Lawrence Berkeley National Laboratory

Recent Work

Title

THEORETICAL STUDY OF THE ALLYL RADICAL: STRUCTURE AND VIBRATIONAL ANALYSIS

Permalink

<https://escholarship.org/uc/item/1mh694pv>

Authors

Takada, T.
Dupuis, M.

Publication Date

1982-04-01

NRCC

NATIONAL
RESOURCE
FOR COMPUTATION
IN CHEMISTRY

RECEIVED
LAWRENCE

BERKELEY LABORATORY

MAY 28 1982

LIBRARY AND
DOCUMENTS SECTION

Submitted to the Journal of the American Chemical
Society

THEORETICAL STUDY OF THE ALLYL RADICAL:
STRUCTURE AND VIBRATIONAL ANALYSIS

T. Takada and M. Dupuis

April 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA

LBL-14314
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THEORETICAL STUDY OF THE ALLYL RADICAL:
STRUCTURE AND VIBRATIONAL ANALYSIS⁺

T. Takada⁺⁺ and M. Dupuis^{*}

National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 USA

⁺This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Grant No. CHE-7721305.

⁺⁺Present address: Department of Chemistry, The University of Chicago, Chicago, Illinois 60637.

^{*}Present address: Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

THEORETICAL STUDY OF THE ALLYL RADICAL:
STRUCTURE AND VIBRATIONAL ANALYSIS

T. Takada and M. Dupuis
National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 USA

Abstract

The electronic structure of the allyl radical CH_2CHCH_2 and its vibrational spectrum have been calculated from ab initio multiconfiguration Hartree-Fock (MCHF) wavefunctions. While the Hartree-Fock (HF) model incorrectly predicts a non-symmetric structure, the MCHF calculations indicate that the allyl radical has C_{2v} symmetry in accord with ESR evidence. Harmonic vibrational frequencies of all the normal modes are reported for the allyl radical and various deuterium substituted analogues. Most noteworthy are the out-of-plane bending mode frequencies calculated at $760\text{--}790\text{ cm}^{-1}$ which are predicted to give rise to a very intense and characteristic band of the allyl radical.

I. Introduction

Allyl-type radicals having delocalized unpaired electrons in a conjugated π system have been the subject of several studies. Of special interest is the fact that the theoretical work of McConnell and Chesnut¹ predicted a negative spin density in the p orbital of the central carbon of an allyl system. The allyl radical is the simplest odd alternate hydrocarbon which exhibits the feature of negative spin density. The ESR study of Fessenden and Schuler² showed that the allyl radical has C_{2v} symmetry and confirmed the negative spin density on the central carbon atom ($\rho = -0.16$) and a positive spin density on the end carbon atoms ($\rho = +0.58$).

The allyl radical is also known to result from ring fission of the cyclopropyl radical. Greig and Thynne³ estimated the activation energy for the ring fission to be about 20 kcal/mol. In fact a spectroscopic observation of the cyclopropyl radical in an Argon matrix was ambiguous probably because of the presence of the allyl radical.⁴

Previously Dupuis and Pacansky⁴ reported a study of the cyclopropyl radical and its vibrational analysis. In this paper we present an ab initio study of the allyl radical and its vibrational analysis. The two studies are complementary and should be a valuable aid for the identification of the IR spectra of the allyl radical and of the cyclopropyl radical.

The electronic structure of the allyl radical has been the subject of numerous theoretical treatments. Early studies focused on the calculation of the unpaired spin density.¹ Recent studies⁵⁻⁷

discussed the doublet instability of the allyl radical, a manifestation of the broken symmetry dilemma.⁸ Kikuchi showed that the instability problem is resolved by using a multiconfiguration Hartree-Fock (MCHF) wavefunction which include the $\pi \rightarrow \pi^*$ singly excited configurations. Within the semiempirical MINDO/3 framework, Kikuchi calculated a C_{2v} structure as the lowest energy structure of the allyl radical. Alternatively, Voter and Goddard⁹ introduced the Generalized Resonating Valence Bond (GRVB) model to describe the resonance interaction of the two bonding structures of the allyl radical (and) which are responsible for the doublet instability.

The organization of this paper is as follows: in Section II we describe the theoretical method used; in Section III we discuss the structure of the allyl radical; and in Section IV we report its vibrational analysis.

II. Computational Method

In this study we used a multiconfiguration Hartree-Fock wavefunction (MCHF) to describe the allyl radical. The configurations included in the wavefunction were obtained by distributing the three π electrons of the allyl radical among the three low lying π orbitals (bonding π , non-bonding π , and antibonding π orbitals) in all possible ways resulting in eight configurations in C_1 symmetry. This wavefunction is closely related to Voter and Goddard's⁹ GRVB wavefunction and contains the recoupling singly excited configuration shown by Kikuchi⁷ to be necessary for a qualitatively correct description of the allyl radical.

In the next sections we compare the allyl radical with the propene molecule. A propene wavefunction of comparable accuracy to the allyl MCHF wavefunction, is one in which the π bond is represented with a GVB pair. This is a two configuration wavefunction which includes the π^2 and π^{*2} configurations.

The one particle basis set used for the molecular orbital expansions is the split valence 3-21G basis set of Binkley, et al.¹⁰ This basis set, efficient computationally, provides reliable equilibrium geometries and vibrational frequencies. The force method of Pulay¹¹ was applied to calculate the force constant matrix (the first derivatives of the MCHF energy with respect to nuclear coordinates is calculated analytically, and the second derivatives are evaluated by finite difference). The computer code used in this work in the HONDO¹² program which includes a Newton-Raphson orbital optimization algorithm¹³ for the MCHF wavefunction calculation.

III. The Structure of the Allyl Radical

A consistent picture of the structure of the alkyl radicals¹⁴ was obtained from experimental and theoretical studies of the radicals. One important feature commonly observed is the shortening of the bonds in position α to the radical center, and a lengthening of the bonds in position β to the radical center. For example, the radical center of the ethyl radical is ethylene-like with short CH bonds and CC bond, while the CH bond eclipsed with the half filled orbital of the radical center is longer than the other CH bonds. In the cyclopropyl radical⁴ the α CH bond is again predicted to be

short, and the CC bond opposite to the radical center is predicted to be long. The shortening and lengthening of bonds in the radicals result in characteristic bands of the IR spectrum. Another feature characteristic of the ethyl radical is a low frequency ($\sim 540 \text{ cm}^{-1}$) pyramidal bending motion of the radical center. This pyramidal distortion of the radical center in the ethyl radical has a lower frequency than the out-of-plane bend of the ethylene molecule ($\sim 960 \text{ cm}^{-1}$). In light of the differences between the ethyl radical and ethane and ethylene, in what follows we compare the structure and vibrational spectrum of the allyl radical with those of propene.

The structure of propene and of the allyl radical are shown in Fig. 1, and the bond lengths and bond angles are given in Table 1. The change in CC bond lengths from propene to allyl is readily noted. In propene the C_1C_2 bond is a double bond ($1.337 \text{ \AA}$), and the C_1C_3 bond is a single bond ($1.512 \text{ \AA}$). The allyl radical has two equivalent C_1C_2 and C_1C_3 bonds intermediate between a single bond and a double bond. The change in bond lengths is the result of the three π electron delocalization over the three carbon atoms because of the resonance interaction of the two bonding structures . In propene the CH bonds fall in two categories: C_1H_1 , C_2H_2 , and C_2H_3 are ethylenic CH bonds ($\sim 1.075 \text{ \AA}$); the three CH bonds of the methyl group in propene are longer ($\sim 1.084 \text{ \AA}$) than the ethylenic CH bonds. For comparison the bond lengths in ethylene and ethane obtained with the same 3-21G basis set are given in Table 2.

Thus upon elimination of a hydrogen atom from the methyl group of propene, the two remaining CH bonds acquire a strong ethylenic

character, the CC bond in α position to the former methyl group becomes shorter, and the CC bond in β position (the double bond in propene) becomes longer. The planar configuration of the allyl radical is the most energetically favorable for delocalization of the electrons. Similar changes in structure had previously been noted for the ethyl radical¹⁴ and the n-propyl radical.¹⁴ In the allyl radical all the CH bonds have approximately the same length (1.073 Å), with the CH bond on the central carbon C₁ slightly longer (1.075 Å).

In the cyclopropyl radical⁴ the CH bond α to the radical center is slightly shorter (1.067 Å) than the other CH bonds (1.073 Å) which are ethylenic (the values were obtained with the 4-31G basis set,¹⁵ also a split valence basis set very similar to the 3-21G basis set used in this study). Thus upon fission of the β CC bond of the cyclopropyl radical, the formerly CH bond of the cyclic radical goes from 1.067 Å to about 1.075 Å while the unpaired electron of the radical center delocalizes over the C-C-C chain.

IV. Vibrational Analysis of the Allyl Radical

Theoretically determined harmonic frequencies are a valuable aid for assigning vibrational spectra.¹¹ Although the calculated values are higher (~ 10-15%) than the observed frequencies, they appear in the correct order. Exceptions to this usually occur when the vibrational frequencies are closely spaced. When this situation arises, it is difficult to make a meaningful comparison between the theoretical and experimental results because the theoretical values are harmonic frequencies while the experimental values are usually the observed frequencies and thus include anharmonicity.

The calculated harmonic frequencies (in cm^{-1}) of the allyl radical and of some deuterium substituted analogues are given in Table 3. The harmonic frequencies of the propene molecule are given in Table 4, along with the experimental frequencies observed by Silvi, et al.¹⁶ As pointed out earlier, the ordering of the calculated harmonic frequencies agrees with the ordering of the observed frequencies for propene. There is a close correspondence between the calculated spectra of propene and allyl. In what follows, we analyze the differences.

The computed structure of the allyl radical shows all five CH bonds to be ethylenic. The stretching frequencies are predicted to be in the region of ethylenic CH stretches (greater than 3300 cm^{-1} for harmonic frequencies). The stretches assigned to the methyl group of propene have shifted to higher frequencies for the allyl radical.

The considerable changes in CC bond length noted upon inspection of the calculated structures of allyl and propene result in characteristic shifts of the stretching frequencies. In propene the double bond CC stretching frequency is 1770 cm^{-1} , the single bond CC stretching is at 946 cm^{-1} . In allyl there are two equivalent CC bonds not as strong as a CC double bond, but stronger than a CC single bond. The asymmetric combination of CC stretches has a frequency of 1204 cm^{-1} . This is the deformation mode responsible for the symmetry breaking of the HF model. In light of the frequency of the CC symmetric stretch assigned to be 1093 cm^{-1} , the magnitude of the CC asymmetric stretch frequency is surprisingly high. Note that both the 1093 cm^{-1} and the 1370 cm^{-1} modes contain a significant

mixture of CC symmetric stretch and asymmetric CH_2 bends. The former mode is described as the CC symmetric stretch because of its larger contribution to the 1093 cm^{-1} vibrational mode.

The weaker CC bonds in allyl (compared to the C=C double bond in propene) result in a softer out-of-plane bending motion of the terminal CH_2 group in allyl than in propene. Indeed the out-of-plane CH_2 bending frequency in propene is 958 cm^{-1} , while the same mode frequencies of allyl are 786 cm^{-1} and 761 cm^{-1} . Alternatively, the CC bond in the allyl radical is stronger than the CC bond in the ethyl radical for which the pyramidal CH_2 bending motion has a frequency of 540 cm^{-1} . The pyramidal bending motion in the ethyl radical, and the out-of-plane bending motion in ethylene give rise to very intense characteristic bands of the IR spectra. The same vibrational mode in the allyl is also predicted to be responsible for a very intense band.

Similarly, the twisting motions of the CH_2 groups in allyl (596 cm^{-1} and 562 cm^{-1}) are slightly "softer" than the same twisting motion in propene (603 cm^{-1}) and in ethylene. However, the barrier to rotation about the CC bond in allyl is expected to be much lower than in ethylene.

The motions associated with the hydrogen atom on the central carbon have nearly identical frequencies in allyl and in propene: (CH stretch = 3327 cm^{-1} in allyl, 3336 cm^{-1} in propene; CH in-plane bend = 1556 cm^{-1} in allyl, 1598 cm^{-1} in propene; CH out-of-plane way = 1051 cm^{-1} in allyl, 1063 cm^{-1} in propene). Furthermore, the CCC bending motion has a frequency of 476 cm^{-1} in allyl, and 469 cm^{-1} in propene.

The vibrational frequencies previously reported for the cyclopropyl radical⁴ are given in Table 5. Compared to the cyclopropyl radical, the allyl radical has several vibrational modes with lower frequency than any of the cyclopropyl frequencies. The most obvious change involves the β CC stretch of the cyclopropyl radical (916 cm^{-1}) which becomes the CCC bend of the allyl radical (476 cm^{-1}). The other low frequency modes of the allyl radical involve the CH_2 groups. The corresponding modes in the cyclopropyl radical have higher frequencies presumably due to the more restricted structure of the cyclic radical. The bending motion with frequency 713 cm^{-1} of the α CH bond in cyclopropyl becomes the wagging motion with frequency 1051 cm^{-1} in allyl. The wagging motion of the the α CH bond at 1208 cm^{-1} in cyclopropyl becomes the bending motion at 1556 cm^{-1} in allyl. No significant differences exist between the CH stretches of the cyclopropyl radical, and those of the allyl radical.

V. Conclusion

We have determined the structure of the allyl radical. It is characterized by five ethylenic CH bonds, and two CC bonds intermediate between a single and double bond. The lowest frequency mode corresponds to the CCC bend (476 cm^{-1}). The out-of-plane bending modes of the CH_2 group in the allyl radical have lower frequencies (786 cm^{-1} and 761 cm^{-1}) than the same mode in propene (959 cm^{-1}), but higher frequency than the pyramidal motion of the radical center in the ethyl radical. These out-of-plane bending motions are predicted to be responsible for a very intense band near

770 cm^{-1} characteristic of the IR spectrum of the allyl radical. Previously, we had reported that the lowest frequency mode in the cyclopropyl radical was the αCH bending model (713 cm^{-1}). The allyl radical has several vibrational modes with lower or similar frequency. The present study should be valuable for the identification of the spectra of the allyl radical and of the cyclopropyl radical.

Acknowledgment

The authors gratefully acknowledge many stimulating discussions with Dr. J. Pacansky (IBM Research Laboratory).

References

1. H. M. McConnell and D. B. Chesnut, J. Chem. Phys. 28 107 (1958).
2. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 39 2147 (1963).
3. G. Grieg and J. C. J. Thynne, Trans. Faraday Soc. 62 3338 (1966).
4. M. Dupuis and J. Pacansky, J. Chem. Phys. 76, 2511 (1982).
5. J. McKelvey and G. Berthier, Chem. Phys. Lett. 41 476 (1976).
6. J. Paldus and A. Veillard, Chem. Phys. Lett. 50 6 (1977); Mol. Phys. 35 445 (1978).
7. O. Kikuchi, Chem. Phys. Lett. 72 487 (1980).
8. P. O. Löwdin, Rev. Mod. Phys. 35 496 (1963); Adv. Chem. Phys. 14 283 (1969).
9. A. F. Voter and W. A. Goddard, III, Chem. Phys. 57 253 (1981); J. Chem. Phys. 75 3638 (1981).
10. J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. 102 939 (1980).
11. P. Pulay, Modern Theoretical Chemistry, Vol. 4, ed. by H. F. Schaefer, III, (Plenum Press, New York, 1977).
12. M. Dupuis, J. Rys, and H. F. King, J. Chem. Phys. 65 111 (1976).
13. L. Yaffe and W. A. Goddard, III, Phys. Rev. A13 1682 (1975).
14. J. Pacansky and M. Dupuis, J. Chem. Phys. 68 4276 (1978); J. Chem. Phys. 71 2095 (1979); J. Chem. Phys. 73 1867 (1980).
15. R. Ditchfield, W. J. Ehre, and J. A. Pople, J. Chem. Phys. 54 724 (1971).
16. B. Silvi, P. Labarbe, and J. P. Perchard, Spectrochem. Acta. 29A 263 (1973).

Table 1. Calculated bond length (Å) and bond angles of propene and allyl.^a

	<u>CH₃ - CH = CH₂</u>	<u>CH₂ - CH[•] - CH₂</u>
R(C ₁ H ₁)	1.076	1.075
R(C ₁ C ₂)	1.337	1.388
R(C ₂ C ₃)	1.512	1.388
R(C ₂ H ₂)	1.075	1.073
R(C ₂ H ₃)	1.073	1.072
R(C ₃ H ₄)	1.083	1.073
R(C ₃ H ₅)	1.086	1.072
∠(C ₂ C ₁ C ₃)	124.3°	124.4°
∠(C ₁ C ₂ H ₂)	121.8°	121.2°
∠(C ₁ C ₂ H ₃)	121.7°	121.4°

a. GVB wavefunction for propene, MCHF wavefunction for allyl (see text).

Table 2. Calculated bond lengths of Ethane and Ethylene.^a

C_2H_6	$R(C - C) = 1.542 \text{ \AA}$	$R(C - H) = 1.084 \text{ \AA}$
C_2H_4	$R(C = C) = 1.315 \text{ \AA}$	$R(C - H) = 1.074 \text{ \AA}$

a. HF wavefunctions for C_2H_6 and C_2H_4 .

Table 3. Harmonic Frequencies (cm^{-1}) of the Allyl Radical and of some Deuterium Substituted Analogues.

<u>Symmetry</u>	<u>Mode</u>	<u>Radical</u>			
		<u>$\text{CH}_2\text{-CH-CH}_2$</u>	<u>$\text{CH}_2\text{-CD-CH}_2$</u>	<u>$\text{CD}_2\text{-CH-CD}_2$</u>	<u>$\text{CD}_2\text{-CD-CD}_2$</u>
a_1	CH stretch	3412	3409	2541	2543
b_2	CH stretch	3407	3407	2538	2538
a_1	.CH stretch	3327	2456	3328	2459
a_1	CH stretch	3318	3320	2414	2409
b_2	CH stretch	3314	3314	2400	2401
a_1	Sym. CH_2 bend (sym.)	1661	1660	1367	1351
b_2	Sym. CH_2 bend (asym.)	1632	1628	1271	1193
b_2	.CH bend	1556	1374	1543	1361
a_1	Asym. CH_2 bend (sym.)	1370	1345	1162	1148
b_2	CC stretch (asym.)	1204	1096	1110	1003
a_1	CC stretch (sym.)	1093	1090	920	920
b_1	.CH out-of-plane bend	1051	844	1016	804
b_2	Asym. CH_2 bend (asym.)	1040	947	803	779
b_1	CH_2 out-of-plane bend (sym.)	786	785	649	640
a_2	CH_2 out-of-plane bend (asym.)	761	761	601	601
a_2	CH_2 twist (asym.)	596	596	424	424
b_1	CH_2 twist (sym.)	562	561	434	433
a_1	CCC bend	476	471	392	389

Table 4. Vibrational Frequencies (cm⁻¹) of the Propene Molecule

<u>Mode</u>		<u>CH₃-CH=CH₂</u>		<u>CH₃-CD=CH₂</u>		<u>CH₃-CH=CD₂</u>		<u>CD₃-CH=CH₂</u>	
		<u>calc.</u>	<u>obs.^a</u>	<u>calc.</u>	<u>obs.</u>	<u>calc.</u>	<u>obs.</u>	<u>calc.</u>	<u>obs.</u>
CH ₂	Stretch	3383	3091	3380	3090	2519	2318	3383	3093
CH	Stretch	3337	3017	2463	2246	3340	3020	3336	3020
CH ₂	Stretch	3298	2991	3298	3000	2413	2225	3298	2988
CH ₃	Stretch	3260	2973	3260	2974	3260	2972	2417	2221
CH ₃	Stretch	3245	2953	3245	2952	3245	2952	2401	2200
CH ₃	Stretch	3190	2932	3190	2924	3190	2928	2291	2120
C=C	Stretch	1770	1653	1751	1635	1718	1614	1763	1645
CH ₃	Sym. bend	1669	1459	1668	1453	1657	1452	1207	1060
CH ₃	Asym. bend	1664	1443	1663	1443	1664	1449	1200	1055
CH ₂	Sym. bend	1598	1420	1571	1412	1177	1053	1596	1419
CH ₃	Sym. bend	1583	1378	1584	1390	1584	1380	1201	1046
CH	In plane bend	1441	1298	1195	830	1440	1303	1442	1300
CH ₂	Asym. bend (+ CH ₃ sym. rock)	1307	1179	1320	1186	1260	1057	1266	1163
CH ₃	Asym. rock	1176	1045	1175	1040	1172	1045	951	868
CH ₂	Asym. bend - CH ₃ sym. rock	1070	935	969	-	981	786	935	769
CH	Out-of-plane bend	1063	990	907	846	973	909	1061	995
CH ₂	Out-of-plane bend	958	912	958	913	760	728	966	916
C-C	Stretch	946	919	914	918	857	906	853	860
CH ₂	Twist	603	575	567	549	493	470	561	521
CCC	Bend	469	428	465	422	424	380	430	392
CH ₃	Rotation	217	188	215	185	215	184	163	149

a. Observed Frequencies from Ref. 15.

Table 5. Computed vibrational frequencies (cm^{-1}) of the cyclopropyl radical.^a

αCH	Stretch	3418
βCH	Stretch	3373
βCH	Stretch	3358
βCH	Stretch	3293
βCH	Stretch	3286
CH_2	Bend	1646
CH_2	Bend	1623
αCC	Sym. stretch	1314
CH_2	Asym. twist	1301
CH_2	Asym. wag	1268
CH_2	Sym. rock + αCH rock	1241
αCH	Wag	1208
CH_2	Sym. wag	1204
αCC	Asym. stretch	995
βCC	Stretch	916
CH_2	Asym. rock + αCH wag	893
CH_2	Sym. twist	870
αCH	Sym. bend	713

^aSee Ref. 4.

Figure Caption

Figure 1. Propene Molecule and Allyl Radical.

XBL 824-304

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720