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# Determination of the Minimum Energy Conformation of Allylbenzene and Its Clusters with Methane, Ethane, Water and Ammonia

by

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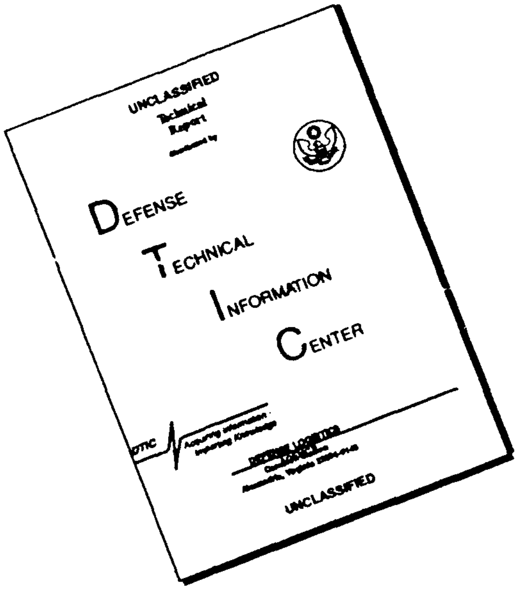

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## Abstract

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# Determination of the Minimum Energy Conformation of Allylbenzene and Its Clusters with Methane, Ethane, Water and Ammonia

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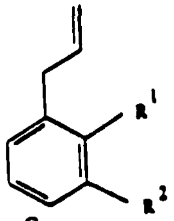
# Abstract

Supersonic molecular jet laser time of flight mass spectroscopy (TOFMS) is employed to determine the minimum energy conformation of the allyl group with respect to the benzene ring of allylbenzene, 1-allyl-2-methylbenzene and 1-allyl-3-methylbenzene. The spectra are assigned and conformations are suggested with the aid of molecular orbital molecular mechanics (MOMM-85) calculations. Based on the experimental and theoretical results, the minimum energy conformer is found to have $\tau_1(C_{ortho}-C_{ipso}-C_\alpha-C_\beta)$ = ca. 90° (i.e., the allyl group is essentially perpendicular to the plane of the benzene ring) and $\tau_2(C_{ipso}-C_\alpha-C_\beta-C_\gamma) = \pm 120^\circ$ (i.e., the olefin C=C bond is eclipsed with the $C_\alpha-H_\alpha$ bond). The TOFMS of allylbenzene clustered with methane, ethane, water and ammonia are also presented. A Lennard-Jones potential energy 6-12-1 atom-atom calculation is used to characterize the structures of these clusters. Experiments and calculations demonstrate that the four different solvent molecules studied can form stable clusters with allylbenzene by coordinating to the $\pi$-system of the allyl substituent in addition to that of the aromatic ring.

## I. Introduction.

Supersonic molecular jet laser spectroscopy has recently been proven to be remarkably capable technique for the observation and structural characterization of a wide variety of alkyl and heteroalkyl substituted benzenes.[1-6] For example, the minimum energy conformations of various ethyl,[1] propyl,[3] butyl[4] and methoxybenzenes[5,6] and styrenes[7] have been observed for the first time and their stable conformations have been experimentally determined. In addition, molecular jet laser spectroscopy has been able to characterize potential energy barriers, typically for aromatic methyl rotors, for some of these molecules in both their ground and excited states.[2,6,8]

In this paper, we focus attention on the effects of a carbon-carbon double bond (an additional π-system) incorporated onto an aromatic ring in terms of the geometry of the minimum energy conformation(s) of the molecule and on the geometry of various van der Waals clusters. The specific systems studied are allylbenzene (1), the allyltoluenes (2 and 3), and the van der Waals clusters formed between allylbenzene and methane, ethane, water and ammonia. Even though the allylbenzene substructure is found in numerous natural products and has value in organic synthetic manipulations, its conformational properties have received little attention.[9] Indeed, there is a dearth of both experimental and theoretical information regarding the conformational preferences of allylbenzene and its derivatives.



1, $R^1 = R^2 = H$

2, $R^1 = CH_3$, $R^2 = H$

3, $R^1 = H$, $R^2 = CH_3$

Spectroscopic studies of these systems are obtained through supersonic molecular jet cooling and isolation of the various species in the gas phase, and one- and two-color time of flight mass spectroscopy (TOFMS) detection. Mass selected excitation spectra of isolated molecules and clusters are thus obtained.[10] In order to determine the conformations and cluster geometries associated with the individual mass selected spectra observed, model calculations of the isolated and clustered species are performed.[12]

Five questions are addressed in this work: 1) can the stable conformations be isolated and spectroscopically observed for benzene and alkyl substituted allylbenzenes? 2) what are the minimum energy conformations of the allyl group in allylbenzenes? 3) what are the configurations of clusters of allylbenzenes with small solvent molecules? 4) does solvation influence the allylbenzene molecular geometry significantly? and 5) does the $\pi$-system of the allyl group influence significantly the solvation of the aromatic ring in substituted benzenes?

## II. Experimental Procedures.

The supersonic jet time of flight mass spectrometer is as described previously.[13] Expansion into the vacuum chamber is achieved with an R.M. Jordan pulsed valve. In the case of the allylbenzene van der Waals clusters, two-color photoionization spectra are obtained by using two Quanta-Ray Nd:YAG-pumped tunable dye lasers to generate the pump and ionization beams. The energy of the tunable pump beam (0.5 to 1.0 mJ/pulse) is typically ~ 37500 $cm^{-1}$ while that of the fixed wavelength ionizing beam (1.0 to 2.0mJ/pulse) is ~34000 $cm^{-1}$. Under these experimental conditions no one-color spectra, due only to the pump beam, are observed. Complications due to fragmentation of higher order clusters are avoided by careful control of the allylbenzene and solvent concentrations so that, in general, higher order clusters are not oberved. Moreover, the ionization energy is determined to be just high enough to oberve spectra but not cause extensive fragmentation into lower mass channels. All peaks in a given spectrum are found to have the same backing pressure dependence.

Ground state potential energy profiles for the allylbenzenes are obtained using Kao's molecular orbital-molecular mechanics MOMM-85 algorithm [14,15], a theoretical approach which has found to be applicable to aromatic molecules [14,16]

The resolution presently available to us (ca. 0.1 $cm^{-1}$) is not sufficient to determine the detailed geometries of allylbenzene clusters from rotational spectroscopy. Instead, potential energy Lennard-Jones (LJ) atom-atom (6-12-1) calculations[17] are used in this endeavor. These calculations are similar to others used in the past, and employ the same set of LJ potential parameters.[18,19] The partial electronic charges centered on each atom of allylbenzene are listed in Table I and are obtained from ab initio STO-3G calculations.

For allylbenzene clustered to methane and ethane, the use of partial charges has no effect on the calculated cluster geometry, and only a small effect (~3 $cm^{-1}$) on the calculated cluster binding energies. The partial charges are therefore omitted in these calculations.

Methane, ethane, water and ammonia are typically mixed with the expansion gas at a concentration of 2% in 50-100 psig of helium.

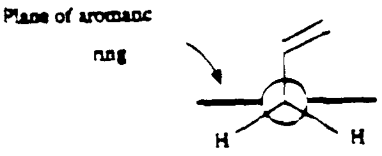
**Allylbenzene (1)** and 1-allyl-2-methylbenzene (2) are purchased from Wiley Organics, Inc. and are used without further purification. The samples are all maintained at ca. 25°C during the experiment.

**1-Allyl-3-methylbenzene (3).**[20] A solution of m-tolylmagnesium bromide, prepared from 3-bromotoluene (8.5 g, 49.7 mmol) and magnesium turnings (2.41 g, 99 mmol) in ether (20 mL), was added at room temperature to a mixture of allylisopropylsulfide (4.0 g, 34.4 mmol) and NiCl$_2$(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$) (0.5 g, 0.92 mmol) in ether (80 mL). The reaction mixture was heated under reflux for 10 h, cooled, and quenched with 1N hydrochloric acid. The organic phase was separated, filtered, dried (sodium sulfate), and concentrated at [illegible] mmHg). The 1-allyl-3-methylbenzene (**3**) was then isolated by distillation to give 3.62 g (80%): bp 24-27 °C (0.07 mmHg); $^1$H NMR (CDCl$_3$) δ 2.32 (s, 3H), 3.34 (d, 2H, *J* = 6.7 Hz), 5.03-5.11 (m, 2H), 5.88-6.00 (m, 1H), 6.97-7.22 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 21.36, 40.20, 115.63, 125.58, 126.78, 128.30, 129.34, 137.77, 137.95, 139.96.

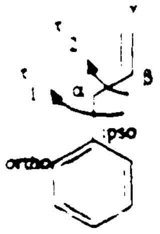
## III. Experimental Results

### A. Allylbenzene and Allyltoluenes.

The time of flight mass spectrum of the $0_0^0$ band region for the $S_0 \leftarrow S_1$ transition of jet-cooled allylbenzene (**1**) is presented in figure 1. The spectrum contains one origin, located at 37492.6 cm$^{-1}$. This single origin indicates that only one energy minimum exists for the orientation of the allyl group with respect to the ring in allylbenzene, as defined in **4a** and **4b**.



**4a**

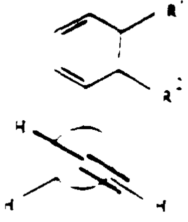


**4b**

Figure 2 is the TOFMS of jet-cooled 1-allyl-3-methylbenzene (**3**). The spectrum exhibits what are assigned as two separate origins, at 36959.2 and 37066.9 cm$^{-1}$, belonging to different conformers. The origin at 36959.2 cm$^{-1}$ appears weak because the laser output at this wavelength (LDS-698 doubled mixed with 1.064 μm) is quite low in intensity. As has been commonly observed for 1-

alkyl-3-methylbenzenes[1-3] the origins appear as doublets [illegible] between internal rotational states of the ring methyl group. This [illegible] is well documented and understood[1-3] and will not be discussed here. [illegible] the low energy side of the origin at 36,939.2 cm$^{-1}$ are possibly [illegible] band of the allyl group. The TOFMS of jet-cooled 1-allyl-2-methylbenzene (**2**) is presented in figure 3 and shows two intense features at [illegible] cm$^{-1}$ which are also assigned as origins.

A portion of the steric energy function for allylbenzene (**1**) based on the MOMM[14,15] algorithm is shown in figure 4. MOMM calculations were also performed on 1-allyl-2-methylbenzene (**2**). In both cases, $\tau_1(C_{ortho}-C_{ipso}-C_{\alpha}-C_{\beta})$ = ca 90°, i.e., the allyl substituent is essentially orthogonal to the plane of the benzene ring (c.f. **4**). This is consistent with the experimental and theoretical findings for $\tau_1$ for other alkyl-substitute aromatics of partial structure $ArCH_2R$[1,3,4,13-22]. The Newman projections for the conformational profile about $\tau_2(C_{ipso}-C_{\alpha}-C_{\beta}-C_{\gamma})$ represent the other important conformational variable for these compounds. The steric energy profile for rotation about $\tau_2$ is shown in figure 4. As can be seen, the vinyl $C_{\alpha}-C_{ipso}$ eclipsed **5** and vinyl $C_{\alpha}-H_{\alpha}$ eclipsed **6** (≡**7**) conformations are predicted to be the energy minima for allylbenzene. Because the energy difference between **5** and **6**/**7** is small (< 1 kcal/mol), certainly within the error range of the MOMM calculations, we cannot specify which of these is the global energy minimum. Much more refined calculations would be required before one could confidently predict which of **5**-**7** is the most stable conformation and what the energy difference between them is. For example, preliminary STO-3G calculations on the geometries of the MOMM-derived energy minima found for **1** (i.e., **5a** vs **6a**) led to a reversal of their potential energies (0.55 kcal/mol by MOMM; -2.40 kcal/mol by STO-3G). The important conclusion here is that the energy minimum is a vinyl $C_{\alpha}-X_{\alpha}$ eclipsed conformation with X representing either the aromatic ring bond (as in 5) or the a hydrogen atom (as in **6** and 7).



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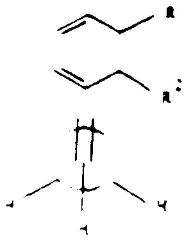

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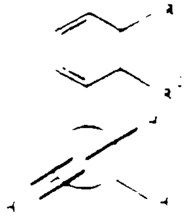

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a $R^1 = R^2 = H$
b $R^1 = CH_3$, $R^2 = H$
c $R^1 = H$, $R^2 = CH_3$

## B **Allylbenzene/Methane**

The TOFMS of allylbenzene clustered with one methane molecule (AB$(CH_4)_1$) is presented in figure 5. Three relatively intense features occur, at 37447.6, 37459.8 and 37477.9 $cm^{-1}$ red shifted from the origin of allylbenzene by 45.0, 32.8 and 14.7 $cm^{-1}$. The first two shifts are similar to those observed for methane clustered to other substituted benzenes such as propylbenzene.[13] For this latter case, shifts of -51 and -26 $cm^{-1}$ are found for methane above and below the ring of the anti conformer.

In order to perform the usual LJ cluster potential energy geometry search calculations for the allylbenzene solvent clusters, a geometry for the allylbenzene portion of the cluster must be assumed. Conformer **6a** is chosen for the allylbenzene minimum energy conformer; arguments in favor of this choice are presented in the Discussion Section and are consistent with the aforementioned spectra. Potential energy calculations for AB$(CH_4)_1$ yield the five cluster geometries illustrated in figure 6. Cluster binding energies are also presented in this figure. For only two of these geometries is the methane molecule coordinated directly to the aromatic π-system of the ring. These two structures are analogous to those observed for propylbenzene $(CH_4)_1$) and presumably are responsible for the 47 cm$^{-1}$ (above the ring) and 22.[illegible] cm$^{-1}$ (below the ring) red shifted features in figure 5.

The remaining three structures in figure 6 all involve coordination to the π-system of the allyl group. Such coordination should have a minimal effect on the energy of the $\pi^* \leftarrow \pi$ transition of the ring π system; therefore at least one of these three remaining cluster geometries must be responsible for the feature at 37177.0 cm$^{-1}$ in figure 5.

## C. Allylbenzene/Ethane

The TOFMS of the allylbenzene$(C_2H_6)_1$ van der Waals cluster $0^0_0$ region is presented in figure 7. The most intense feature of this spectrum occurs at 37489.8 cm$^{-1}$ and is red shifted from the allylbenzene origin by only 2.8 cm$^{-1}$. Some of the other features present in figure 7 occur at 37418.8, 37451.0, 37499.1 and 37512.4 cm$^{-1}$ with corresponding shifts from the allylbenzene origin of -73.8, -41.6, 6.5 and 19.8 cm$^{-1}$.

LJ potential energy calculations of allylbenzene$(C_2H_6)_1$ yield nine separate cluster geometries; these are depicted in figure 8$^a$ and figure 8$^b$. The first four of these are the familiar "perpendicular" and "parallel" configurations of the ethane molecule over the benzene ring, and have been observed for ethane coordinated to benzene[17] and propylbenzene[13]. The "perpendicular" and "parallel" configurations of the benzene$(C_2H_6)_1$ cluster produce **red shifts of the** $6^1_0$ transition of 57.2 and 30.8 cm$^{-1}$, respectively. Thus **these cluster** geometries for allylbenzene$(C_2H_6)_1$ clusters are most likely **responsible for** the features at 37418.8 and 37451.0 cm$^{-1}$ (red shifts of 73.8 and 41.6 cm) in figure 7.

The most intense features of the spectrum in figure 7 lie quite close to the allylbenzene origin. Such small red shifts are to be expected for clusters in which the aromatic π-system of the ring is not coordinated or solvated.[13]

The features at 37429.8, 37499.1 and 37512.4 cm$^{-1}$ in figure 7 are therefore most likely due to the coordination of the ethane molecule to the π-system of the allyl substituent.

### D. Allylbenzene/Water.

Figure 9 depicts the TOFMS of allylbenzene$(H_2O)_1$ in the region of the allylbenzene $0_0^0$ transition. The first four intense features of the spectrum occur at 37523.5, 37540.4, 37577.7 and 37582.9 cm$^{-1}$, with corresponding blue shifts relative to the allylbenzene origin of 30.9, 47.8, 85.1 and 90.3 cm$^{-1}$. LJ potential energy calculations reveal four separate allylbenzene$(H_2O)_1$ configurations, as shown in figure 10. Two of these involve the coordination of the water molecule to the aromatic π-system above and below the ring. A cluster of similar geometry produces an 84.6 cm$^{-1}$ blue shift of the $0_0^0$ transition in benzene.[18] The features in figure 9 which are blue shifted from the allylbenzene origin by 85.1 and 90.3 cm$^{-1}$ are therefore most likely due to the coordination of the water molecule to the π-system of the ring. The features which are blue-shifted by 30.9 and 47.8 cm$^{-1}$ are presumably due to coordination of the water molecule to the π-system of the allyl group.

### E. Allylbenzene/Ammonia.

The TOFMS of the $0_0^0$ transition of allylbenzene$(NH_3)_1$ is presented in figure 11. Intense features occur at 37490.6, 37542.7 and 37566.3 cm$^{-1}$ shifted by -2.0, +50.1 and +73.7 cm$^{-1}$, respectively from the origin of allylbenzene. LJ *potential* ***energy*** *calculations predict the existence the four cluster configurations* **illustrated** in figure 12. As for water, two of these clusters involve coordination of the ammonia molecule to the π-system of the ring, while the other two involve ammonia coordination to the π- system of the allyl group. The TOFMS of ammonia coordinated to benzene is complex and difficult to interpret,[18] but an assignment of these data has been presented.[18] The red-most feature in the TOFMS is 100 cm$^{-1}$ to lower energy of the benzene $0_0^0$ transition. Other data for ammonia coordinated to alkyl-substituted benzenes are not presently available.

An ammonia molecule coordinated directly over the π-system of the aromatic ring of allylbenzene would unlikely produce only a 2 cm$^{-1}$ red shift of the cluster $0_0^0$ transition. Since solvation of or coordination to the aromatic ring π-system typically produces the largest cluster (red or blue) shifts, we assign the features in figure 11 which are blue shifted 50.1 and 72.7 cm$^{-1}$ from the allylbenzene origin to transitions belonging to clusters in which the ammonia is positioned directly over the ring. The 2.0 cm$^{-1}$ red shifted feature is most likely due to a cluster in which the ammonia molecule is directly coordinated to the allyl substituent.

## IV. Discussion.

### A. Allylbenzene Conformation.

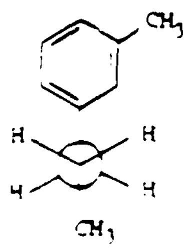
In previous studies, we have demonstrated that laser jet spectroscopy can be employed to observe stable conformational isomers, even if the energy barriers for conformational interconversion are very low[1-6]. In each spectrum, the origin transition is associated with a specific stable ground state conformation; conversely, each stable conformation corresponding to a potential energy minimum generates, at least in principle, its own spectroscopic $0_0^0$ transition. Hence, by examining the spectra of specifically substituted allylbenzenes, one can in principle "count" the number of stable ground state conformations and thereby establish their molecular geometries.[1-7] For allylbenzenes, this may lead to a distinction between **5** and **6**/**7**, or the possible presence of both in the jet.

As shown in figure 4, a variety of stable conformations can be proposed for **1-3**; however, only conformations for which the allyl substituent is essentially perpendicular to the plane of the benzene ring are considered in this discussion, since MOMM calculations indicate $\tau_1 \sim 90°$. Moreover, such orientations are found experimentally and theoretically to be the energy minima for all other arylprimary alkyl (Ar-$CH_2$-R) compounds (e.g., ethyl, propyl, isobutyl, neopentyl, etc.)[1,3,4,15,22] The MOMM results point to **5** and **6**,**7** as stable ground state conformations.

Since only a single origin transition is observed for **1**, either **5a** or **6a** but not both conformations obtain for allylbenzene; analogously, only **5** or the 'mixture' of [**6** and **7**] obtains for **2** and **3**. To distinguish between these possibilities, we have utilized these asymmetrically substituted allylbenzenes following the strategy employed previously by us to uncover the minimum energy conformations of alkyl and methoxy substituted benzenes.[1-6]

Consider 1-allyl-2-methylbenzene **2**: the TOFMS of this compound would contain only one origin transition if conformation **5b** were the energy minimum, while conformations **6b** and **7b** would yield two distinct origins. Since the actual TOFMS of 1-allyl-2-methylbenzene, presented in figure 3, contains two origins, at 37179.5 and 37250.8 cm$^{-1}$, conformation **5c** is ruled out. Thus conformations **6c** and **7c** are assigned as the stable conformations of **2**.

Similar logic obtains for 1-allyl-3-methylbenzene (**3**). As shown in figure 2 and discussed above, two origin transitions are observed and assigned as **6c** and **7c**. Although we have made assignments linking specific conformations with individual transitions for other systems, as in the case of the anti **8** and two gauche **9a** and **9b** conformations observed for propylbenzene[3], we cannot at this time assign the individual transitions observed for **2** and **3** to specific conformations **6** or **7**.



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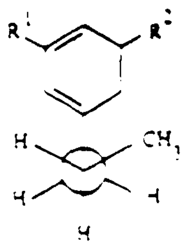

9a. $R^1$ = H $R^2$ = $CH_3$

9b. $R^1$ = $CH_3$ $R^2$ = H

## B. Allylbenzene Clusters

The π-system of the double bond in allylbenzene can and does compete effectively with the π-system of the aromatic ring to coordinate incoming solvent molecules. Coordination with this olefinic π-system results in stable clusters with various solvent molecules. In addition, the geometries of clusters in which the solvent molecule is coordinated to the ring are influenced by the double bond of the allyl group, which tends to pull the solvent molecule to the allyl side of the ring. Thus, the early (and perhaps later) stages of nucleation and solvation of olefin-substituted benzene derivatives may well differ substantially from those of alkane-substituted benzene derivatives.

Allylbenzene water and ammonia clusters for which the solvent is coordinated to the aromatic ring apparently generate blue shifted $0_0^0$ transitions with respect to the allylbenzene isolated molecule. This excited state reduced binding energy is probably related in the fact that these solvent molecules contain lone pairs of electrons which can destabilize the $\pi^*$ state of the ring relative to the ground state. Very similar behavior is found and characterized for other aromatic systems.[12,13,17,18,19]

Finally, the fact that the coordination of solvent molecules to the allyl substituent generally has only minor effects on the energy of the ring $\pi^* \leftarrow \pi$ transition indicates that the two π-electronic systems are indeed reasonably isolated from each other

## V. Conclusions.

We have observed spectra of the isolated allylbenzenes **1**-**3** and allylbenzene itself solvated by various small molecules ($CH_4$, $C_2H_6$, $NH_3$, $H_2O$). Based on both spectroscopic and theoretical results the ground state energy minimum geometry of isolated allylbenzene is determined to be **6a** (= **7a**). For **2**, conformations **5a** and **6b** are found to be the ground state energy minima. Similarly, for **3**, conformations **5c** and **6c** are the ground state energy minima. Allylbenzene clusters appear to have two very distinct types of spectra: those well shifted (red or blue) from the comparable allylbenzene feature and those relatively near the comparable allylbenzene feature. The former spectra we have associated with clusters in which the solvent is directly coordinated to the aromatic ring and the latter spectra we have associated with clusters in which the solvent is coordinated to the allyl group $\pi$-system, well removed from the ring and the $\pi^* \leftarrow \pi$ transition. Solvation does not appear to disrupt in any way the conformation of the isolated allylbenzene molecule, as the spectral shifts characterized for the clusters are all relatively small and well within the range found for other simple aromatic systems. And finally, since much of the cluster spectroscopic intensity seems to be found in features associated with allyl group direct solvation (origin features with small cluster shifts), we suggest that the allyl $\pi$-system has a significant influence upon how allylbenzene interacts with and is solvated by small solvent molecules.

**Acknowledgments.** We thank J. Kao for providing the STO-3G results and for developing and making available the MOMM-85 algorithm and associated CHMLIB software, R. Ferguson, B. LaRoy, and A. C. Lilly for helpful discussions and support, and Professor Paul v. R. Schleyer for providing the MNDO and AM1 results and for helpful discussions. Parts of this effort were supported by ONR.

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10a. The name "one (and two) color time of flight mass spectroscopy" is generally employed to describe the following experiment. A sample is irradiated with a laser of energy $\nu_1$, resulting in the generation of the first excited singlet state ($S_1 \leftarrow S_0$). A second photon $\nu_2$ subsequently ionizes those molecules in $S_1$ ($S_1 \rightarrow I^+$). The ions are detected in given mass channels by time of flight mass spectroscopy, such that only ion current representing a chosen $\underline{m}/\underline{z}$ is recorded. The energy of the $\nu_1$ laser is changed, and a mass selected excitation spectrum is obtained.

b. In early pioneering work, Smalley and coworkers[11a,11b] and Ito and coworkers[11c-11e] have reported the fluorescence excitation (FE) spectra and dispersed fluorescence spectra of various aromatic compounds. Because FE results are not mass selected, ambiguity may exist regarding the source of some of the transitions.

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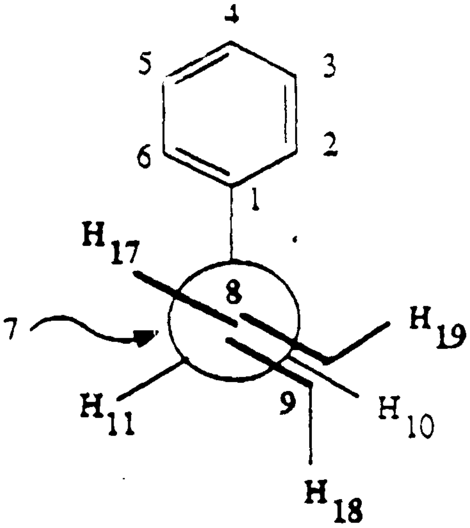
**23**. For allylbenzene, MNDO calculations reveal a minimum at $\tau_2 = 120^{\circ}$ and maxima at $\tau_2 = 0^{\circ}$ and $180^{\circ}$, while AM1 calculations reveal a global minimum at $\tau_2 = 140^{\circ}$, a less stable minimum at $\tau_2 = 0^{\circ}$ MOMM MNDO, and AM1 are reasonably consistent in that each predicts the energy minimum to be ca. $\tau_2 = 120^{\circ}$. We thank Professor Paul v.R. Schleyer for providing the MNDO and AM1 results.

## Table I

## Partial Electronic Charges for Allylbenzene[a]

| Atom[b] | q |
|---|---|
| 1 (C) | -0.01 |
| 2 (C) | -0.064 |
| 3 (C) | -0.060 |
| 4 (C) | -0.063 |
| 5 (C) | -0.060 |
| 6 (C) | -0.065 |
| 7 (C) | -0.106 |
| 8 (C) | -0.046 |
| 9 (C) | -0.128 |
| 10 (H) | 0.057 |
| 11 (H) | 0.059 |
| 12 (H) | 0.058 |
| 13 (H) | 0.057 |
| 14 (H) | 0.056 |
| 15 (H) | 0.057 |
| 16 (H) | 0.062 |
| 17 (H) | 0.059 |
| 18 (H) | 0.057 |
| 19 (H) | 0.055 |



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[a] From STO-3G calculations using the MOMM-85 derived energy minimum

[b] Other attached atoms, not shown in diagram, are 2-12, 3-13, 4-14, 5-15, and 6-16.

# Figure Captions

Figure 1 One-color TOFMS of the $0_0^0$ region $S_1 \leftarrow S_0$ for jet-cooled allylbenzene. The single intense feature is assigned as the origin and occurs at 37192.6 $cm^{-1}$. The weak features to higher energy of the origin are presumed to be due to torsional motion of the allyl group. The solitary origin demonstrates that only one molecular conformation exists as an energy minimum for this molecule.

Figure 2 One-color TOFMS of the $0_0^0$ region of $S_1 \leftarrow S_0$ for jet-cooled 1-allyl-3-methylbenzene. The spectrum contains two origins, at 36959.2 and 37066.9 $cm^{-1}$. The origins appear as doublets due to transitions between internal rotational states of the ring methyl group.

Figure 3 One-color TOFMS of the $0_0^0$ region of $S_1 \leftarrow S_0$ for jet-cooled 1-allyl-2-methylbenzene. The spectrum contains two intense features at 37179.5 and 37250.8 $cm^{-1}$ which are assigned as origins. The presence of two origins eliminates the conformation 5 as the correct geometry of the energy minimum.

Figure 4 MOMM-derived steric energy profile for allylbenzene for rotation about $\tau_2$.

Figure 5 Two-color TOFMS of the $0^0_0$ region of $S_1 - S_0$ for jet-cooled allylbenzene$(CH_4)_1$. The three intense peaks occur at [illegible] [illegible] and 15 $cm^{-1}$ to lower energy of the allylbenzene origin and are due to three different cluster configurations.

Figure 6 Minimum energy cluster configurations and binding energies for allylbenzene$(CH_4)_1$ obtained from the Lennard-Jones potential energy calculation.

Figure 7 Two-color TOFMS of the $0^0_0$ region of $S_1 - S_0$ for jet-cooled allylbenzene$(C_2H_6)_1$. The intense features centered around 37500 $cm^{-1}$ are within 20 $cm^{-1}$ of the allylbenzene origin and are due to clustering of the ethane molecule on the allyl substituent.

Figure 8 Minimum energy configurations and binding energies for allylbenzene$(C_2H_6)_1$ obtained from LJ potential calculations. (A) Complexation of ethane with aromatic $\pi$-system. (B) Complexation of ethane with olefin $\pi$-system.

Figure 9 Two-color TOFMS of the $0^0_0$ region of $S_1 - S_0$ for jet-cooled allylbenzene$(H_2O)_1$. The spectrum contains four intense features at 37523.5, 37540.4, 37577.7 and 37582.9 $cm^{-1}$ corresponding to four different cluster configurations.

Figure 10 Minimum energy configurations and binding energy for allylbenzene$(H_2O)_1$ obtained from LJ potential calculations.

Figure 11 Two-color TOFMS of the $0_0^0$ region of $S_1 \leftarrow S_0$ for jet-cooled allylbenzene$(NH_3)_1$. The intense features at 37490.8, 37532.7 and 37566.3 $cm^{-1}$ are due to different cluster configurations.

Figure 12 Minimum energy configurations and binding energies for allylbenzene$(NH_3)_1$ obtained from LJ potential calculations.

TOFMS of allylbenzene

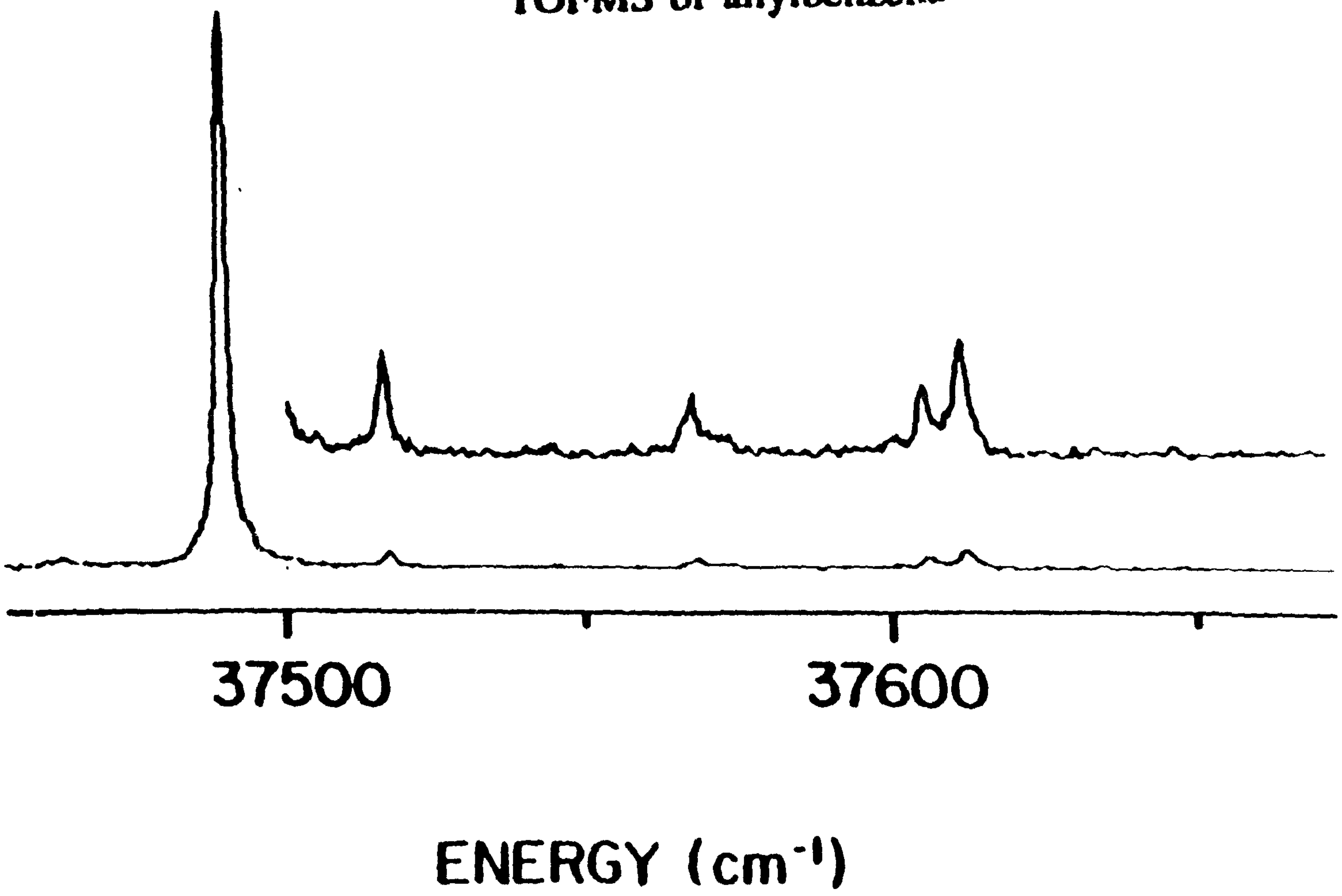


Figure 1

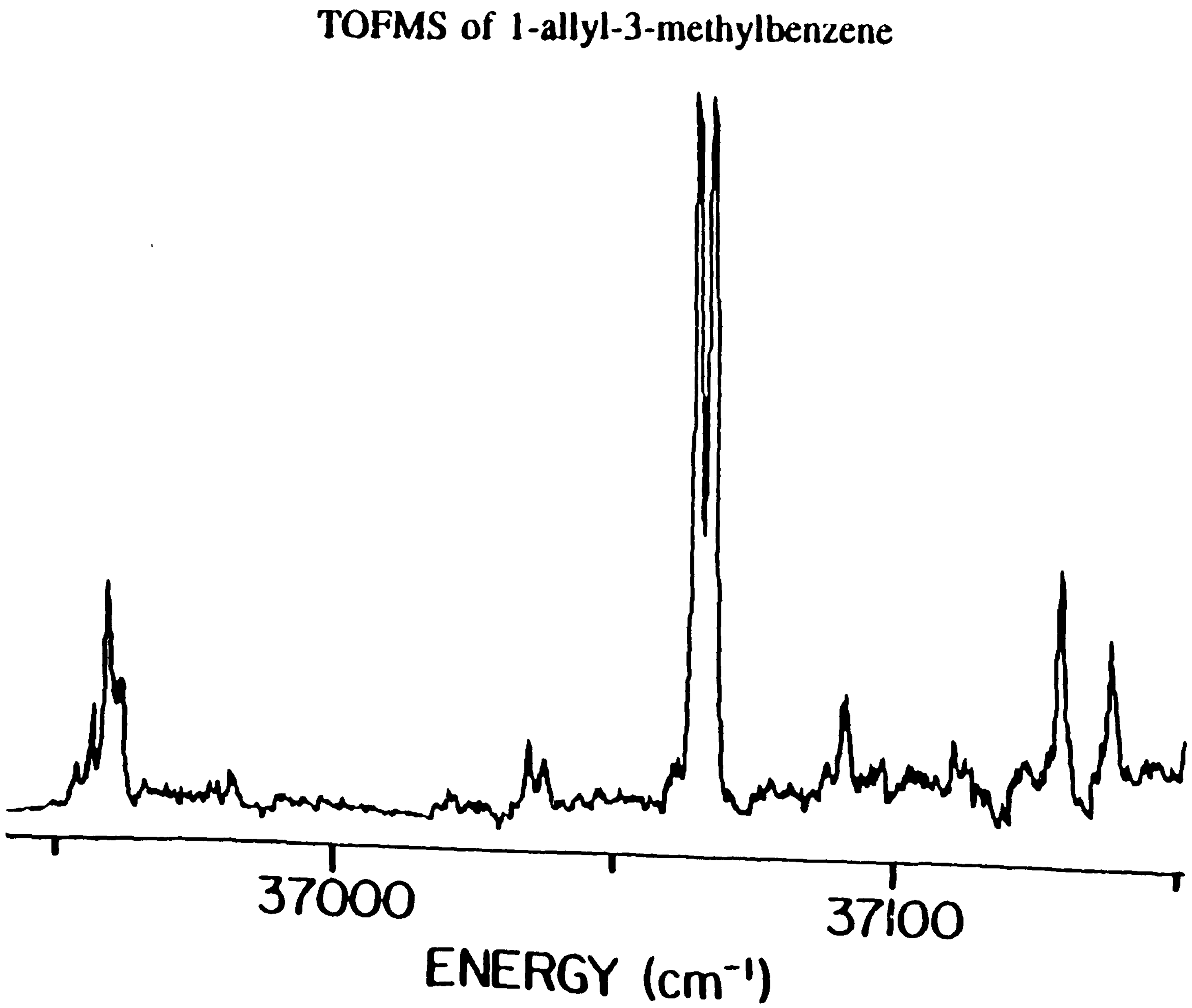


Figure 2

TOFMS of 1-allyl-2-methylbenzene

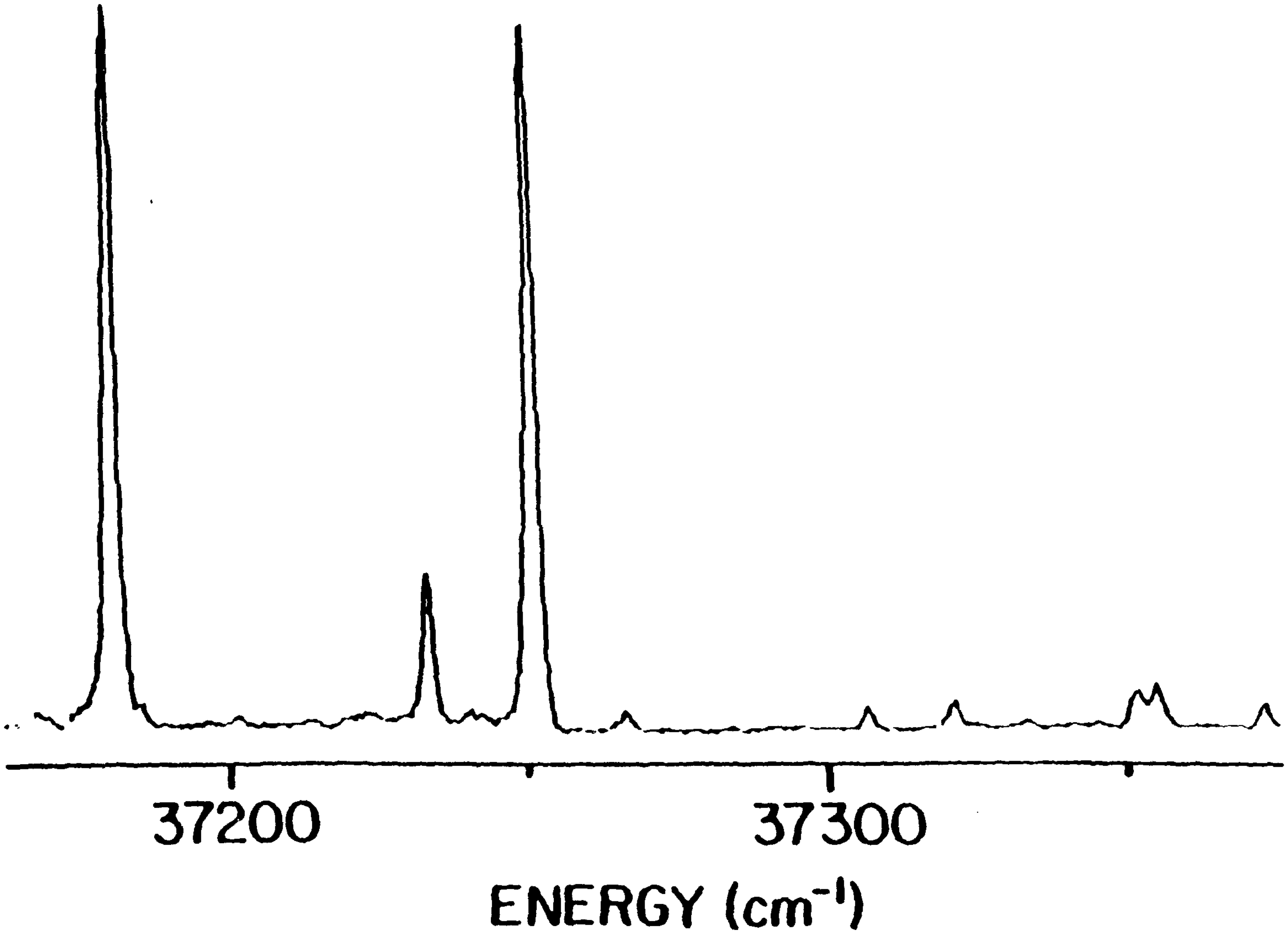


Figure 3

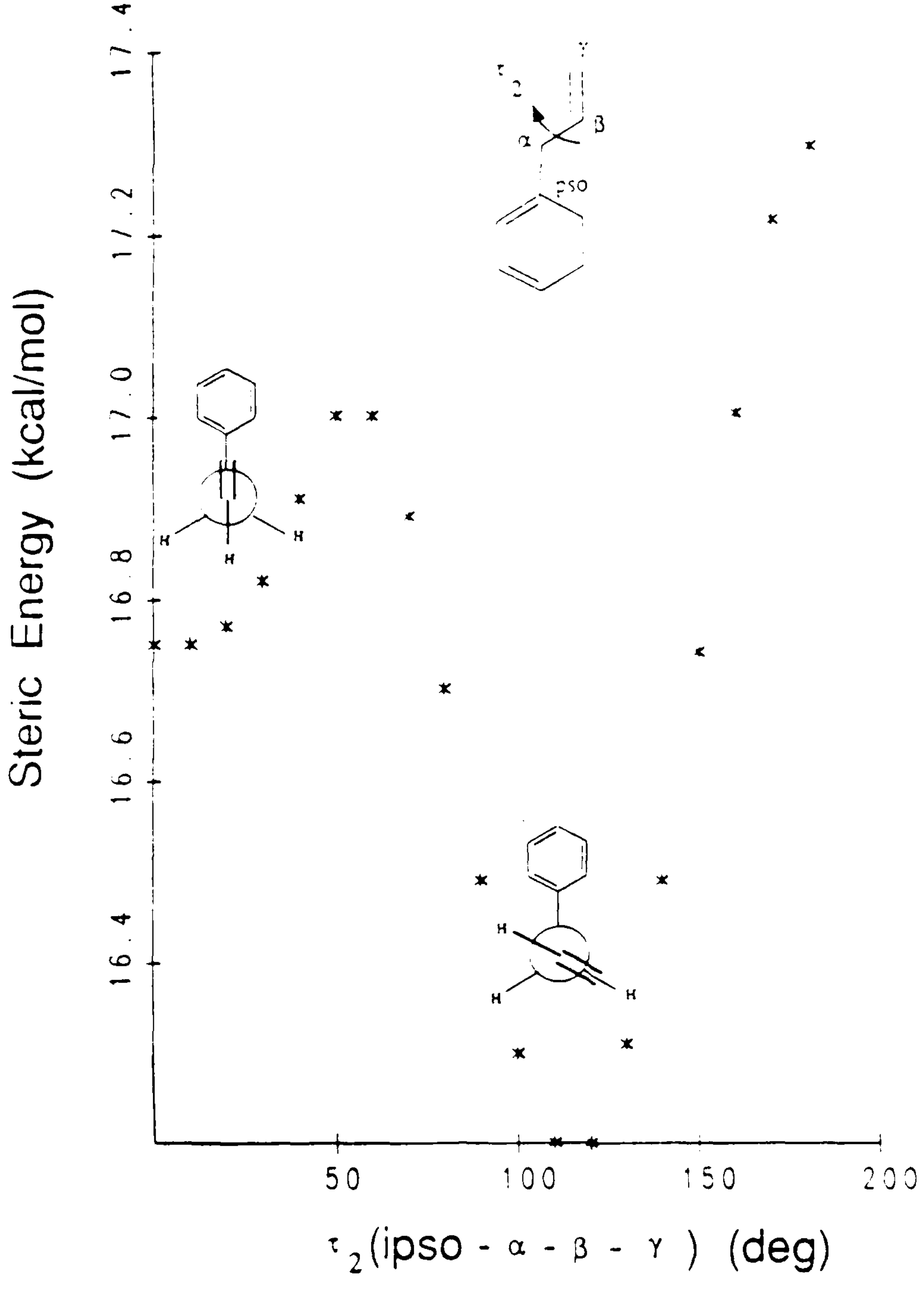

Steric Energy (kcal/mol)
16.4
16.6
16.8
17.0
17.2
17.4
50
100
150
200
τ2(ipso - α - β - γ) (deg)
τ2
α
β
γ
ipso
H
H
H
H
H
H

Figure 4

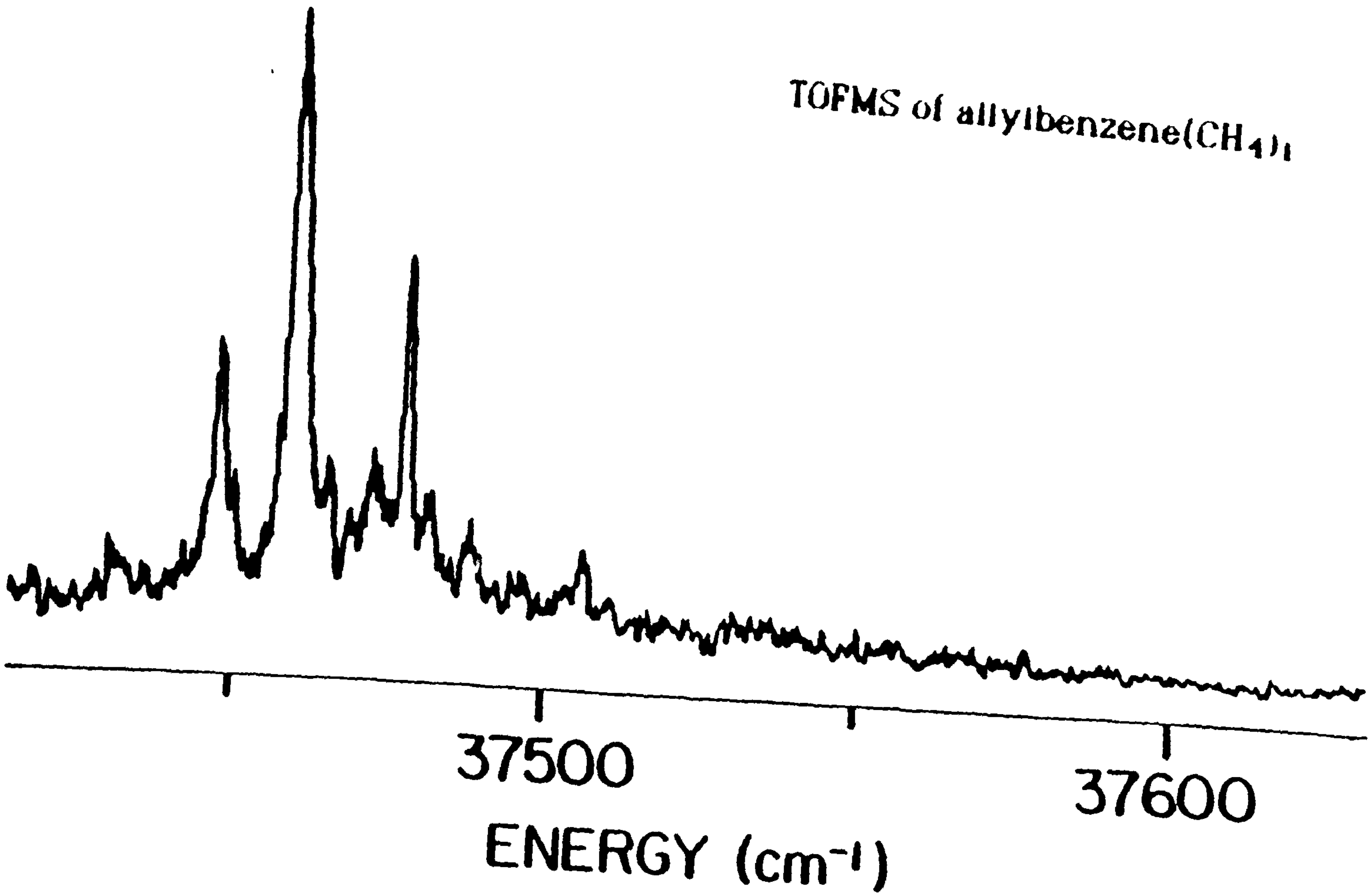


Figure 5

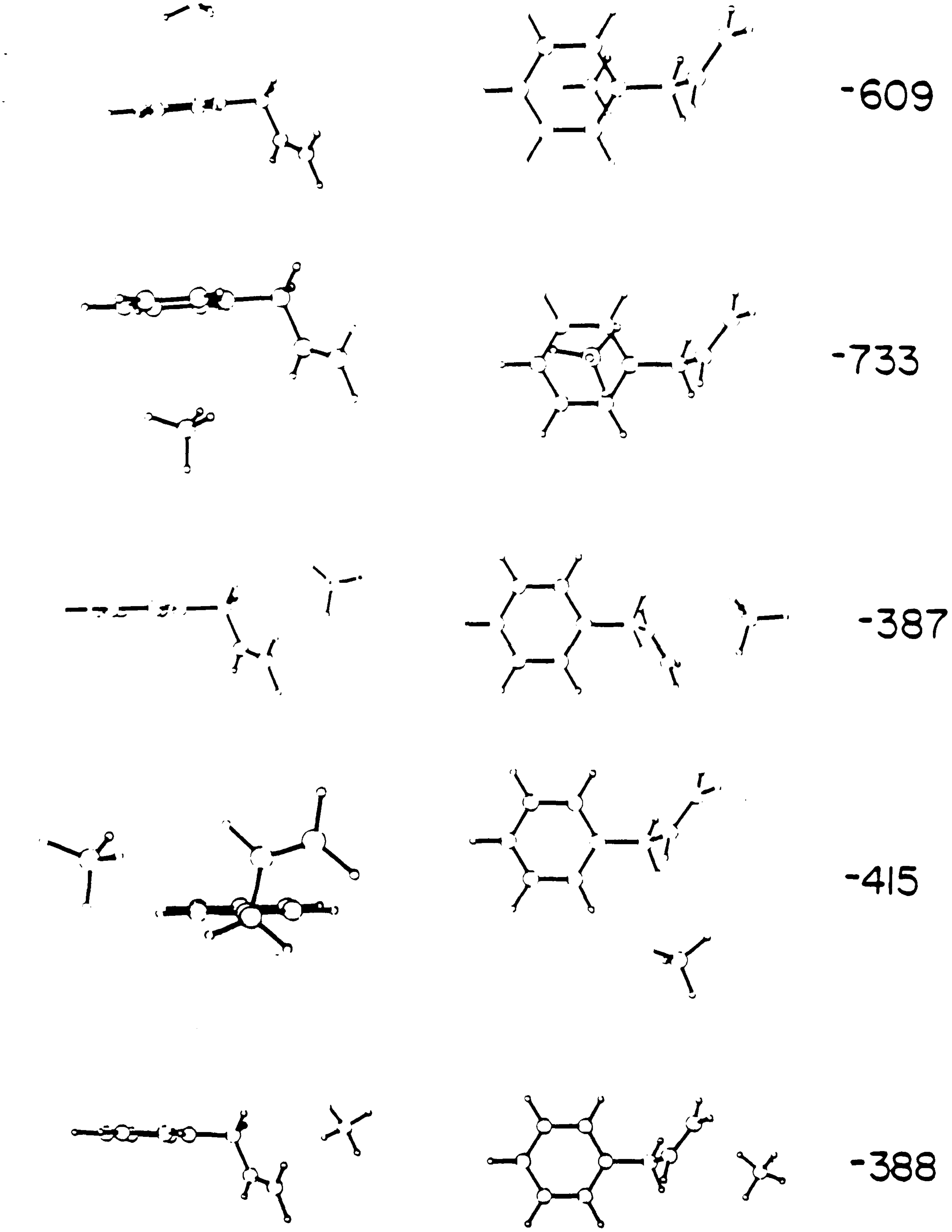


Figure 6

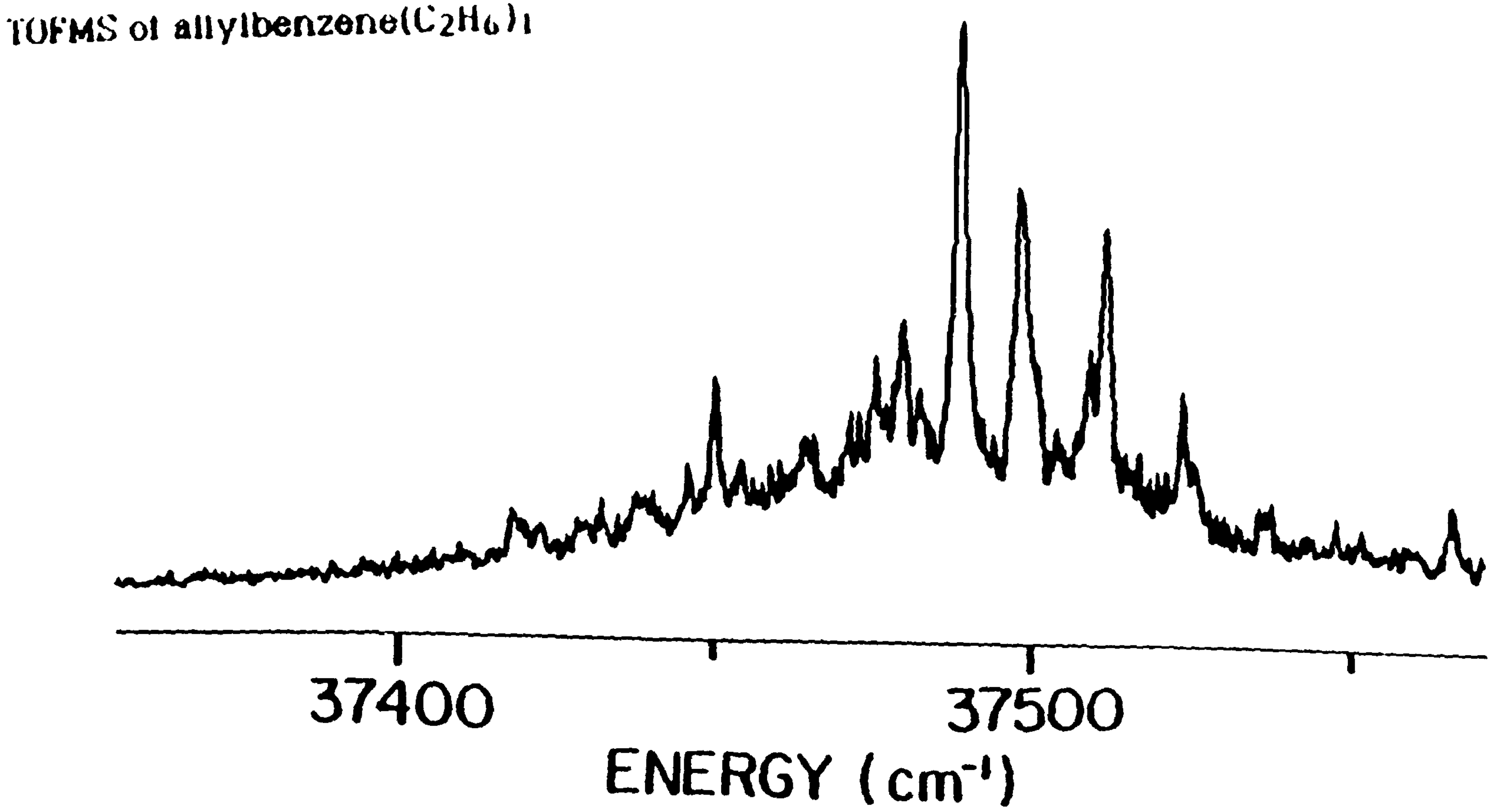


Figure 7

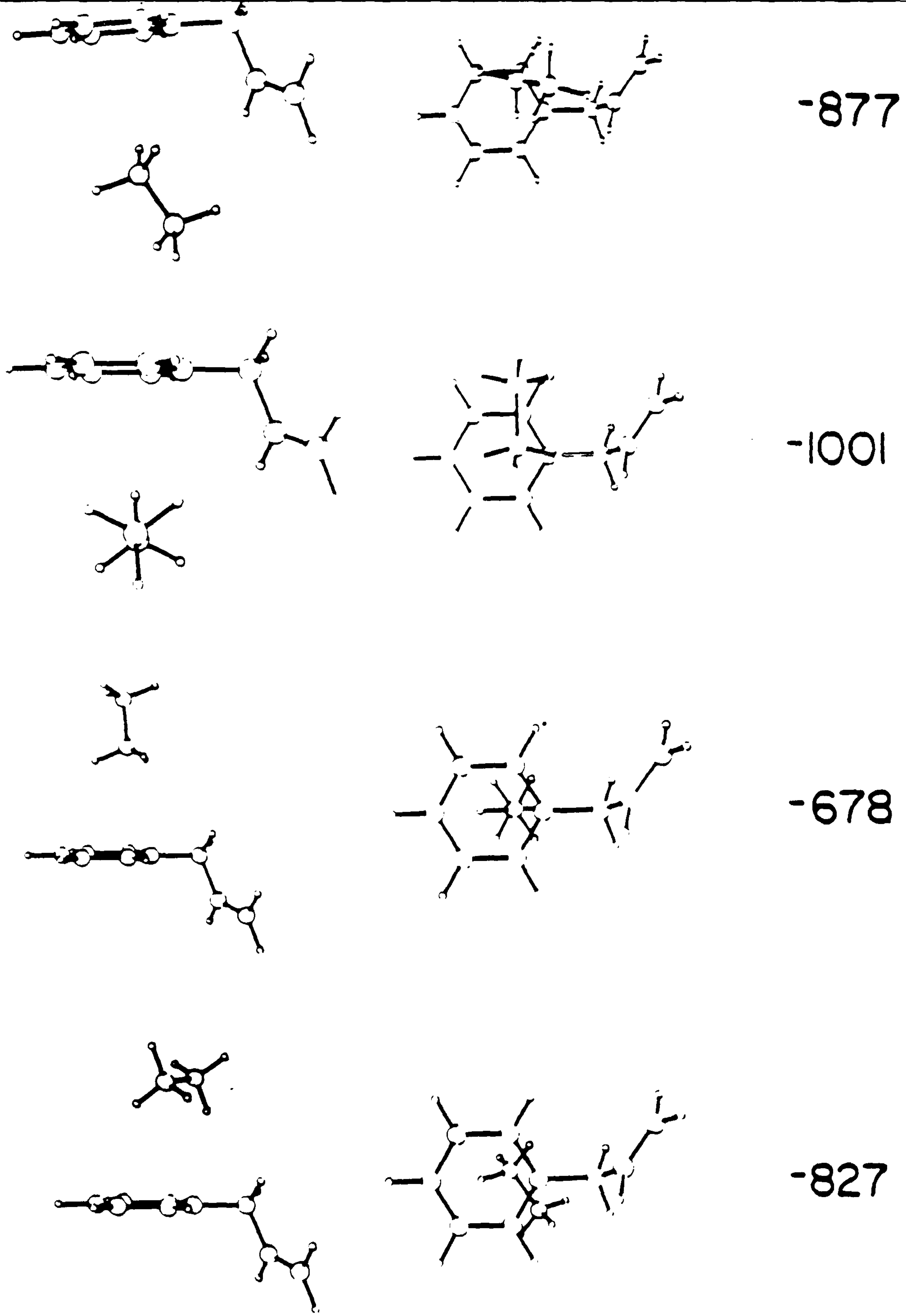


Figure 8a

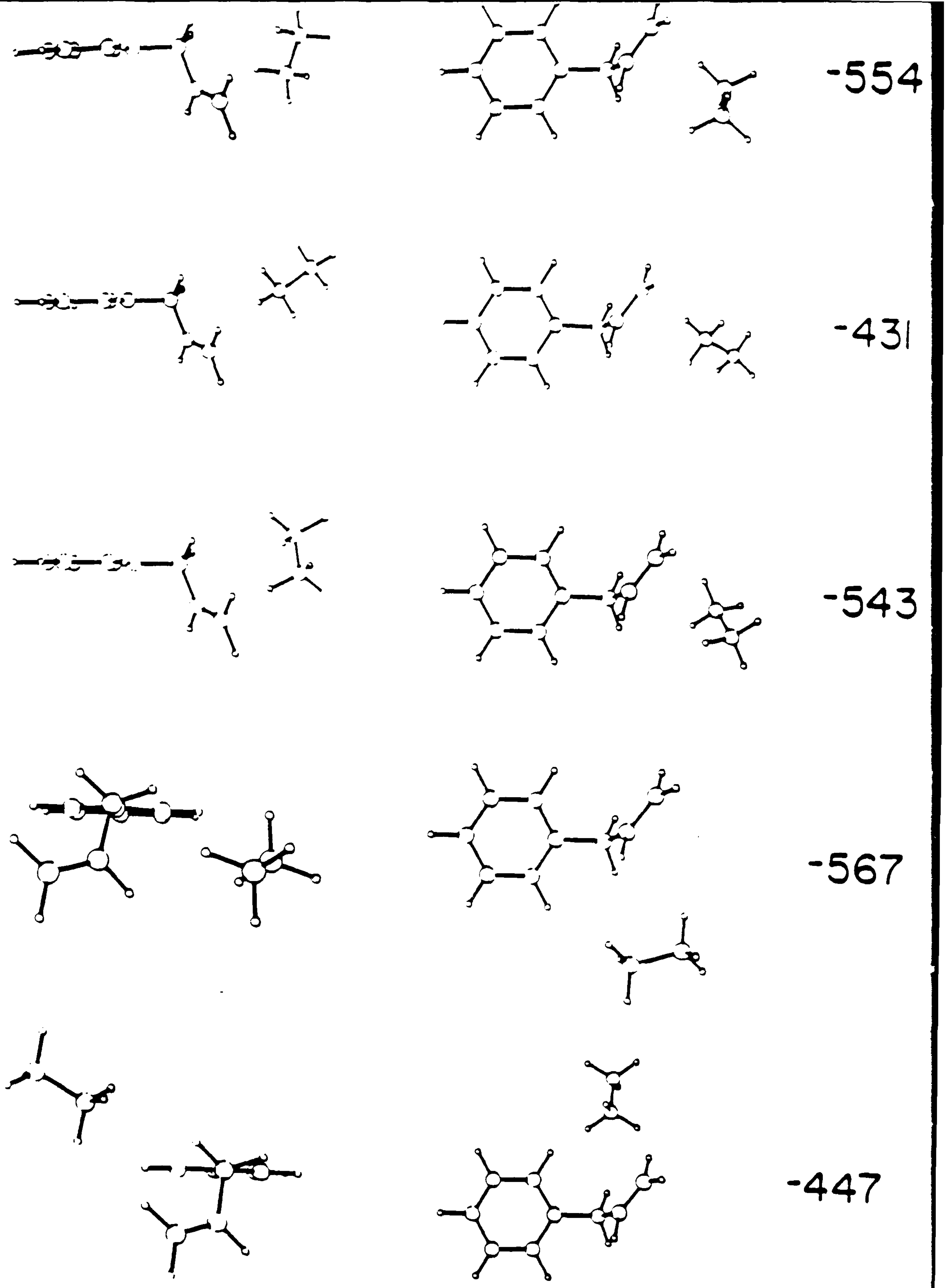
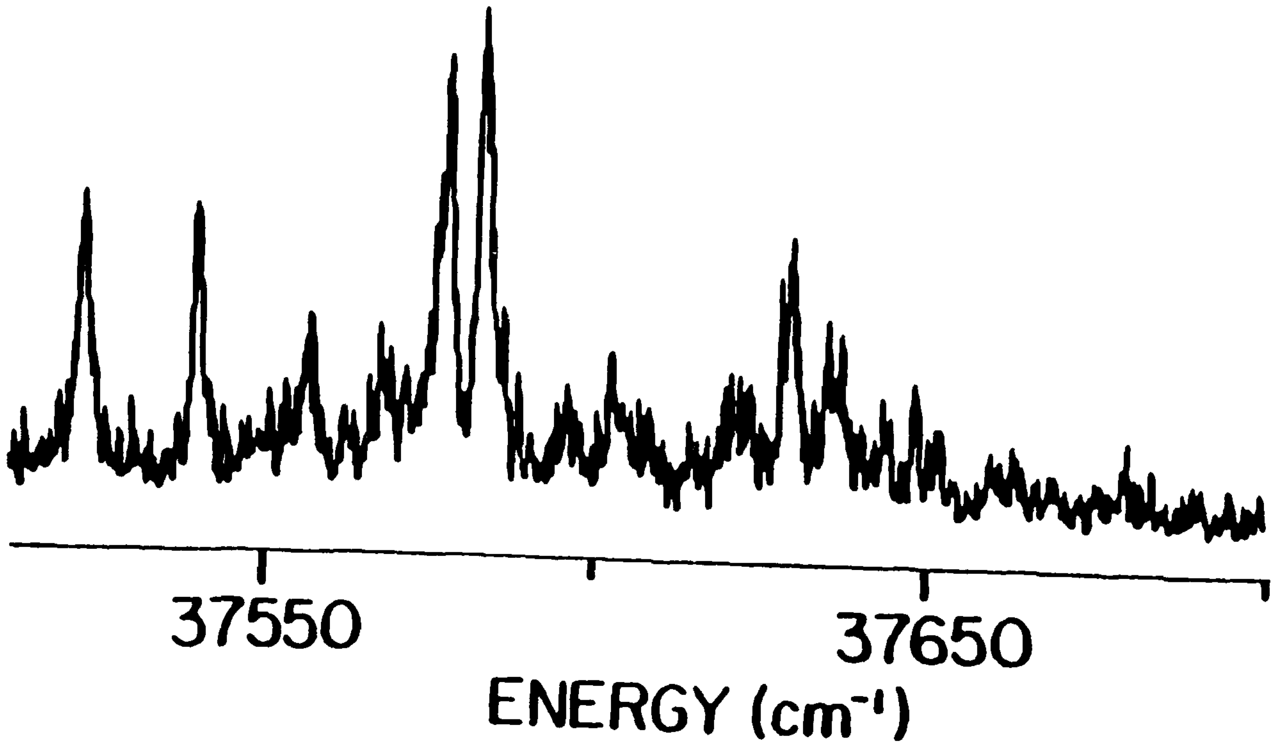


Figure 8b



TOFMS of allylbenzene($H_2O$)$_1$

Figure 9

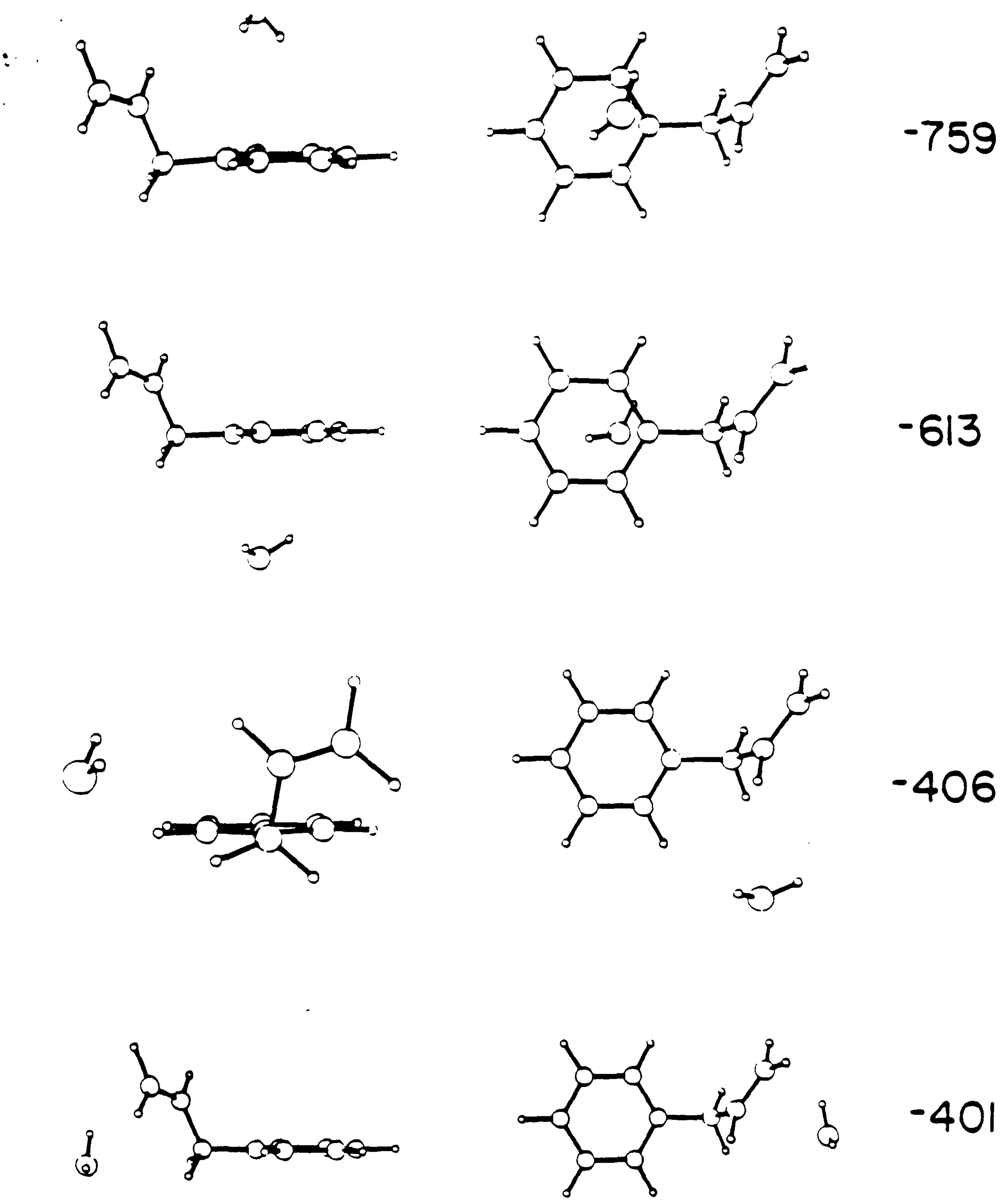


Figure 10

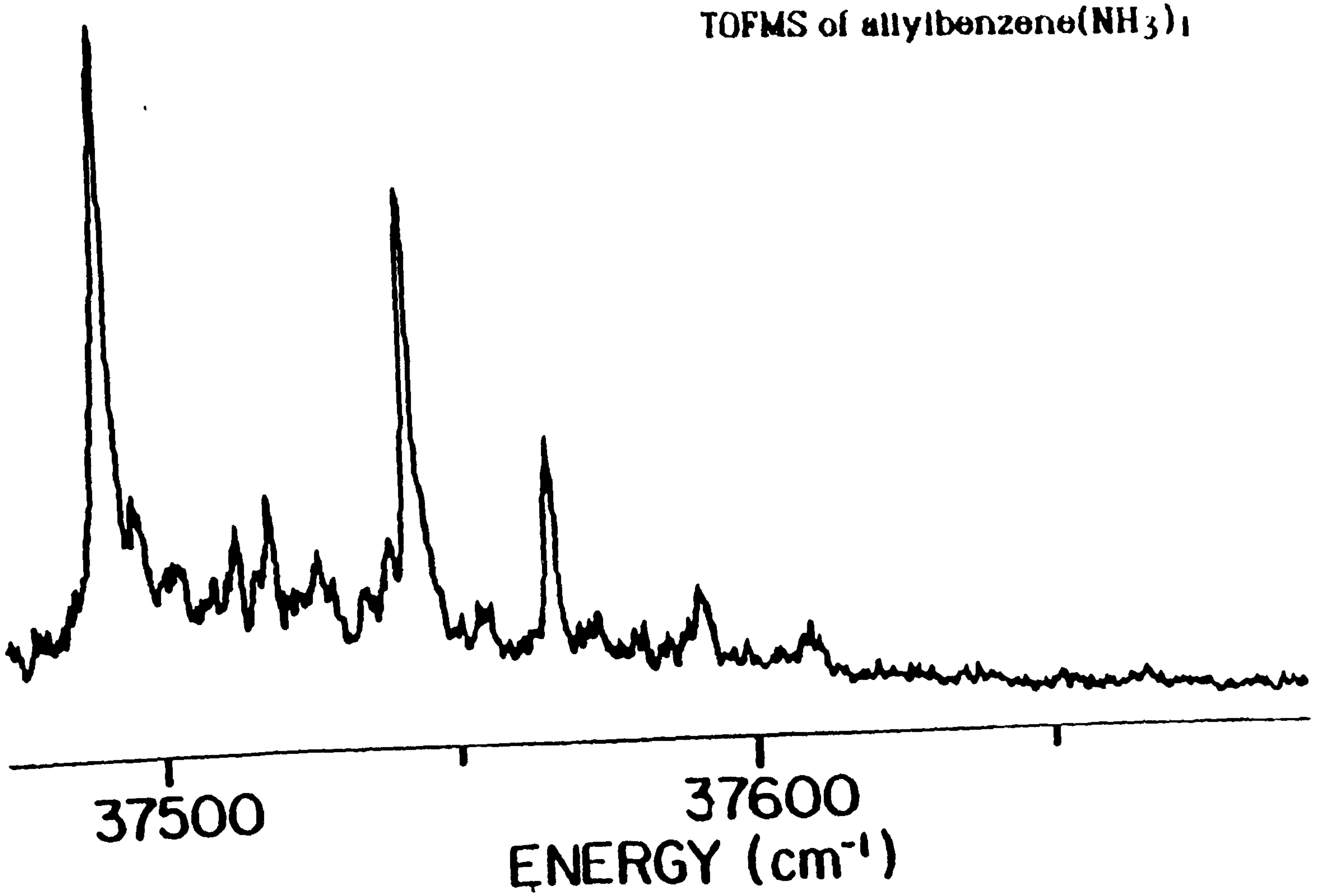

TOFMS of allylbenzene$(NH_3)_1$

Figure 11

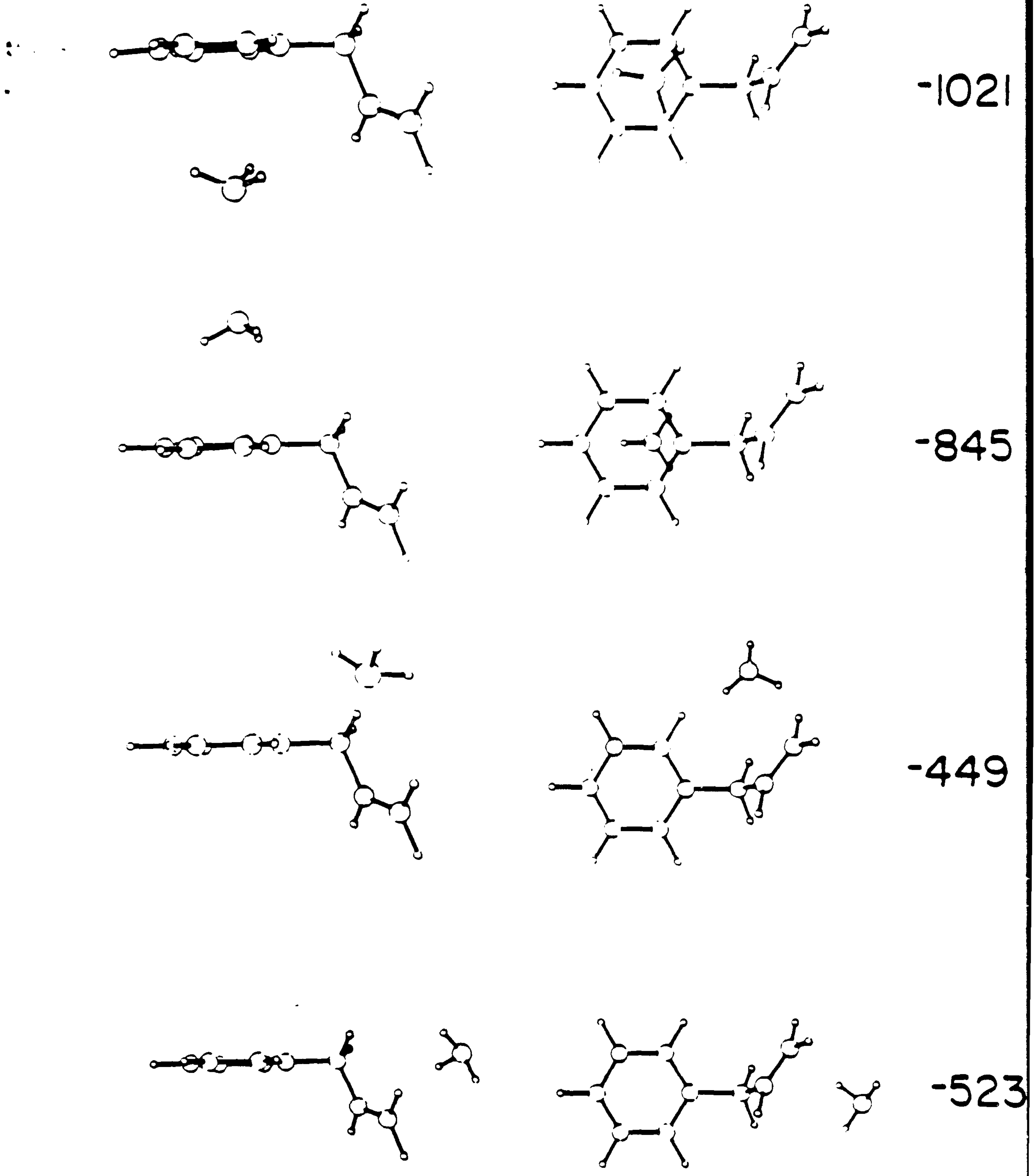


Figure 12

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