI calculations because it is not completely clear how large the effect of dynamic correlation is. Also, having larger systems in mind, it may turn out to be cheaper to perform SR-CI instead of CAS-MCSCF calculations. The results of various alternatives are collected in Table III. Since we regarded these calculations as informative tests, we were not interested in complete geometry optimizations. Instead, we used the geometries from the calculations with the respective reference sets (SCF or MCSCF) and reoptimized solely the C–C bond distance under C_{2v} symmetry constraint. Afterwards, we checked whether the antisymmetric C–C stretching motion ($R_{C_1C_2}-R_{C_1C_3}$) leads to an energy lowering. In all cases the C_{2v} structure remained stable with respect to this distortion. This is of particular significance in the case where symmetry-broken orbitals were chosen as a starting point (second column of Table III): again a C_{2v} structure and a reasonable C–C bond distance results from the CI calculation.

Since MR-CI calculations are much more expensive than SR-CI calculations we investigated yet another approach as an alternative to SCF-CI. The basic purpose of doing a three-orbital CAS MCSCF calculation is to resolve the instability problem. In this wave function the $...b_1^2 a_2$ configuration is dominating, the same way as in the SCF-CI case. Thus, we used it as reference configuration in an alter-

native SR-CI approach. These results are shown in the third column of Table III. Compared to the SCF-CI result (first column of Table III) one arrives at a practically identical bond length. The remaining entries in Table III show the results of MR-CI and SR- and MR-ACPF calculations. The computed C–C bond distance is now elongated by about 0.01 Å. This is the well-known effect of size-extensivity corrections stemming from higher excitations in the wave function.

For comparison with experiment we have also performed a complete geometry optimization at the highest level of theory presented here, the three-orbital CAS-MCSCF/MR-ACPF approach. The calculated structural results are compared with the electron diffraction data of Vajda *et al.*[13] in Table IV (for a better overview, the MCSCF values are also repeated here). The C–C bond distance we obtained at this level ($r_e = 1.395$ Å) is not significantly different from our own MCSCF result ($r_e = 1.388$ Å). However it is still shorter than the experimental result of $r_g = 1.428(10)$ Å. Naturally, there is a fundamental difference between r_e and r_g structures, the latter containing vibrational effects (depending on a rather ill-defined temperature in Ref. 13). Still, even if we consider the uncertainties in the theoretical treatment (specifically, a relatively small basis set), the discrepancy is disturbingly large. Thus we feel that—besides eventual calculations with larger basis sets on the theoretical part—the experimental result is also in doubt and a thorough reinvestigation would be justified.

TABLE IV. MCSCF (three-orbital CAS) and MR − ACPF optimized geometries of allyl.[a]

	MCSCF	MR-ACPF	ED exp. (Ref. 13)
C_1C_2	1.388	1.395	1.428
C_1H_4	1.087	1.103	1.069
C_2H_5	1.082	1.098	1.069
C_2H_7	1.084	1.101	1.069
$\angle C_2C_1C_3$	124.9	124.5	124.6
$\angle H_5C_2C_1$	121.4	121.6	120.9
$\angle H_7C_2C_1$	121.2	120.9	120.9
E[b]	− 0.277 96	− 0.657 79	

[a] Bond distances in Å, bond angles in degree. For numbering scheme of atoms see Fig. 1.
[b] Total energy + 116 hartree.

TABLE V. MCSCF(five-orbital CAS) and MR-ACPF optimized geometries of pentadienyl.[a]

	SCF	MCSCF	MR-ACPF
C_1C_2	1.408	1.420	1.419
C_2C_4	1.342	1.364	1.371
C_1H_6	1.085	1.086	1.102[b]
C_2H_7	1.087	1.087	1.103[b]
C_4H_9	1.085	1.085	1.101[b]
C_4H_{11}	1.083	1.083	1.099[b]
$\angle C_2C_1C_3$	124.4	124.0	124.0[b]
$\angle C_1C_2C_4$	124.5	124.8	124.8[b]
$\angle H_7C_2C_1$	117.1	116.9	116.9[b]
$\angle H_9C_2C_4$	121.4	121.5	121.5[b]
$\angle H_{11}C_2C_4$	121.7	121.5	121.5[b]
E[c]	− 0.002 59	− 0.069 69	− 0.686 06

[a] Bond distances in Å, bond angle in degree. For numbering scheme of atoms see Fig. 2.
[b] Corrected MCSCF value, see the text.
[c] Total energy + 193 hartree.

The calculated C–C bond length of the allyl radical lies between the length of the single and double bonds of butadiene (1.459 and 1.339 Å, obtained at a similar level of theory[28]). The CCC bond angle ($\sim 125°$) is typical for molecules with π electronic structure (e.g., $\sim 124°$ in butadiene and hexatriene[29]).

2. 1,4-Pentadienyl radical

According to the analysis of Čížek and Paldus,[5] a doublet instability does not exist for the pentadienyl radical. Extensive *ab initio* test calculations in connection with the treatment of longer polyene radicals[30] showed that symmetry breaking effects are indeed absent in the pentadienyl case. Thus, the situation here is much simpler and, as a great advantage, the SCF method should be applicable in a straightforward manner. Therefore, C_{2v} symmetry was assumed for the minimum energy structure in the subsequent calculations.

Three methods have been employed for the geometry optimization of pentadienyl: complete optimization was performed at the SCF and the five-orbital (three b_1 and two a_2) CAS-MCSCF level and, in addition, the C–C bond lengths were reoptimized using the MR-ACPF method. In this latter case the other parameters were held constant at corrected MCSCF values. The corrections were determined by comparing the MCSCF (three-orbital) and MR-ACPF results for allyl (Table IV). This gave an offset value of $+0.016$ Å for the C–H bond lengths while no correction was necessary for the bond angles. The resulting equilibrium geometries are compiled in Table V.

The central C–C bonds of pentadienyl (1.420 and 1.419 Å from MCSCF and MR-ACPF, respectively) are longer by about 0.03 Å than the corresponding bonds of allyl (1.388

and 1.395 Å, respectively). The terminal C–C bond lengths (1.364 from MCSCF and 1.371 Å from MR-ACPF calculation) are definitely shorter than even the allyl bond. They are, however, significantly longer than the bond in ethylene (1.31 Å) or butadiene (1.32 Å) using a comparable basis set and the CPF method.[29] All this is in accordance with qualitative expectations: in terms of resonance structures, pentadienyl has an extra covalent structure—in addition to the allyl type structures—in which the unpaired electron is on the central CH group, giving simultaneously single bonds in the center and double bonds on both terminal CC bonds. As compared to the allyl radical, the effect of including dynamic correlation is smaller on the central bond (0.001 vs 0.007 Å), while for the double bond it is again 0.007 Å. The latter difference is comparable to that found in butadiene (0.01 Å).[28] The variations of the C–H bond distances from allyl to pentadienyl are very small. The CCC bond angles are close to those in the allyl radical.

B. Force fields

1. Allyl radical

We have calculated the complete force field of allyl by means of the MCSCF method. With the higher level MR-ACPF calculations some compromise had to be done because—having no analytical gradients—the complete pointwise calculation would have been too expensive. Therefore, we calculated the dominant terms of the force field only, namely all diagonal force constants and those of the coupling constants which were large enough to contribute significantly to the vibrational frequencies. The latter were selected as follows: $F_{1,2}$ (CC stretch/CC stretch), $F_{1,8}$ (CC stretch/CCC bend), $F_{1,9}$ (CC stretch/CH rock) and $F_{1,10}$ (CC stretch/CH_2 scissor) (see also the definition of internal

TABLE VI. MCSCF and MR-ACPF force constants of allyl.[a]

i,j	$F_{i,j}$ MCSCF[b]	$F_{i,j}$ MR-ACPF	i,j	$F_{i,j}$ MCSCF[b]	$F_{i,j}$ MR-ACPF	i,j	$F_{i,j}$ MCSCF[b]	$F_{i,j}$ MR-ACPF
1,1	6.407	6.500	4,5	0.033	0.037[c]	8,11	-0.105	-0.122[c]
1,2	1.530	1.390	4,6	0.004	0.004[c]	9,9	0.530	0.559
1,3	0.081	0.087[c]	4,7	-0.001	-0.002[c]	9,10	-0.017	-0.020[c]
1,4	0.050	0.054[c]	4,8	0.056	0.063[c]	9,11	0.049	0.058[c]
1,5	0.078	0.084[c]	4,9	-0.007	-0.008[c]	10,10	0.443	0.457
1,6	-0.010	-0.011[c]	4,10	0.056	0.065[c]	10,12	0.005	0.006[c]
1,7	-0.011	-0.012[c]	4,11	-0.087	-0.101[c]	10,13	-0.006	-0.007[c]
1,8	0.213	0.216	4,12	-0.002	-0.003[c]	11,11	0.505	0.540
1,9	0.177	0.188	4,13	0.010	0.012[c]	11,13	-0.011	-0.013[c]
1,10	-0.186	-0.197	5,5	5.147	5.250		out-of-plane	
1,11	-0.012	-0.013[c]	5,6	-0.001	-0.002[c]	14,14	0.284	0.284
1,12	-0.021	-0.023[c]	5,7	0.009	0.011[c]	14,15	-0.045	-0.030
1,13	0.058	0.063[c]	5,8	-0.054	-0.061[c]	14,17	0.003	0.003
3,3	5.022	5.120	5,9	0.032	0.037[c]	15,15	0.187	0.159
3,4	0.018	0.020[c]	5,10	0.055	0.064[c]	15,16	-0.004	0.000
3,5	-0.002	-0.002[c]	5,11	0.093	0.108[c]	15,17	0.007	0.002
3,8	-0.147	-0.168[c]	5,12	-0.006	-0.007[c]	15,18	0.009	0.007
3,10	-0.012	-0.014[c]	5,13	-0.003	-0.004[c]	17,17	0.068	0.079
3,11	0.039	0.045[c]	8,8	1.075	1.118	17,18	0.000	-0.001
4,4	5.215	5.330	8,10	-0.013	-0.016[c]			

[a] Force constants are given in aJ Å^{-2} for stretch–stretch, aJ Å^{-1} rad^{-1} for stretch-bend, and aJ rad^{-2} for bend–bend couplings. See Table I for definition of coordinates. Only the independent and nonzero values are given.
[b] Scaled force constants. See Table VII for the scaling factors.
[c] The unscaled MCSCF value is taken (see the text).

TABLE VII. Scale factors for MCSCF force constants optimized for the MCSCF force field of allyl.

Type	Value
CC stretchings	0.99
CH stretchings	0.88
CCC bending	0.88
Bendings involving hydrogen	0.85
CC,CC coupling	0.82[a]
CH wagging	1.00[b]
CH_2 wagging	1.45
CH_2 twisting	0.78

[a] The coupling constants are independently scaled (see the text).
[b] Not optimized (see the text).

coordinates in Table I). Except for the coupling between the two CC stretches we did not find any significant effect of the dynamic correlation on the coupling force constants. So the use of the MCSCF values for the remaining in-plane coupling force constants instead of the MR-ACPF values has a negligible influence on the calculated vibrational frequencies. On the other hand, we have computed the complete MR-ACPF out-of-plane force field because of the problems to be discussed below.

In Table VI the complete harmonic force field of allyl is given. The MCSCF values are those obtained after empirical scaling (see below), from which the original theoretical results can simply be recalculated with the scale factors listed in Table VII. First we compare the unadjusted theoretical MCSCF and MR-ACPF results in order to investigate the influence of dynamic correlation. For the following discussion it should be realized that in "normal" closed-shell systems simple SCF calculations systematically overestimate the force constants, so that the inclusion of electron correlation lowers their values. Basically, we expect similar trends in the present case between the two levels of theory, but—as we will see—the situation is less clear-cut.

Particularly interesting are the CC stretching force constants. The diagonal MCSCF force constant before scaling is 6.44 aJ $Å^{-2}$ and it changes insignificantly in the MR-ACPF force field (6.50 aJ $Å^{-2}$). In contrast, the coupling between the two CC stretchings becomes considerably smaller: its (unscaled) MCSCF value is 1.86 aJ $Å^{-2}$, while the MR-ACPF result is 1.39 aJ $Å^{-2}$. The same effect, a significant overestimation of the CC/CC coupling constants was found in the case of the SCF force field of benzene.[31] On the other hand, the inclusion of dynamic correlation causes an increase in the CC stretching couplings in butadiene and hexatriene.[29] It seems that dynamic correlation has a negative effect if we have a single-minimum potential (CC bond lengths are the same) and a positive effect for alternating bonds where in the limiting case we have a double minimum potential.

For the remaining in-plane diagonal force constants we find a rather uniform decrease of about 10%–15% when going from the MCSCF to the MR-ACPF results. Those of the off-diagonal force constants which have been calculated at the MR-ACPF level show changes of a few percent only.

The changes in the out-of-plane force constants are less

systematic. The diagonal CH wagging force constant ($F_{14,14}$) does not change (0.284 aJ rad^{-2}), the CH_2 twist force constant ($F_{17,17}$) is reduced from 0.087 (unscaled MCSCF) to 0.079 aJ rad^{-2} (MR-ACPF). For the CH_2 wagging force constant, $F_{15,15}$ the unscaled MCSCF value is 0.129 aJ rad^{-2} which increased, rather than decreased, after including correlation (MR-ACPF value: 0.159 aJ-rad^{-2}). Thus, contrary to the usual overestimation, the MCSCF result underestimates this force constant. As will be shown in Sec. III C 1 the increase of the CH_2 wagging force constant as obtained by the MR-ACPF method is still not large enough in order to give completely satisfactory agreement of calculated and experimental frequencies. One possible source of error is a deficiency in the basis set. From our experience with calculations on excited states of butadiene[28] we suspected that especially *p* functions on carbon at the lower end of the series of exponents of the MIDI3 basis (and also of similar basis sets) could have a significant influence. MCSCF test calculations in which the MIDI3* basis was augmented by *p* functions with exponents of 0.07 showed the expected effect: the diagonal CH_2 wagging force constant increased from 0.129 aJ rad^{-2} to 0.156 aJ rad^{-2}. Calculations with even more diffuse functions (exponents 0.02) did not have any influence on the force constant worth mentioning. More detailed investigations with even much larger basis sets (second *d* set, *p* functions on the hydrogen atoms, etc.) would be desirable, go, however, far beyond the scope of our present investigations. Moreover, as will be seen in Sec. IV C 1 the assignment of the calculated IR active wagging frequency to the experimental one does not pose any problem at all because of the large intensity of that mode. Additionally, the empirical scaling (see below) reasonably corrected for the basis set errors. Therefore, we renounced in further extensions of the basis and kept the MIDI3* basis.

As indicated in the introduction, from a pragmatic point of view a reasonable approach to obtain reliable force fields is to use lower level (less expensive) calculations and combine them with the experimental information. This is the philosophy of the method of SQM force fields,[18] which have proven very successful in SCF calculations of closed-shell molecules. In this spirit, we have also determined a scaled MCSCF force field for allyl by fitting the direct theoretical force constants to the experimental frequencies through a few scale factors. Most of the frequencies were taken from the matrix infrared work of Holtzhauer and Oth.[16] However, some frequencies were reassigned by us based on the theoretical MR-ACPF results (see below). For some vibrational modes no experimental frequencies were available. Here we have replaced them by the MR-ACPF frequencies (see Sec. III C). For the in-plane coordinates we used four scale factors assigned to the various types of coordinates.[18] Deviating from the standard scheme, we also introduced a separate scale factor for the CC/CC stretching coupling $F_{1,2}$. This extra scaling has turned out to be necessary for molecules with conjugated π system.[29,31,32] For the out-of-plane coordinates the optimization of the scale factors was not straightforward: there are only three measured frequencies of b_1 symmetry, while the a_2 modes are IR inactive. Additionally, there is a large kinetic coupling between the

CH wagging and CH_2 twisting coordinates. These two facts make the optimization ill-conditioned. As a compromise, we made use of the fact that the CH wagging force constant is practically the same at the MCSCF and MR-ACPF levels and that the corresponding MR-ACPF frequency agrees well with experiment (see below). Thus, we fixed the CH wagging scale factor at 1.00 and optimized the remaining two factors. All scale factors used in this empirical adjustment of the MCSCF force field are listed in Table VII.

We consider the scaled MCSCF and the purely theoretical MR-ACPF force fields, given in Table VI, as roughly equivalent in quality. They are very similar to each other and—as we will see—give frequencies in good agreement with experiment. The differences in the scaled MCSCF and the MR-ACPF results are an indication of the residual uncertainties in the present determination of the force field of allyl.

At this point, it is of interest to compare allyl with some analogous (although closed-shell) molecules. In the following a comparison will be made with the scaled force fields of butadiene and hexatriene obtained by the CPF method using double zeta basis sets with polarization functions[29] and with the scaled SCF force field of benzene[31] using the smaller 4-21 basis set. The CC diagonal stretching force constant of allyl is 6.4–6.5 aJ $Å^{-2}$ (Table VI). This is between the values typical for a double bond (8.4 aJ $Å^{-2}$ in butadiene and 8.3–8.1 aJ $Å^{-2}$ in hexatriene) and a single bond (5.0 aJ $Å^{-2}$ in both butadiene and hexatriene[29]). The force constant thus clearly shows (as well as the bond length discussed above) that the CC bond is between a single and a double bond due to a strong delocalization of the unpaired electron. In fact, allyl is fairly close to benzene in which the CC stretching force constant is 6.5–6.6 aJ $Å^{-2}$.[31]

Especially interesting is the extremely high value found for the CC/CC coupling ($F_{1,2}$). Based on the scaled MCSCF and the MR-ACPF results of Table VI, the final estimate may be 1.4–1.5 aJ $Å^{-2}$. This is much higher than any of its counterparts in related molecules. We have found a value of 0.4 aJ $Å^{-2}$ for the $C=C/C-C$ couplings in butadiene and hexatriene,[29] and even in benzene this force constant is only 0.6–0.7 aJ $Å^{-2}$.[31,33]

The various CH stretching force constants are in the range 5.02 to 5.21 aJ $Å^{-2}$ (MC-SCF) and 5.12 to 5.33 aJ $Å^{-2}$ (MR-ACPF). They are close to their counterparts in butadiene or in hexatriene and are in line with the trend in the corresponding bond lengths. All bending force constants of allyl show also close analogy with those in hexatriene and butadiene.

As concerns the out-of-plane force field the CH wagging force constant (0.28 aJ rad^{-2}) is similar to those in related molecules: in butadiene it is 0.25 aJ rad^{-2},[18] in hexatriene 0.24–0.26 aJ rad^{-2}.[32] The CH_2 wagging—taking the range for it as 0.19–0.16 aJ rad^{-2}—is much lower than in any comparable system, e.g., 0.24 aJ rad^{-2} in both butadiene[18] and hexatriene.[32] The value of 0.07 to 0.08 aJ rad^{-2} for $F_{17,17}$ is reasonable for a torsion around a CC bond of partial double bond character: in hexatriene, for example,the torsion around the formally single bond has a force constant of $\sim$0.03, while that around the double bond is 0.12 aJ rad^{-2}.[32]

2. 1,4-Pentadienyl radical

For pentadienyl only the MCSCF force field was calculated which was then scaled by the scale factors taken over from allyl. Thus, the final scaled force field is a pure *a priori*

TABLE VIII. Comparison of the vibrational frequencies of allyl calculated by different methods.[a]

		MCSCF		MR-ACPF	UMP2 (Ref. 12)	
		unscaled	scaled		unscaled	scaled
in-plane						
A_1	ν_1	3324	3115	3146	3333	3113
	ν_2	3239	3035	3066	3222	3016
	ν_3	3220	3017	3045	3246	3028
	ν_4	1610	1490	1491	1595	1480
	ν_5	1328	1251	1269	1301	1255
	ν_6	1077	1022	1035	1048	1005
	ν_7	447	417	418	437	452
B_2	ν_8	3320	3111	3142	3329	3109
	ν_9	3226	3024	3055	3238	3021
	ν_{10}	1583	1480	1498	1579	1465
	ν_{11}	1497	1389	1400	1444	1385
	ν_{12}	1180	1183	1206	1230	1179
	ν_{13}	980	903	913	918	886
out-of-plane						
A_2	ν_{14}	670	803	738	801	773
	ν_{15}	581	517	547	595	624
B_1	ν_{16}	1020	969	985	1123	1088
	ν_{17}	677	805	751	823	794
	ν_{18}	550	519	524	557	584

[a] Frequencies in cm^{-1}.

prediction for pentadienyl. Concerning details of the scaling the following remarks are in order: the extra scale factor introduced for the CC/CC stretching coupling in allyl was used here for the central CC bonds, while no extra scaling was applied on the other CC/CC couplings. Application of the extra scale factor for the latter would be questionable because, as we have seen above, even the direction of the correction depends on the type of bonds involved in the coupling. This somewhat arbitrary choice introduces a slight inaccuracy in the in-plane force field whose effect on the vibrational frequencies will be tested in the next section. In the case of the out-of-plane force field the unusual behavior of the CH_2 wagging in allyl discussed above makes the transferability of scale factors less reliable.

In order to save space, we have not compiled the complete force field of pentadienyl. Only the most interesting force constants will be discussed in the following. We compare the force field of pentadienyl with allyl, quoting the scaled MCSCF results. Note that, the scaling being the same for both radicals, this does not influence the relative values. Hence the same conclusions hold for the original, direct theoretical results (except for some insignificant effects on the various CC/CC couplings whose scaling was not exactly uniform).

The CC stretching force constant of allyl (6.41 aJ Å^{-2}) splits into two different force constants in pentadienyl, corresponding to the two different CC bonds (5.64 aJ Å^{-2} for C_1C_2 and 7.66 aJ Å^{-2} for C_2C_4; see Fig. 2 for numbering). This is in agreement with the trends in bond lengths showing that the inner bond in pentadienyl is much weaker than in allyl. The most interesting finding is that also the coupling between the innermost CC stretchings in pentadienyl (0.67 aJ Å^{-2}) is less than half of its counterpart in allyl (1.53 aJ Å^{-2}). On the other hand the coupling between adjacent inner and terminal CC stretchings (C_1C_2/C_2C_4) is 1.49 aJ Å^{-2}, almost as large as in allyl. This is a sign that the "allyl-like" part of pentadienyl is not the central one. The large extent of conjugation in the whole carbon backbone is shown by the large values of the other CC/CC couplings ($C_4C_2/C_1C_3 = -0.51$ aJ Å^{-2}, $C_4C_2/C_3C_5 = 0.43$ aJ Å^{-2}). The alternation of signs and even the magnitudes resemble benzene fairly closely.[31,33] The CH stretching force constants are in the range $5.02 - 5.20$ aJ Å^{-2}, practically the same as in allyl. Both kinds of CCC bending force constants are equal to the CCC bending force constant of allyl (~ 1.07 aJ rad^{-2}). The same is true for the CH bending, CH_2 rocking and scissoring diagonal force constants and also for the coupling force constants, except those of the CC stretchings discussed above.

Let us now turn to the out-of-plane force field. In allyl the CH wagging force constant was calculated to be 0.28 aJ rad^{-2}. In pentadienyl we have, of course, two types of CH waggings, those in the vinyl groupings (on atoms C_2 and C_3), and the central one on C_1. For these, the force constants are 0.28 and 0.19 aJ rad^{-2}, respectively. It is thus the vinyl CH wagging, rather than the central one which is close to (practically identical with) allyl. This fact confirms the concept that the terminal part of pentadienyl is the allyl-like structure. In pentadienyl the CH_2 wagging force constant is

still low (0.17 aJ rad^{-2}), but significantly larger than in allyl (0.13 aJ rad^{-2}). The transferability of the scale factor seems rather uncertain here. Accepting it for pentadienyl, the scaled force constant is 0.25 aJ rad^{-2}. This is a quite realistic value, close to the corresponding force constants in butadiene (0.24 aJ rad^{-2})[18] or hexatriene (0.25 aJ-rad^{-2}).[32] The twisting (torsional) force constants show good correspondence with the bond lengths (bond strengths): the torsion around the terminal CC bond has a force constant of 0.089 aJ rad^{-2}, that around the inner CC bond is 0.048 aJ rad^{-2}. As compared to allyl (0.068 aJ-rad^{-2}), they are thus split corresponding to the bond strengths (see stretching force constants above), the stronger bond leading to a higher torsional force constant.

C. Vibrational frequencies

1. Allyl radical

In C_{2v} symmetry the 18 vibrational fundamentals of allyl are distributed as $7a_1 + 6b_2 + 3b_1 + 2a_2$, the first two species representing the in-plane modes and the other two species the out-of-plane modes. According to the selection rules the a_1, b_2 and b_1 vibrations are IR active, while the a_2 species would only be active in the Raman spectrum which has not been measured. The matrix IR spectrum of the allyl radical has been studied by three groups.[14-16] Our discussion will be based on the two more complete investigations by Holtzhauer and Oth[16] and Maltsev *et al.*[15]

We have calculated three lists of vibrational frequencies according to the three sets of calculated force constants as discussed above, namely unscaled and scaled MCSCF, and MR-ACPF. In the comparison the unscaled and scaled UMP2 results of Cometta–Moroni *et al.*[12] will also be included. Note that Cometta–Moroni *et al.* calculated only the diagonal force constants at the UMP2 level, while the off-diagonal ones were those determined from the UHF calculation. All these results are compiled in Table VIII while our MR-ACPF results are compared with experiment in Table IX. We compare first the direct, unadjusted results at these three levels of theory.

We start our discussion with the in-plane frequencies. Evidently, the general trends follow from the trends observed in the force constants: inclusion of electron correlation systematically lowers the frequencies. Definitely overestimated numbers are seen in the MCSCF results, while the MR-ACPF frequencies are typically 5%–6% lower and, as we will see, approximate the experimental results. Due to the different couplings in the two sets, the frequency lowering is, of course, not a strict rule, and one of the frequencies, v_{12} in species b_2, which is sensitive to the CC/CC coupling, has increased slightly in the MR-ACPF results. Partial inclusion of electron correlation in the UMP2 calculation gives frequencies roughly in between the MCSCF and MR-ACPF results. Notable is again v_{12} which is here even higher than its MR-ACPF value, here too, this is probably related with the difference in the CC/CC coupling but we cannot check this explicitly because force constants are not given in Ref. 12.

The largest discrepancies in the out-of-plane force field

are found mainly for the frequencies ν_{14} and ν_{17} which are dominated by the (antisymmetric and symmetric) CH_2 waggings. As a result of the underestimated wagging force constant (the coupling is negligible), these frequencies are far too low in the unscaled MCSCF results; inclusion of electron correlation improves the situation somewhat and the MR-ACPF frequencies are higher, but still too low. It is remarkable that the UMP2 result[12] around 800 cm^{-1} looks very good. Considering, however, that all other frequencies are systematically overestimated at this level, this seems a fortuitous cancellation of errors.

Comparison with experiment is investigated in Table IX. Of the various theoretical frequencies the MR-ACPF results, which represent the highest level of theory, are listed. Assignation of the experimental spectrum was based on these results (which then laid the basis for scaling the MCSCF force constants). The calculated infrared intensities are also given (second column in Table IX). The latter are considered as semiquantitative results which are, however, very useful in making the assignation more reliable. (Corresponding to the experimental characterization, the information we need is only whether a band is, roughly speaking, weak, medium or strong). It should be noted that the MCSCF intensities—not listed—agree qualitatively with the MR-ACPF intensities. (Concerning the more detailed results, the dipole moment derivatives agree well for the carbon backbone. The same was found for the force constants, indicating that this part of the molecule is well described already by the MCSCF calculation, in which we concentrated on the good description of the π-electron system. More significant differences are found for the CH stretch-

ings, because electron correlation is satisfactorily accounted for only by the MR-ACPF treatment in this case).

Now we discuss the assignment of the infrared spectrum of allyl (Table IX). In cases where, based on arguments given below, we have changed the assignation of an experimental band, the original assignation made in the experimental studies is given in parentheses. According to our calculations, the lowest frequency mode (predominantly the CCC bending) is at 418 cm^{-1}, below the range investigated experimentally. The next four frequencies represent out-of-plane modes, for which our results (as discussed above) are less reliable. Still, the ν_{18} b_1 mode (CH_2 twisting) seems safely identifiable with the absorption at 510 cm^{-1}, especially if the agreement of calculated and observed intensities (both strong) is considered. This supports the assignment in Ref. 16, and not that of Maltsev.[15] The next two modes, being of a_2, symmetry, are IR inactive. As follows from the discussion of the force constants, the CH_2 wagging frequency ν_{17} is underestimated (by about 50 cm^{-1}), but the assignation is, in fact, unambiguous based on the intensities: in agreement with the experiment, this is the most intense band in the spectrum.

From about 900 cm^{-1} upwards we consider the theoretical predictions as very reliable: this is the range of the in-plane vibrations for which the force field is well defined, and the only out-of-plane force constant which affects this region, the CH wagging, was also very stable in the various theoretical results above. We calculate the CH_2 rocking at about 910 cm^{-1} and thus cannot accept either of the experimental assignments (810 and 980 cm^{-1}, respectively). On the basis of the calculated very low intensity it seems justified

TABLE IX. Assignation of the fundamental frequencies of allyl using the calculated MR-ACPF force field.[a]

			Matrix IR experiment[b]		
	Characterization[g]	MR-ACPF[f]	HO (Ref. 16)	MKN (Ref. 15)	
$\nu_7\, a_1$	CCC bending	418 [1]	$\cdots$[c]	$\cdots$[c] (510)	
$\nu_{18}\, b_1$	CH_2 twisting,CH wagging	524 [1457]	511	510($-$)	s
$\nu_{15}\, a_2$	CH_2 twisting	547 [$\cdots$]	$\cdots$[d]	$\cdots$[d]	
$\nu_{14}\, a_2$	CH_2 wagging	738 [$\cdots$]	$\cdots$[d]	$\cdots$[d]	
$\nu_{17}\, b_1$	CH_2 wagging	751 [6440]	802	801	vs
$\nu_{13}\, b_2$	CH_2 rocking	913 [34]	$\cdots$[e] (810)	$\cdots$[e] (983)	
$\nu_{16}\, b_1$	CH wagging,CH_2 twisting	986 [2233]	984	983(809)	m
$\nu_6\, a_1$	CH_2 rocking,CC stretching	1035 [29]	$\cdots$[e] (1183)	$\cdots$[e] (973)	
$\nu_{12}\, b_2$	CC stretching	1206 [34]	1183(1284)	1184(1284)	w
$\nu_5\, a_1$	CC stretching,CH_2 rocking	1269 [89]	1242	1242	w
$\nu_{11}\, b_2$	CH rocking,CH_2 scissoring	1400 [830]	1389	1389	m
$\nu_4\, a_1$	CH_2 scissoring	1491 [297]	1478	1477(1463)	m
$\nu_{10}\, b_2$	CH_2 scissoring,CH rock,CC stretching	1498 [1]	1478(1464)	1477	m
$\nu_3\, a_1$	CH stretching	3045 [223]	3019	3019	m
$\nu_9\, b_2$	CH_2 sym. stretching	3055 [251]	3019	3019	m
$\nu_2\, a_1$	CH_2 sym. stretching	3066 [204]	3051	3051	w
$\nu_8\, b_2$	CH_2 asym. stretching	3142 [512]	3109	3107	w
$\nu_1\, a_1$	CH_2 asym. stretching	3146 [3942]	3109	3107	m

[a] Frequencies in cm^{-1}.
[b] New assignation on the basis of the present calculations. Original assignation is given in parentheses if it is different from the present one.
[c] This region was not measured.
[d] Inactive in IR experiment.
[e] Should be very weak based on our calculations.
[f] Calculated intensities (cm/mmol) in square brackets.
[g] Based on the present calculations.

TABLE X. Vibrational frequencies and IR intensities of 1,4-pentadienyl.[a]

Symm.	Characterization	MC-SCF	MCSCF	scaled
A_1	CH stretching	3317 [2043]	3111	[2043]
	CH stretching	3233 [2723]	3034	[1676]
	CH stretching	3232 [909]	3032	[1904]
	CH stretching	3217 [1498]	3018	[1550]
	C=C stretching	1665 [243]	1589	[154]
	CH₂ scissoring,CH rocking	1526 [10]	1418	[53]
	CH rocking,C=C stretching	1353 [179]	1284	[231]
	C–C stretching	1291 [24]	1229	[18]
	CH₂ rocking	954 [33]	897	[31]
	CCC bending cent.	513 [10]	490	[11]
	CCC bending term.	206 [3]	194	[3]
B_2	CH stretching	3316 [720]	3111	[726]
	CH stretching	3228 [1613]	3030	[1569]
	CH stretching	3214 [290]	3015	[327]
	C=C stretching	1614 [128]	1509	[107]
	CH cent. rocking,CH rocking	1544 [529]	1444	[563]
	C=C stretching,CH₂ scissoring	1374 [10]	1294	[78]
	CH rocking	1319 [62]	1267	[31]
	C–C stretching	1127 [121]	1118	[99]
	CH₂ rocking	1053 [95]	978	[63]
	CCC bending term.	467 [171]	437	[173]
B_1	CH wagging	1042 [4514]	992	[8510]
	CH₂ wagging	767 [6115]	915	[2079]
	CH cent. wagging	796 [32]	782	[544]
	CH₂ twisting	654 [1093]	594	[651]
	C–C torsion	157 [105]	146	[75]
A_2	CH wagging	1004 [···]	968	[···]
	CH₂ wagging	766 [···]	905	[···]
	CH₂ twisting	604 [···]	562	[···]
	C–C torsion	248 [···]	220	[···]

[a] Frequencies in cm⁻¹, intensities (square brackets) in cm/mmol.

that no absorption is assigned to this vibration. In the light of our result for the CH wagging, $v_{16} \approx 980$ cm⁻¹, Maltsev's assignment of 809 cm⁻¹ is far too low, while Holtzhauer's assignment of 984 cm⁻¹ is definitely confirmed. This is the more significant because the UMP2 calculation by Cometta–Moroni *et al.*[12] considerably overestimated this frequency. The calculated fairly large intensity is in accord with the experimental intensity quoted as medium. For the next two modes, v_6 and v_{12}, the theoretical intensities are very low, it is thus not surprising that previous assignments were uncertain here. We assign the weak absorption around 1180 cm⁻¹ to the higher frequency mode, rather than the lower one, and leave v_6 unobserved. For the last four modes in the medium frequency range we agree basically with previous assignments. A minor question concerns the exact identification of the two CH₂ scissoring modes around 1470 cm⁻¹: in our calculation their splitting is negligible and the b_2 mode has practically no intensity; we thus think that the absorption in this region comes from one mode only, the a_1 vibration. In the high frequency range of the CH stretchings, it is well known that anharmonicity may complicate the spectrum so that assignment of the individual modes, although listed in Table IX, is only tentative.

The above modification of the assignment leaves three experimental frequencies, used in previous assignments, un-

assigned. Considering that the 809 cm⁻¹ band is only a shoulder on the most intense absorption at 801 cm⁻¹,[15] and the bands at 973 and 1284 cm⁻¹ are both very weak, it seems justifiable to assume that these are not fundamentals.

Once the assignment, as just discussed, was established, this laid the basis for fitting the MCSCF force field to the experimental frequencies. This optimization yielded the scale factors discussed above and given in Table VII. A similar, but in its details slightly different, scaling was also applied on the UMP2 force field by Cometta–Moroni *et al.*[12] Considering the in-plane frequencies in Table VIII, the agreement of the two sets of scaled results is quite excellent: the standard deviation is 10 cm⁻¹ and, what is more significant, even the maximum deviation is below 20 cm⁻¹ (leaving v_7 out of consideration, since for this frequency no experimental data was available, and we thus fitted it to the MR-ACPF theoretical frequency). The in-plane results are thus very reassuring and show the justification of such empirical adjustments of lower level theoretical calculations.

2. 1,4-Pentadienyl radical

As described above,the MCSCF force field of pentadienyl was scaled by the scale factors taken over from allyl. The scaled force field thus gives the possibility of making *a priori* predictions for the vibrational frequencies of pentadienyl, for which no experimental data are available yet. The predicted spectrum is given in Table X.

It is, of course, important to judge the expected reliability of our results. Due to the relatively large correction for the CH₂ wagging force constant, the out-of-plane frequencies are considered less reliable. We think that uncertainties of about 100 cm⁻¹ are possible, especially in the two modes dominated by the waggings. These facts should not disturb the assignation, because this band is very intense in the infrared spectrum. At the same time our predictions for the in-plane frequencies should be very safe. Here the only uncertainty in the force field concerns the CC/CC coupling constants which are fairly large along the complete carbon backbone and for which the scaling, as discussed above, was rather uncertain. We therefore checked numerically the sensitivity of the frequencies to slight changes in these couplings with the following result. The coupling of the two terminal stretchings, although fairly large, has a small effect on the frequencies (this is not surprising, considering that they do not couple in the G matrix). The same is true for the coupling C_1C_2/C_3C_5. The sensitivity of the frequencies to the couplings of neighboring stretchings, viz. C_1C_2/C_2C_4 and C_1C_2/C_1C_3 is considerable. The largest sensitivity is found for the frequency at 1118 cm⁻¹ (e.g., it changes more than 20 cm⁻¹ if we use the extra scale factor instead of the standard scaling). In summary, the uncertainty in the CC/CC couplings may cause an uncertainty up to 30 cm⁻¹ in the medium frequency range. Such an error is tolerable from the point of view of the assignment and we hope that our predicted spectrum of pentadienyl will be useful in eventual future experimental works.

Finally, a few observations about the calculated frequencies may be of interest. It is interesting to see that the lowest-frequency CCC bending, at about 200 cm⁻¹, lies

much lower than in allyl (~ 500 cm^{-1}). Considering that the three CCC force constants in pentadienyl are very close to their counterpart in allyl, the low frequency can be explained by strong kinetic couplings. The situation is analogous to hexatriene where the corresponding mode is at 150 cm^{-1}.[32] From the point of view of the nature of bonding a notable finding is that the two C=C stretchings can be identified as fairly well isolated vibrations in the region 1500–1600 cm^{-1}, the range typical for (relatively weak) double bonds.

IV. CONCLUSION

We have determined the structure, force constants and vibrational frequencies of the allyl and pentadienyl radicals by *ab initio* calculations.

The investigation of the doublet instability of allyl leads to the conclusion that—beyond the well known Hartree–Fock instability—even a π-CAS MCSCF wave function may be subject to instability: while the three-orbital and five-orbital CAS wave functions are stable the four-orbital CAS wave function is unstable with respect to the asymmetric distorsion of the CC bonds. This fact was explained in terms of a near degeneracy of the $2a_2$ and $3b_1$ orbitals. The CI wave functions are always stable even if one uses the symmetry broken SCF orbitals in the calculations.

The three-orbital CAS MCSCF and MR-ACPF methods were used to calculate the force constants of allyl. As judged by the good reproduction of the experimental frequencies, the MR-ACPF method gives remarkably accurate force constants. To the MCSCF force field an empirical scaling was applied by fitting it through a few scale factors to the experimental frequencies. The scaled MCSCF and the purely theoretical MR-ACPF force field are our best estimate for the force constants of allyl. We consider the in-plane force constants as very well established, while the out-of-plane force field is somewhat less reliable due to the larger corrections which had to be applied to the CH$_2$ wagging force constant. On the basis of the MR-ACPF calculation we give a reassignation of some vibrational modes in the experimental infrared spectrum.

A five-orbital CAS MCSCF force field has been calculated for the 1,4-pentadienyl radical. Using the scale factors for allyl, the vibrational spectrum of pentadienyl is predicted for the first time. The reliability of these frequencies should greatly facilitate the future measurement and assignment of the spectrum.

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