

Indeed, in certain instances the less active enantiomer may even possess undesirable properties.<sup>20</sup> Thus, enantiomeric purity is an important criterion for establishing the pharmaceutical acceptability of such drugs.

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**Registry No.** I, 92984-07-1; II, 92984-08-2; IV, 67492-08-4; *dl*-phenylethanolamine, 1936-63-6; (*R*)-phenylethanolamine, 2549-14-6; (*S*)-phenylethanolamine, 56613-81-1; *dl*-phenylpropanolamine, 14838-15-4; 1(*R*),2(*S*)-(-)-phenylpropanolamine, 492-41-1; 1(*S*),2(*R*)-(+)-phenylpropanolamine, 37577-28-9; *dl*-pseudophenylpropanolamine, 54680-46-5; 1(*R*),2(*R*)-(-)-pseudophenylpropanolamine, 37577-07-4; 1(*S*),2(*S*)-(+)-pseudophenylpropanolamine, 492-39-7; *dl*-norepinephrine, 138-65-8; (*R*)-(-)-norepinephrine, 51-41-2; (*S*)-(+)-norepinephrine, 149-95-1; *dl*-nordefrin, 74812-63-8; 1(*R*),2(*S*)-(-)-nordefrin, 829-74-3; 1(*S*),2(*R*)-(+)-nordefrin, 829-75-4; *dl*-normetanephrine, 709-52-4; (*R*)-normetanephrine, 2282-53-3; (*S*)-normetanephrine, 35778-41-7; *dl*-1-amino-2-propanol, 1674-56-2; (*R*)-(-)-1-amino-2-propanol, 2799-16-8; (*S*)-(+)-1-amino-2-propanol, 2799-17-9; *dl*-valinol, 16369-05-4; (*R*)-(-)-valinol, 4276-09-9; (*S*)-(-)-valinol, 2026-48-4; *dl*-alaninol, 6168-72-5; L-proline, 2812-46-6;  $\omega$ -undecenal, 112-45-8; dimethylchlorosilane, 1066-35-9; copper, 7440-50-8.

## Photoelectron Spectroscopy of the Allylic Anion

John M. Oakes and G. Barney Ellison\*

Contribution from the Department of Chemistry, Campus Box 215, University of Colorado, Boulder, Colorado 80309. Received June 8, 1984

**Abstract:** We have examined the photodetachment spectra of the allylic anion ( $\text{CH}_2\text{CHCH}_2^-$ ) and two of its deuterated isotopes,  $\text{CH}_2\text{CDCH}_2^-$  and  $\text{CD}_2\text{CDCD}_2^-$ . The electron affinities (EA) of the corresponding allyl radicals are  $\text{EA}(\text{CH}_2\text{CHCH}_2) = 0.362 \pm 0.020$  eV,  $\text{EA}(\text{CH}_2\text{CDCH}_2) = 0.373 \pm 0.020$  eV, and  $\text{EA}(\text{CD}_2\text{CDCD}_2) = 0.381 \pm 0.026$  eV. The photoelectron spectra of these ions show only one active vibronic mode which we assign as the in-plane C-C-C bend. This leads us to conclude that the anion has a planar, symmetric  $C_{2v}$  geometry. Computational modeling yields a geometry for the  $\text{CH}_2\text{CHCH}_2^-$  ion with a C-C-C bond angle  $16^\circ$  greater than that of the allyl radical.

Almost since radicals have been known to exist, the allyl radical ( $\text{CH}_2\text{CH}=\text{CH}_2$ ) has been of fundamental interest to chemists because it is the simplest of conjugated hydrocarbon radicals. For this reason much work has been done to study its thermochemistry and spectroscopy, in addition to a great deal of theoretical effort directed at understanding its electronic structure. The geometry of the allyl radical is qualitatively understood from electron spin resonance (ESR) studies<sup>1-3</sup> and matrix infrared absorption spectra of this important hydrocarbon. All experimental and theoretical studies of allyl radical find it to be a planar molecule with  $C_{2v}$  symmetry. A detailed computational study of its geometry and vibrational spectrum has been published recently.<sup>4</sup> The electron affinity has been reported<sup>5</sup> for the allyl radical in an ion cyclotron resonance (ICR) threshold photodetachment experiment, but this is in slight disagreement with flowing afterglow results.<sup>6-8</sup>

The corresponding anion ( $\text{CH}_2=\text{CHCH}_2^-$ ) has also generated much study. Of fundamental interest is the question of whether the geometry of the allylic anion still has  $C_{2v}$  symmetry. Earlier studies<sup>9</sup> have focused on a related simple organic radical which is a flat, symmetric, resonance stabilized molecule, the propargyl radical ( $\text{CH}_2-\text{C}\equiv\text{CH}$ ). It is found that the corresponding ion,

$\text{CH}=\text{C}=\text{CH}^-$ , is a nonplanar molecule and not conjugatively stabilized. Rather little is known about the structure of the allylic anion. There is some chemical evidence that the two ends of the negative ion behave similarly in the gas-phase experiments.<sup>10</sup> This would lead one to suspect it still has a symmetric,  $C_{2v}$  structure. Theoretical structural studies have predicted both planar and nonplanar structures. A multiphoton infrared photodetachment study has recently been made of this ion as well.<sup>11</sup>

Using negative ion photoelectron spectroscopy,<sup>12,13</sup> we have studied the allylic anion ( $m/z$  41) using both propene and 1,5-hexadiene as ion precursors. We have also studied two deuterium-substituted isomers,  $\text{CH}_2\text{CDCH}_2^-$  ( $m/z$  42) and  $\text{CD}_2\text{CDCD}_2^-$  ( $m/z$  46), from the corresponding propenes. From the appearance of the photoelectron spectrum of the allylic ion and by comparison to those of the two deuterated isomers, we conclude that the allylic anion retains its planar,  $C_{2v}$  structure. The major structural change observed is the opening of the skeletal C-C-C bond angle. Our analysis quantifies this geometry change and also yields a refined electron affinity of  $\text{CH}_2=\text{CH}-\text{CH}_2$ .

### Experimental Section

The negative ion photoelectron spectrum is obtained by intersecting a mass-selected ion beam with a laser of fixed frequency ( $h\nu_0$ ) and determining the distribution of kinetic energy (KE) for the detached electrons  $\text{M}^- + h\nu_0 \rightarrow \text{M} + \text{e}^-$  (KE). Although the photoelectron

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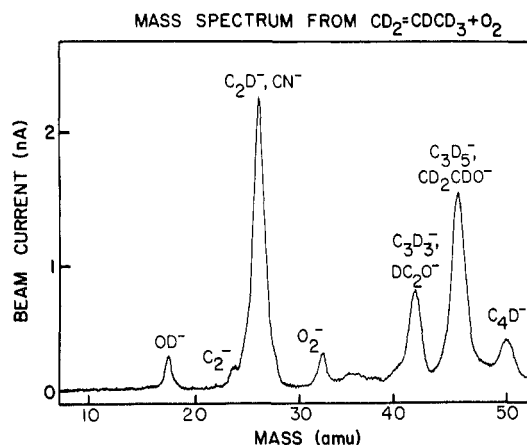


Figure 1. Negative ion mass spectrum resulting from a mixture of  $\text{CD}_2=\text{CD}-\text{CD}_3/\text{O}_2$ .

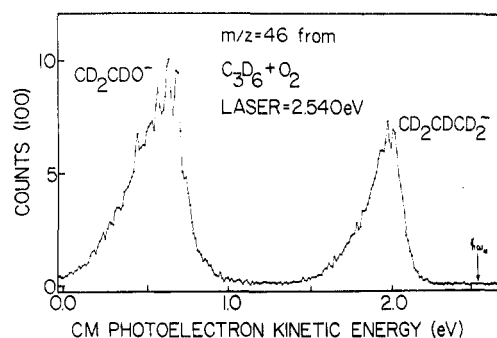


Figure 2. A survey photoelectron spectrum of the  $\text{C}_3\text{D}_5^-$  ion (roughly 11 meV between data points). The center of mass (CM) photoelectron kinetic energy of the scattered electrons is plotted against the total number of electron counts.

spectrometer used in this experiment has been described in detail previously,<sup>14</sup> we will briefly outline our procedure. A beam of negative ions is extracted from a high-pressure discharge ion source which contains the ion precursor(s). The beam is dispersed according to mass by a Wien filter before entering a high-vacuum region ( $10^{-9}$  torr). This mass-selected beam ( $\approx 1$  nA) is intersected at  $90^\circ$  by a fixed frequency (4880 Å, 75 W) beam from an argon ion laser. Those electrons scattered at right angles to both the ion and the laser beams enter our double hemispherical electron energy analyzer. The resolution of this analyzer (fwhm) is roughly 20 meV.

The allylic anion is produced in our ion source with use of a tungsten filament by adding either approximately a 1:1 mixture of propylene (Matheson Gas Products) and  $\text{O}_2$  or neat 1,5-hexadiene (Aldrich) to our ion source. The deuterated allyl ions were produced from a 1:1 mixture of either propene-2- $d_1$  ( $\text{CH}_3-\text{CD}=\text{CH}_2$ ) or perdeuteriopropylene plus  $\text{O}_2$ . Both propenes were obtained from Merck, Sharpe and Dohme. Their purity (99%) was confirmed by infrared spectroscopy, and the compounds were used without further purification.

It is important to discuss the manner in which we identified the allylic ions. Approximately 200 pA of  $\text{C}_3\text{H}_5^-$  was obtained from neat 1,5-hexadiene. The mass of the ion we believe to be allylic ( $m/z$  41) was confirmed by detaching the ion of  $m/z$  39 near it in the spectrum. This ion is the allenyl anion ( $\text{C}_3\text{H}_3^-$ ) which has been studied previously.<sup>9</sup>

From propylene/ $\text{O}_2$  we obtain about 1.5 nA of the  $m/z$  41 ion. This proves to consist of roughly a 1:1 mixture of  $\text{HCCO}^-$  and  $\text{C}_3\text{H}_5^-$ . Identifying the mass is straightforward because the spectrum<sup>15</sup> of  $\text{HCCO}^-$  has been reported previously. From propene-2- $d_1$  and  $\text{O}_2$  we obtain a 1-nA beam of an ion with  $m/z$  42. We assign this as  $\text{CH}_2\text{CDCH}_2^-$  and confirm the mass identity by detachment of neighboring ions with  $m/z$  41 ( $\text{HCCO}^-$ ) and  $m/z$  44 ( $\text{CH}_2\text{CDO}^-$ ). The photoelectron spectrum of  $\text{CH}_2\text{CHO}^-$  has been reported,<sup>16</sup> and the monodeuterated isomer has a similar spectrum.

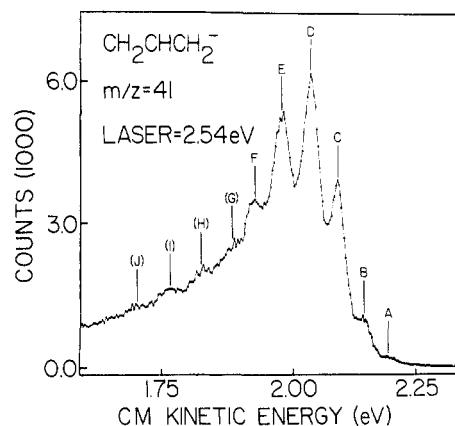


Figure 3. A higher signal-to-noise photoelectron spectrum of the  $d_0$  allylic ion; the data points are roughly 2.8 meV apart.

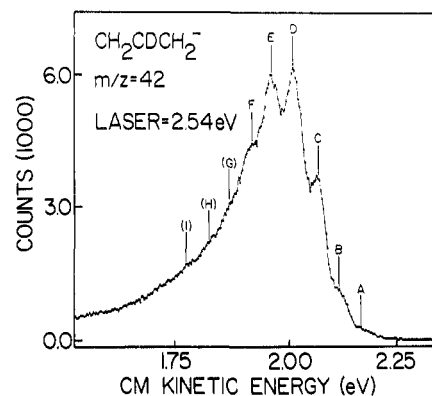


Figure 4. A higher signal-to-noise photoelectron spectrum of the  $d_1$  allylic ion; the data points are roughly 2.8 meV apart.

Figure 1 is the mass spectrum of ions resulting from a mixture of  $\text{O}_2$  and perdeuteriopropene. Several of the ions are absolutely identified by their photodetachment spectra ( $\text{OD}^-$ ,  $\text{O}_2^-$ ,  $\text{C}_3\text{D}_3^-$ , and  $\text{DC}_2\text{O}^-$ ). The ions at  $m/z$  46 are positively assigned as  $\text{CD}_2\text{CDO}^-$  and  $\text{C}_3\text{D}_5^-$ . The perdeuteriovinyl anion ( $\text{CD}_2\text{CDO}^-$ ) has been studied earlier<sup>16</sup> so that the assignment of our mass peak as  $m/z$  46 is secure. Figure 2 is a low-resolution photoelectron spectrum resulting from detachment of the  $m/z$  46 ion beam. The spectrum shows a set of features at low electron energy due to detachment<sup>16</sup> of  $\text{CD}_2\text{CDO}^-$  [ $\text{EA}(\text{CD}_2\text{CDO}) = 1.819$  eV]. Electrons are also seen at relatively high energy which we assign as arising from another  $m/z$  46 ion,  $\text{C}_3\text{D}_5^-$ .

All photoelectron spectra we report are calibrated with a reference ion (generally  $\text{OH}^-$  or  $\text{OD}^-$ ). The spectra are transformed to a center-of-mass (CM) frame by the following relationship.

$$\text{KE} = \text{KE}_{\text{cal}} + \gamma(V - V_{\text{cal}}) + mW[(1/M_{\text{cal}}) - (1/M)] \quad (1)$$

Here KE is the CM kinetic energy at the point in the spectrum desired,  $W$  is the ion beam energy, and  $m$  is the mass of the electron.  $\text{KE}_{\text{cal}}$  refers to the kinetic energy of the calibration ion ( $2.540 - E_{\text{cal}}$ ). We have used  $\text{OH}^-$  and  $\text{OD}^-$  as our marker ions; the EA of the hydroxyl radical is well-known.<sup>17</sup>  $V$  and  $V_{\text{cal}}$  are the energy analyzer acceleration voltages at the peak in the spectrum, and  $M$  and  $M_{\text{cal}}$  are the masses of the ion being studied and the calibration ion, respectively. An energy scale compression factor is  $\gamma$ ; this factor is determined from the photoelectron spectrum<sup>18</sup> of  $\text{Cr}^-$  and is typically in the range  $1.00 \pm 0.01$ .

## Results

Photodetachment spectra of  $\text{CH}_2\text{CHCH}_2^-$ ,  $\text{CH}_2\text{CDCH}_2^-$ , and  $\text{CD}_2\text{CDO}^-$  are presented in Figures 2–6. Figure 2 is a survey spectrum of  $\text{C}_3\text{D}_5^-$  (roughly 11 meV between data points). Besides identifying the mass of the ion, this trace indicates that we are only able to access the ground  $\tilde{X}$  state of the radical; our laser

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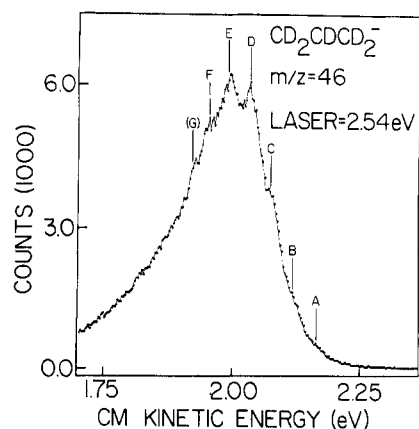


Figure 5. A higher signal-to-noise photoelectron spectrum of the  $d_5$  allylic ion; the data points are roughly 2.8 meV apart.

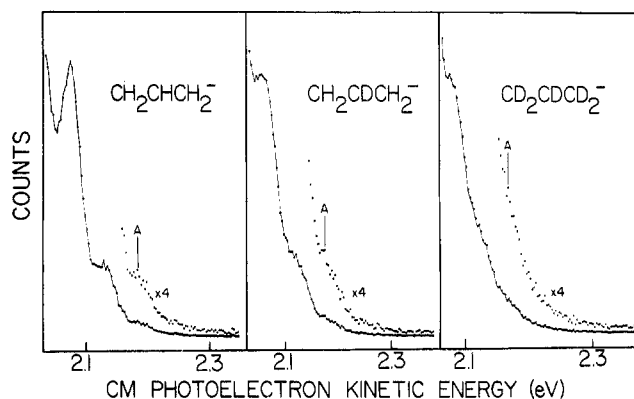


Figure 6. Enhanced plots of the photodetachment origins for the three isotopic allylic ions; the data points are approximately 2.8 meV apart.

is not energetic enough to reach the  $\text{CD}_2\text{CDCD}_2$   $\tilde{A}$  state. Figures 3–6 are high signal-to-noise spectra (about 2.8 meV between points) which display the features in the spectra more clearly. Figure 6 is a trace through the detachment origin of each of the isomeric ions. In all cases the photoelectron spectrum is a plot of the CM kinetic energy of the electrons detached vs. the number of electrons counted. Electron energy increases to the right, with the highest possible energy being that of the laser photons,  $\hbar\omega_0 = 2.540$  eV.

Each of the spectroscopic features in Figures 3–6 are labeled; Table I collects together data from all isomeric ions. The errors quoted in the table are absolute and include contributions from all experimental parameters. Splittings between the peaks will have smaller uncertainties than Table I would indicate (typically 2–4 meV) since many of the factors contributing to the total error bars (such as drifts in ion beam voltage, shifts in  $\gamma$ , and the like) are likely to cancel when differences are computed.

Each of the more detailed spectra (Figures 3–5) shows detachment of the ion to only a single electronic state of allyl radical. From the long Franck–Condon profiles, we deduce that there is a significant geometry difference between the allylic anion and the allyl radical. We will return to this question in a later section of the paper.

The first feature marked in Figures 3–5 is peak A which we believe to be the origin of each of the spectra. Figure 6 depicts this region of the spectrum with a scale enhancement of a factor of 4. Peak A is a prominent in  $\text{CH}_2\text{CHCH}_2^-$  and  $\text{CH}_2\text{CDCH}_2^-$  but is poorly evident in the  $d_5$  ion,  $\text{CD}_2\text{CDCD}_2^-$ . This region of the photoelectron spectrum of the allylic ion always appears the same in each of the numerous scans we have taken. It is invariant to ion source conditions, type of filament, or ion precursor. We do not think that peak A results from detachment of a vibrationally excited ion ("hot bands"). Hot band features generally express themselves by different frequency intervals and irregular intensities (see ref 14 for a clear example). The constancy of peak A as well

Table I. Measured CM Kinetic Energy (eV) of Allylic Ions  
Laser  $\lambda_0 = 488$  nm

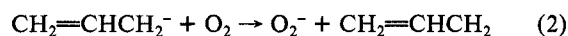
| peak | $\text{CH}_2=\text{CH}-\text{CH}_2^-$ | $\text{CH}_2=\text{CD}-\text{CH}_2^-$ | $\text{CD}_2=\text{CD}-\text{CD}_2^-$ |
|------|---------------------------------------|---------------------------------------|---------------------------------------|
| A    | $2.178 \pm 0.019$                     | $2.167 \pm 0.019$                     | $2.159 \pm 0.025$                     |
| B    | $2.129 \pm 0.014$                     | $2.114 \pm 0.014$                     | $2.112 \pm 0.017$                     |
| C    | $2.074 \pm 0.010$                     | $2.066 \pm 0.011$                     | $2.068 \pm 0.012$                     |
| D    | $2.031 \pm 0.009$                     | $2.005 \pm 0.009$                     | $2.011 \pm 0.009$                     |
| E    | $1.982 \pm 0.009$                     | $1.959 \pm 0.011$                     | $1.969 \pm 0.011$                     |
| F    | $1.931 \pm 0.011$                     | $1.916 \pm 0.014$                     | $1.927 \pm 0.016$                     |
| G    | $1.885 \pm 0.019$                     | $1.873 \pm 0.016$                     | $1.897 \pm 0.016$                     |
| H    | $1.833 \pm 0.019$                     | $1.825 \pm 0.018$                     |                                       |
| I    | $1.783 \pm 0.021$                     | $1.776 \pm 0.024$                     |                                       |
| J    | $1.726 \pm 0.021$                     |                                       |                                       |

as the regularity of the vibrational progression over the Franck–Condon envelopes in Figures 3–5 leads us to assign the A features as the (0,0) transitions. The difference between the photon energy ( $\hbar\omega_0 = 2.540$  eV) and CM kinetic energy is the binding energy; the binding energy of the (0,0) band is the experimental electron affinity. From the values tabulated in Table I, the uncorrected electron affinities are  $\text{EA}(\text{CH}_2\text{CHCH}_2) = 0.362 \pm 0.019$  eV,  $\text{EA}(\text{CH}_2\text{CDCH}_2) = 0.373 \pm 0.019$  eV, and  $\text{EA}(\text{CD}_2\text{CDCD}_2) = 0.381 \pm 0.025$  eV.

## Discussion

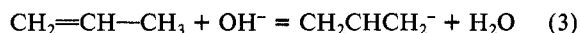
**A. Thermochemistry.** To help support our conclusion that peak A is indeed the first in a vibrational progression in the allyl radical, we must compare the EA resulting from this conclusion ( $0.362 \pm 0.019$  eV) to the results of other experiments. Zimmerman and Brauman<sup>5</sup> have reported the electron affinity of allyl radical in an ICR threshold photodetachment experiment to be  $0.550 \pm 0.054$  eV. Both of our peaks A and B lie outside of this range and peak C is just barely within it; the ICR number falls between peaks E and D in Figure 3. In determining the EA, however, the ICR detachment cross section was extrapolated by modeling the threshold behavior. It was necessary to do this since a tunable light source of long enough wavelength to directly probe the origin was not available.

On the other hand, ion chemistry studies in a flowing afterglow device have shown<sup>6,8</sup> that the charge-transfer reaction



proceeds rapidly, indicating that  $\text{EA}(\text{O}_2) > \text{EA}(\text{allyl})$ . The electron affinity of  $\text{O}_2$  is well-known<sup>19</sup> to be  $0.440 \pm 0.008$  eV; this implies a bound of  $0.0 < \text{EA}(\text{CH}_2\text{CHCH}_2) < 0.440$  eV.

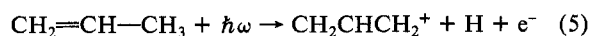
In separate flowing afterglow experiments,<sup>7</sup> the reactions of propene and hydroxide ion were scrutinized to ascertain the gas-phase acidity ( $\Delta H^\circ_{\text{acid}}$ ) of the alkene.



MacKay et al.<sup>7</sup> have measured the equilibrium constant for (3); from  $K_{\text{equil}}$  and the known<sup>20</sup>  $\Delta H^\circ_{\text{acid}}(\text{HO}-\text{H})$ , they deduce that  $\Delta H^\circ_{\text{acid}}(\text{CH}_2\text{CHCH}_2-\text{H}) = 391.3 \pm 0.5$  kcal/mol. The gas-phase acidity is simply related to the homolytic bond dissociation energy (DH), EA, and the ionization potential of H [ $\text{IP}(\text{H}) = 313.605$  kcal/mol].

$$\Delta H^\circ_{\text{acid}}(\text{CH}_2\text{CHCH}_2-\text{H}) = \text{DH}^\circ(\text{CH}_2\text{CHCH}_2-\text{H}) + \text{IP}(\text{H}) - \text{EA}(\text{CH}_2\text{CHCH}_2) \quad (4)$$

Photoionization mass spectroscopy has provided a value for  $\text{DH}^\circ(\text{CH}_2\text{CHCH}_2-\text{H})$ . The mass spectrometric appearance potential of  $\text{CH}_2\text{CHCH}_2^+$  from propene has been found<sup>21</sup> to be  $\text{AP} = 11.880 \pm 0.030$  eV.



The photoelectron spectrum<sup>22</sup> of the allyl radical shows the IP-

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Table II. Final Experimental Values

|  |
|--|
| EA(CH <sub>2</sub> CHCH <sub>2</sub> ) = 0.362 ± 0.020 eV                              |
| EA(CH <sub>2</sub> CDCH <sub>2</sub> ) = 0.373 ± 0.020 eV                              |
| EA(CD <sub>2</sub> CDCH <sub>2</sub> ) = 0.381 ± 0.026 eV                              |
| $\Delta H_f^\circ{}_{298}(\text{CH}_2\text{CHCH}_2^-) = 29.5 \pm 0.9 \text{ kcal/mol}$ |

(CH<sub>2</sub>CHCH<sub>2</sub>) = 8.13 ± 0.02 eV. The appearance potential, IP, and DH are all related as follows.

$$\text{AP}(\text{CH}_2\text{CHCH}_2^+) = \text{DH}^\circ(\text{CH}_2\text{CHCH}_2\text{-H}) + \text{IP}(\text{CH}_2\text{CHCH}_2) \quad (6)$$

Thus the bond dissociation of propene, DH<sup>°</sup>(CH<sub>2</sub>CHCH<sub>2</sub>-H), is found to be 86.5 ± 0.8 kcal/mol. With use of relationship 4, this suggests a value for EA(CH<sub>2</sub>CHCH<sub>2</sub>) of 8.8 ± 0.9 kcal/mol [or 0.38 ± 0.04 eV]. This number is significantly smaller than the ICR photodetachment result but is consistent with our assignment of the A peak as the origin.

There are some corrections to be made to our raw electron affinity of 0.362 eV for CH<sub>2</sub>CHCH<sub>2</sub>. We know little about the rotational constants or vibrational frequencies of CH<sub>2</sub>CHCH<sub>2</sub> or CH<sub>2</sub>CHCH<sub>2</sub><sup>-</sup>; consequently, we can only estimate spin-orbit and rotational corrections to our error bars. We adopt a rotational correction of ±0.005 eV as well as a spin-orbit contribution of ±0.001 eV to our final error bars. Since we can assign no hot bands, there is no vibrational sequence band correction<sup>23</sup> to apply. The final value for the EA(CH<sub>2</sub>CHCH<sub>2</sub>) derived from peak A is 0.362 ± 0.020 eV. Using this value of the EA, we can also compute the  $\Delta H_f^\circ{}_{298}$  of the allylic ion. From the DH<sup>°</sup>(CH<sub>2</sub>CHCH<sub>2</sub>-H) we know that  $\Delta H_f^\circ{}_{298}(\text{CH}_2\text{CHCH}_2)$  is 39.3 ± 0.8 kcal/mol. The ion heat of formation is obtained<sup>24</sup> from the EA as follows:

$$\Delta H_f^\circ{}_{298}(\text{CH}_2\text{CHCH}_2) - \Delta H_f^\circ{}_{298}(\text{CH}_2\text{CHCH}_2^-) = \text{EA}(\text{CH}_2\text{CHCH}_2) + 5/2RT \quad (7)$$

In (7) 5/2RT is the integrated heat capacity of the electron, 1.481 kcal/mol, consistent with the JANAF convention.<sup>24</sup> We find  $\Delta H_f^\circ{}_{298}(\text{CH}_2\text{CHCH}_2^-)$  to be 29.5 ± 0.9 kcal/mol. Table II collects our final experimental values for the electron affinities and heats of formation of allyl radicals and the allylic ion.

**B. Vibrational Analysis.** The structure displayed in the spectra shown in Figures 3–5 belongs to allyl radical and not CH<sub>2</sub>CH-CH<sub>2</sub><sup>-</sup>. Each of the individual peaks represents detachment of the allylic anion to a different vibrational state of the ground  $\tilde{X}^2A_2$  state of CH<sub>2</sub>CHCH<sub>2</sub>. The molecular spectroscopy of allyl radical has not yet been exhaustively studied. Currie and Ramsay<sup>25</sup> have studied the UV absorption spectrum of the allyl radical produced in flash photolysis of allyl bromide. In this experiment, the  $\tilde{A}^2B_1 \leftarrow \tilde{X}^2A_2$  ( $T_e = 3.04$  eV) transition was studied. Four vibronic modes in the excited state were observed but not assigned. All the lines were broadened due to predissociation. Little was learned about the vibrational spectroscopy of the ground state of allyl radical.

More recently, Maier et al.<sup>26</sup> have used infrared spectroscopy of matrix-isolated allyl radical from flash pyrolysis using several precursors. All the allowed infrared transitions were observed and assigned. These experimental results are collected in Table III. Of interest is the low-frequency modes seen in the infrared spectrum of allyl.

ESR studies of matrix-isolated CH<sub>2</sub>CHCH<sub>2</sub> yield spectra<sup>1–3</sup> consisting of 18 lines, consistent with a C<sub>2v</sub> radical structure having 3 distinct H atoms in a 1:2:2 ratio. A number of ab initio electronic

structure calculations<sup>4,27,28</sup> all find the allyl radical to be a flat, planar species with C<sub>2v</sub> symmetry. Takada and Dupuis<sup>4</sup> have carried out a careful multiconfigurational Hartree-Fock (MCHF) calculation on CH<sub>2</sub>CHCH<sub>2</sub> and then extracted a complete set of harmonic force constants for the  $\tilde{X}$  state. These harmonic constants then yield a set of vibrational frequencies for the radicals (Takada and Dupuis consider 3 different isotopically substituted species). We have collected their calculated frequencies in Table III where they are labeled by symmetry and local mode. Although these frequencies may be in error by 10 to 15%, the calculated values in Table III should be a reasonable guide in assigning the vibrational modes of allyl. The calculated frequencies for the deuterated isomers will be a useful guide in assigning the mode we see excited in photodetachment of the selectively isotopically substituted allyl anions.

A qualitative examination of the high-resolution spectrum for CH<sub>2</sub>CHCH<sub>2</sub><sup>-</sup> in Figure 3 suggests that only one vibrational mode of allyl radical (out of 18 possible) is excited upon detachment of the ion. This mode has a low frequency of about 400 cm<sup>-1</sup>. A glance at Table III suggests only 3 possible assignments:  $\omega_7$ , the CCC bend;  $\omega_9$ , the CH<sub>2</sub> asymmetric twist combination; and  $\omega_{12}$ , the CH<sub>2</sub> symmetric twist combination. The asymmetric twist was not assigned in the experimental IR studies, while the symmetric twist and the CCC bend were identified. As we will shortly see, the active vibration is the CCC bending mode,  $\omega_7$ .

We have carried out a least-squares fitting analysis to the peak positions tabulated in Table I. Rather than fit the CM kinetic energy for each of the features (A–J), we have fit to the peak binding energies (BE). The BE for a peak is related to the CM kinetic energy through the laser energy,  $\hbar\omega_0 = 2.540$  eV. If we subtract the CM kinetic energy from the laser frequency, we recover an experimental BE. These values are collected together in Table IV. We initially fit the BE values to a function of the form:<sup>29</sup>

$$E(v') = T_0 + \omega_7'(v' + 1/2) + x_{77}'(v' + 1/2)^2 \quad (8)$$

If we fit the experimental BE values to a function of the form of (8), we find excellent agreement. It turns out that the anharmonicity constant for eq 8 which fits our data is on the order of  $x_{77}' = 0.0019$  eV or less for all isotopic ions. This is smaller than the experimental peak uncertainties; consequently, we have ignored anharmonicity constants in our energy expression ( $x_{77}' \equiv 0$ ). The final functions for CH<sub>2</sub>CHCH<sub>2</sub>, CH<sub>2</sub>CDCH<sub>2</sub>, and CD<sub>2</sub>CDCH<sub>2</sub> are listed in Table IV; we also tabulate the calculated  $E(v')$ , the difference between the experimental BE and  $E(v')$ , and the experimental splitting between the various transitions (in cm<sup>-1</sup>). A glance at the column of differences shows that our fitted, harmonic functions [ $E(v')$ ] match the experimental data to within 10 meV or better in all cases but one.

On the basis of the data of Table IV and the calculated frequencies in Table III, we can assign the active mode in our photoelectron spectra. Of the three low-frequency modes possible,  $\omega_7$  most nearly matches our fitted constants:  $\omega'(\text{CH}_2\text{CHCH}_2^-) = 398 \text{ cm}^{-1}$ ,  $\omega'(\text{CH}_2\text{CDCH}_2^-) = 391 \text{ cm}^{-1}$ ,  $\omega'(\text{CD}_2\text{CDCH}_2^-) = 360 \text{ cm}^{-1}$ . From Table III one can see the extent of the isotope shifts for each isomer. The crucial ratios for us to consider are the following:  $\omega_7(\text{CH}_2\text{CHCH}_2/\text{CD}_2\text{CDCH}_2) = 0.82$ ;  $\omega_9(\text{CH}_2\text{CHCH}_2/\text{CD}_2\text{CDCH}_2) = 0.71$ ;  $\omega_{12}(\text{CH}_2\text{CHCH}_2/\text{CD}_2\text{CDCH}_2) = 0.77$ . The experimentally observed shift is 0.90 (360 cm<sup>-1</sup>/398 cm<sup>-1</sup>); this is closest to the value for  $\omega_7$ . Strictly speaking we should contrast the calculated values in Table III with the (1,0) or fundamental frequencies in Table IV. This is a demanding comparison to make; the first discernible peak (A) in Figures 3–5 is rather weak and difficult to locate precisely. With the proper concern for uncertainties, the fundamental intervals are the following: (0,1) CH<sub>2</sub>CHCH<sub>2</sub> = 395 ± 165 cm<sup>-1</sup>; (0,1)

(22) F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **100**, 3290 (1978).

(23) P. C. Engelking and W. C. Lineberger, *J. Chem. Phys.*, **66**, 5054 (1977).

(24) S. G. Lias, In "Kinetics of Ion-Molecule Reactions", P. Ausloos, Ed., Plenum Publishing, New York and London, 1979, pp 246–249, Appendix.

(25) C. L. Currie and D. A. Ramsay, *J. Chem. Phys.*, **45**, 488 (1966).

(26) G. Maier, H. P. Reisenauer, B. Rohde, and K. Dehnicke, *Chem. Ber.*, **166**, 732 (1983).

(27) O. Kikuchi, *Chem. Phys. Lett.*, **72**, 487 (1980).

(28) (a) G. Levin and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 1649 (1975); (b) A. F. Voter and W. A. Goddard III, *Chem. Phys.*, **57**, 253 (1981).

(29) G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, NJ, 1967 p 142.

**Table III.** Vibrational Frequencies (cm<sup>-1</sup>) of Allyl Radical<sup>a</sup>

| $\omega$ | symmetry       | mode                            | CH <sub>2</sub> CHCH <sub>2</sub> |       | calcd | calcd |
|----------|----------------|---------------------------------|-----------------------------------|-------|-------|-------|
|          |                |                                 | exptl                             | calcd |       |       |
| 1        | a <sub>1</sub> | CH stretch                      | 3105                              | 3412  | 3409  | 2543  |
| 2        | a <sub>1</sub> | CH stretch                      | 3048                              | 3327  | 2456  | 2459  |
| 3        | a <sub>1</sub> | CH stretch                      | 3016                              | 3318  | 3320  | 2409  |
| 4        | a <sub>1</sub> | CH <sub>2</sub> scis (sym)      | 1463                              | 1661  | 1660  | 1351  |
| 5        | a <sub>1</sub> | CH <sub>2</sub> rock (sym)      | 1403                              | 1370  | 1345  | 1148  |
| 6        | a <sub>1</sub> | CC stretch (sym)                | 1242                              | 1093  | 1090  | 920   |
| 7        | a <sub>1</sub> | CCC                             | 511                               | 476   | 471   | 389   |
| 8        | a <sub>2</sub> | CH <sub>2</sub> umbrella (asym) |                                   | 761   | 761   | 601   |
| 9        | a <sub>2</sub> | CH <sub>2</sub> twist (asym)    |                                   | 596   | 596   | 424   |
| 10       | b <sub>1</sub> | CH out-of-plane bend            | 985                               | 1051  | 844   | 804   |
| 11       | b <sub>1</sub> | CH <sub>2</sub> umbrella (sym)  | 802                               | 786   | 785   | 640   |
| 12       | b <sub>1</sub> | CH <sub>2</sub> twist (sym)     | 810                               | 562   | 561   | 433   |
| 13       | b <sub>2</sub> | CH stretch                      | 3104                              | 3407  | 3407  | 2538  |
| 14       | b <sub>2</sub> | CH stretch                      | 3016                              | 3314  | 3314  | 2401  |
| 15       | b <sub>2</sub> | CH <sub>2</sub> scis (asym)     | 1463                              | 1632  | 1628  | 1193  |
| 16       | b <sub>2</sub> | CH bend                         | 1285                              | 1556  | 1374  | 1361  |
| 17       | b <sub>2</sub> | CC stretch (asym)               | 1477                              | 1204  | 1096  | 1003  |
| 18       | b <sub>2</sub> | CH <sub>2</sub> rock (asym)     | 1389                              | 1040  | 947   | 779   |

<sup>a</sup>The experimental values for C<sub>3</sub>H<sub>5</sub> are from the matrix IR spectra of ref 26. The calculated harmonic frequencies of allyl radical based on ab initio MCS-CF wave functions. These values are taken from Table III of ref 4.

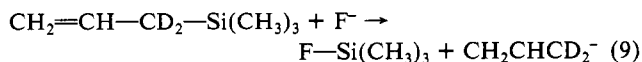
**Table IV.** Experimental and Calculated Binding Energies (BE)<sup>a</sup>

| transition   | BE, eV        | $E(v')$ , eV | diff, eV | exptl splitting, cm <sup>-1</sup> |
|--|---------------|--------------|----------|-----------------------------------|
| CH <sub>2</sub> =CH-CH <sub>2</sub> <sup>-</sup> $E(v') = 0.3380 + 0.0493(v' + 0.5)$ |               |              |          |                                   |
| (0,0)  | 0.362 ± 0.019 | 0.3626       | 0.0006   | 395                               |
| 7 <sub>0</sub> <sup>1</sup>  | 0.411 ± 0.014 | 0.4119       | 0.0009   | 445                               |
| 7 <sub>0</sub> <sup>2</sup>  | 0.466 ± 0.010 | 0.4613       | -0.0047  | 350                               |
| 7 <sub>0</sub> <sup>3</sup>  | 0.509 ± 0.009 | 0.5106       | 0.0016   | 395                               |
| 7 <sub>0</sub> <sup>4</sup>  | 0.558 ± 0.009 | 0.5599       | 0.0019   | 410                               |
| 7 <sub>0</sub> <sup>5</sup>  | 0.609 ± 0.009 | 0.6092       | 0.0002   | 370                               |
| 7 <sub>0</sub> <sup>6</sup>  | 0.655 ± 0.019 | 0.6586       | 0.0036   | 420                               |
| 7 <sub>0</sub> <sup>7</sup>  | 0.707 ± 0.019 | 0.7079       | 0.0009   | 400                               |
| 7 <sub>0</sub> <sup>8</sup>  | 0.757 ± 0.021 | 0.7572       | 0.0002   | 460                               |
| 7 <sub>0</sub> <sup>9</sup>  | 0.814 ± 0.021 | 0.8065       | -0.0075  |                                   |
| CH <sub>2</sub> =CD-CH <sub>2</sub> <sup>-</sup> $E(v') = 0.3576 + 0.0485(v' + 0.5)$ |               |              |          |                                   |
| (0,0)  | 0.373 ± 0.019 | 0.3818       | 0.0088   |                                   |
| 7 <sub>0</sub> <sup>1</sup>  | 0.426 ± 0.014 | 0.4303       | 0.0043   | 430                               |
| 7 <sub>0</sub> <sup>2</sup>  | 0.474 ± 0.011 | 0.4788       | 0.0048   | 385                               |
| 7 <sub>0</sub> <sup>3</sup>  | 0.535 ± 0.009 | 0.5273       | -0.0077  | 490                               |
| 7 <sub>0</sub> <sup>4</sup>  | 0.581 ± 0.011 | 0.5758       | -0.0052  | 370                               |
| 7 <sub>0</sub> <sup>5</sup>  | 0.624 ± 0.014 | 0.6243       | 0.0003   | 345                               |
| 7 <sub>0</sub> <sup>6</sup>  | 0.667 ± 0.016 | 0.6728       | 0.0058   | 345                               |
| 7 <sub>0</sub> <sup>7</sup>  | 0.715 ± 0.018 | 0.7213       | 0.0063   | 390                               |
| 7 <sub>0</sub> <sup>8</sup>  | 0.764 ± 0.024 | 0.7698       | 0.0058   | 395                               |
| CD <sub>2</sub> =CD-CD <sub>2</sub> <sup>-</sup> $E(v') = 0.3661 + 0.0446(v' + 0.5)$ |               |              |          |                                   |
| (0,0)  | 0.381 ± 0.025 | 0.3884       | 0.0075   |                                   |
| 7 <sub>0</sub> <sup>1</sup>  | 0.428 ± 0.017 | 0.4331       | 0.0051   | 380                               |
| 7 <sub>0</sub> <sup>2</sup>  | 0.472 ± 0.012 | 0.4777       | 0.0057   | 355                               |
| 7 <sub>0</sub> <sup>3</sup>  | 0.529 ± 0.009 | 0.5223       | -0.0067  | 460                               |
| 7 <sub>0</sub> <sup>4</sup>  | 0.571 ± 0.011 | 0.5670       | -0.0040  | 340                               |
| 7 <sub>0</sub> <sup>5</sup>  | 0.613 ± 0.016 | 0.6116       | -0.0014  | 340                               |
| 7 <sub>0</sub> <sup>6</sup>  | 0.643 ± 0.016 | 0.6562       | 0.0132   | 240                               |

<sup>a</sup>BE = 2.540 - CM kinetic energy. See Table I for CM KE.

CH<sub>2</sub>CDCH<sub>2</sub> = 430 ± 165 cm<sup>-1</sup>; (0,1) CD<sub>2</sub>CDCH<sub>2</sub> = 380 ± 225 cm<sup>-1</sup>. The comparison of these values with the calculated frequencies in Table III is uneven. The observed fundamentals are lower than any calculated modes but are close enough to be within the proper range for  $\omega_7$ . Certainly our fitted frequencies (Table IV) match these intervals reasonably well and the observed fundamentals (Table IV) are acceptably close. Nevertheless, the large error bars accompanying the observed fundamentals (on the order of ±150 cm<sup>-1</sup>) indicate that this assignment should be taken cautiously. In addition, comparison to the matrix-perturbed IR spectra strongly favors the  $\omega_7$  identity because it is the only mode observed below 800 cm<sup>-1</sup>. Certainly no other modes tabulated in Table III fit our spectra nearly as well as  $\omega_7$ .

**C. Ion Structure.** What is the structure of allyl carbanion? Direct evidence on this matter is quite sparse. An ICR study of CH<sub>2</sub>CHCD<sub>2</sub><sup>-</sup> suggests that the ion is symmetric.<sup>10</sup> This result follows from a study of the ion chemistry of the labeled anion, CH<sub>2</sub>CHCD<sub>2</sub><sup>-</sup>.



It is known that carbanions will react with organic nitrites.<sup>30</sup>

(30) G. K. King, M. M. Maricq, V. M. Bierbaum, and C. H. DePuy, *J. Am. Chem. Soc.*, **103**, 7133 (1981).

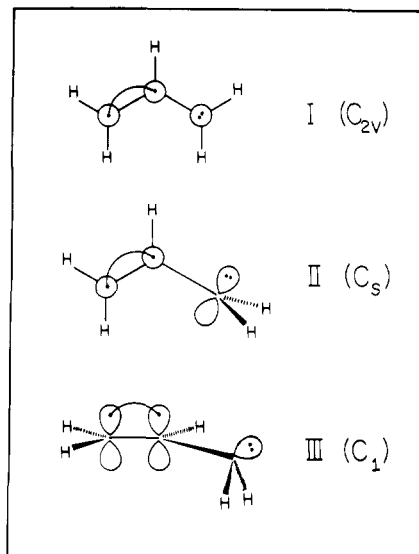
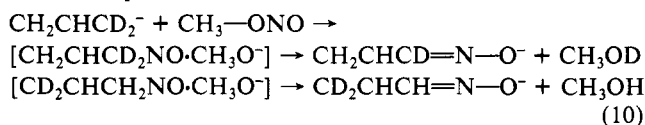


Figure 7. Three different models for the geometry of the  $\text{CH}_2\text{CHCH}_2^-$  ion.

When this deuterated ion was condensed with  $\text{CH}_3\text{—ONO}$ , a 1:1 mixture of product ions was detected.



This experiment implies that  $\text{CH}_2\text{CHCH}_2^-$  is a symmetric anion.

Several computational studies of the allylic ion have been reported. Two restricted Hartree–Fock (RHF) calculations report<sup>31,32</sup> a planar,  $C_{2v}$  structure for the negative ion and a C–C–C bond angle of roughly  $133^\circ$ . One minimal basis RHF calculation suggests<sup>33</sup> that the  $\text{CH}_2\text{CHCH}_2^-$  is a nonplanar molecule; it reports a pyramidal structure for the ion with the terminal hydrogens bent out of the molecular plane by approximately  $10^\circ$ . There is a general feeling that accurate calculations on weakly bound negative ions are quite difficult.<sup>34</sup> We should consider several possible ionic structures as we interpret the photoelectron spectra of  $\text{CH}_2\text{CHCH}_2^-$ .

Three qualitatively different structures for the carbanion come to mind; these are drawn in Figure 7. The first structure is the familiar  $C_{2v}$  ion (I). The second is a  $C_s$  structure with one methylene group twisted  $90^\circ$  out of the molecular plane (II). The last structure is a pyramidal carbanion with  $C_1$  (or no) symmetry (III). The label of the  $\tilde{X} \text{CH}_2\text{CHCH}_2^-$  state is  $^1A_1$  in any case. The  $C_{2v}$  ion is a fully conjugated species (I) while the  $C_s$  and  $C_1$  structures have the ionic center uncoupled from or only partially conjugated to the  $\text{CH=CH}_2$  group. One conjectures that the EA of a species such as II or (particularly) III would be quite small; for comparison<sup>35</sup> the EA( $\text{CH}_3$ ) is known to be 0.080 eV. Detachment of I might be expected to show active CCC skeletal modes in the resultant  $\text{CH}_2\text{CHCH}_2$ ,  $\omega_6$  and  $\omega_7$ . If other carbanion structures such as II or III were important, one might expect the vibronic signature to include twisting modes ( $\omega_9$  or  $\omega_{12}$ ) and rocking modes ( $\omega_5$  and  $\omega_{18}$ ) as active vibrations.

We are inclined to favor structure I as that describing allyl carbanion. This is suggested by two features of the spectra in Figures 3–5: (a) the simplicity of the Franck–Condon profile (only one active mode) and (b) the active vibration is an  $a_1$  mode,  $\omega_7$ .

(31) A. Pross, D. J. DeFrees, B. A. Levi, S. K. Pollack, L. Radom, and W. J. Hehre, *J. Org. Chem.*, **46**, 1693 (1981).

(32) A. C. Hopkinson and M. H. Lien, *Int. J. Quantum Chem.*, **18**, 1371 (1980).

(33) D. W. Boerth and A. Streitwieser, *J. Am. Chem. Soc.*, **100**, 750 (1978).

(34) L. Radom, In "Methods of Electronic Structure Theory", Vol. 4, H. F. Schaefer, III, Ed., Plenum Press, New York, 1977, p 333.

(35) G. B. Ellison, P. C. Engelking, and W. C. Lineberger, *J. Am. Chem. Soc.*, **100**, 2556 (1978).

The structural differences between allyl radical and structure I (Figure 7) are small; one expects the C–C bond lengths and the CCC angle of carbanion I to be greater than the corresponding dimensions of  $\text{CH}_2\text{CHCH}_2$ . Structures II and III are qualitatively different than allyl radical; neither exhibits  $C_{2v}$  symmetry. Detachment of II or III might be expected to excite numerous skeletal modes and methylene vibrations.

The spectra in Figures 3–5 are dominated by a long progression in  $\omega_7$ , the C–C–C bending mode. Each of the peaks in the photoelectron spectra is proportional to a Franck–Condon factor, FCF. Franck–Condon factors are dominated by the overlap of the vibrational wave function of the ion ( $\Theta_i$ ) with that of the neutral radical ( $\Theta_r$ ):  $\text{FCF} = \langle \Theta_i | \Theta_r \rangle^2$ . As we have argued earlier, no transitions in Figures 3–5 originate from vibrationally excited ions; consequently  $|\Theta_i\rangle = |0\rangle$ . Thus active vibrational modes in the radical ( $\langle \Theta_r |$ ) must belong to the totally symmetric representation of a common point group encompassing both the ion and radical. This implies that if structure I of Figure 7 describes  $\text{CH}_2\text{CHCH}_2^-$ , the active modes in the photoelectron spectra will be confined to the  $a_1$  block of  $\text{CH}_2\text{CHCH}_2$  (see Table III). On the other hand, if structure II represents the allylic ion, vibrational activity is allowed in both the  $a_1$  and  $b_1$  blocks since both are totally symmetric under  $C_s$ . If  $\text{CH}_2\text{CHCH}_2^-$  has the nonsymmetric structure III, excitation of all 18 modes of allyl radical is allowed. We have identified the sole active vibration in our photoelectron spectra as  $\omega_7$ , and  $a_1$  mode. The lack of vibronic activity in nonsymmetric modes ( $a_2$ ,  $b_1$ , and  $b_2$ ) suggests to us that the  $\text{CH}_2\text{CHCH}_2^-$  has  $C_{2v}$  symmetry. Our qualitative picture of  $\text{CH}_2\text{CHCH}_2^-$  is given by I in Figure 7; the major difference between allyl radical and the allylic ion is the enlarged C–C–C bond angle in the anion.

In an attempt to quantify the geometry change between the allyl radical and the corresponding negative ion, we have undertaken the modeling of the Franck–Condon factors for  $\text{CH}_2\text{C—HCH}_2^-$ ,  $\text{CH}_2\text{CDCH}_2^-$ , and  $\text{CD}_2\text{CDCD}_2^-$ . Our first task is to fit the experimental spectra in Figures 3–5 to a set of Gaussian peaks. The intensity of a peak centered at an energy  $E_k$  (see Table I) is fitted to a form:

$$I_k(E) = A_k \exp[-(E - E_k)^2/B_k] \quad (11)$$

The parameter  $A_k$  is a height and  $B_k$  is a width, typically 40 to 60 meV. The entire photoelectron spectrum is synthesized by simply summing these Gaussians. Using this method, we have generated excellent fits to the data. The fitted, empirical spectra for  $\text{CH}_2\text{CHCH}_2^-$ ,  $\text{CH}_2\text{CDCH}_2^-$ , and  $\text{CD}_2\text{CDCD}_2^-$  are presented in Figure 8 and match the experimental data (Figures 3–5) very closely. From these fitted spectra we are able to extract the areas (and thus the Franck–Condon factors (FCF)) of the peaks from the relation

$$\text{FCF} = A(\pi B)^{1/2}/2 \quad (12)$$

The Franck–Condon factors are scaled such that the top peak (C) has an area of 1.0. The final experimental FCF's are presented in Table V.

We would like to use our experimental FCF's from our fitted spectra (Figure 8, Table V) to extract an ion geometry for the allyl anion. In order to do this, we must calculate  $|\Theta_i\rangle$  and  $|\Theta_r\rangle$ , the vibrational wave functions for the ion and neutral. The appropriate dimension is the in-plane skeletal bend of allyl. The Schrödinger equation then is

$$[2^{-1}\hbar g_{\phi\phi}^3 \partial^2/\partial \rho^2 + V(\rho)]|\Theta(\rho)\rangle = E|\Theta(\rho)\rangle \quad (13)$$

where  $V(\rho)$  is the potential energy for the bending motion of a molecule of the type Y–X–Y. In light of our observation of a harmonic spectrum for allyl, we have used  $V(\rho) = [K_{\text{vib}}/2](\rho - \rho_0)^2$  where  $\rho$  is the supplement to the Y–X–Y bond angle and  $\rho - \rho_0$  is the displacement from the equilibrium Y–X–Y angle in radians. The kinetic energy term contains the G-matrix element  $g_{\phi\phi}^3$ . The G element<sup>36</sup> is

$$g_{\phi\phi}^3 = r_3^{-2}\{m_x + m_y(1 + \cos \rho_0)\}/m_x m_y \quad (14)$$

(36) T. Barrow, R. N. Dixon, and G. Duxbury, *Mol. Phys.*, **27**, 1217 (1974).

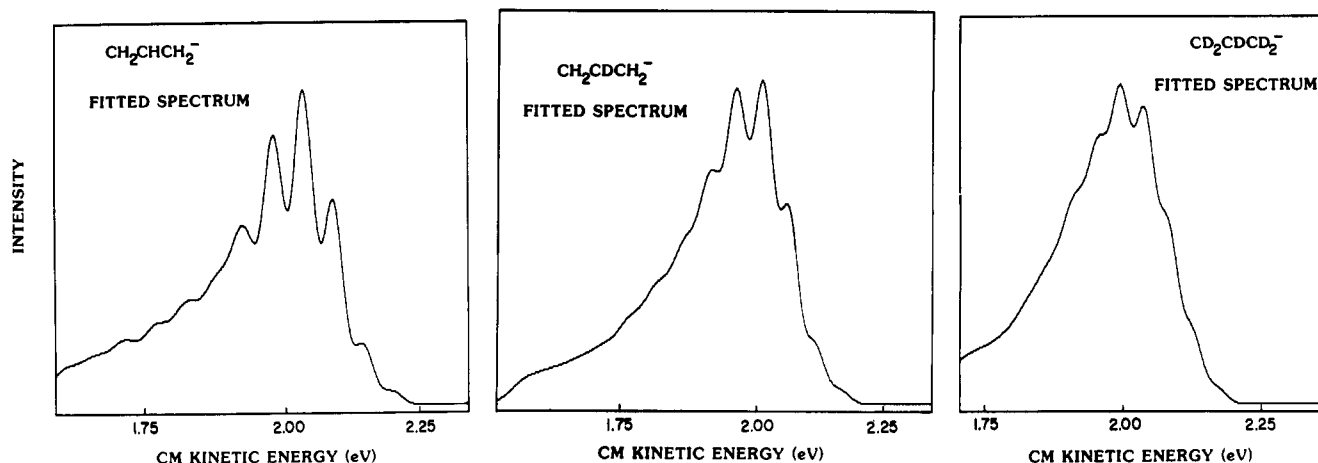


Figure 8. Fitted photoelectron spectra resulting from a Gaussian synthesis using eq 11.

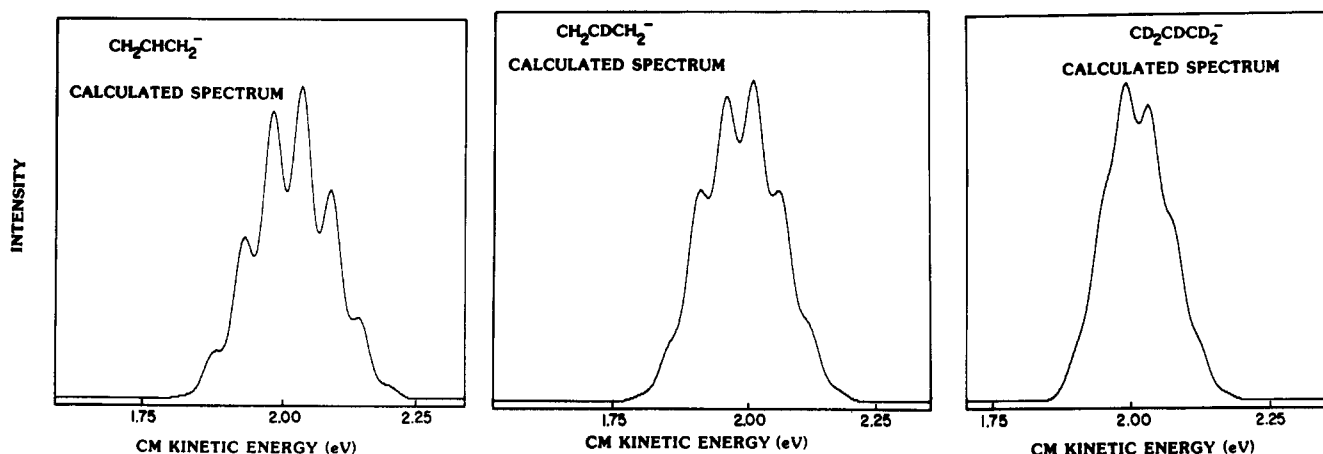


Figure 9. Calculated photoelectron spectra resulting from modeled Franck-Condon factors originating from eq 13.

The Y-X bond length is  $r_0$ . We have ignored off-diagonal elements in both the kinetic energy matrix ( $G$ ) and the force constant matrix ( $F$ ). In doing this we make the approximation that  $\omega_7$  is a pure bend without any contribution from stretching motion.

Using the Hamiltonian described above, we solve for the wave function  $|\Theta\rangle$  variationally using a basis set of cubic B splines.<sup>37,38</sup> Fifty splines were sufficient for our calculations. As a check for the validity of this technique, we have applied it to the  $\text{SO}_2$  molecule. The Franck-Condon factors for the bending motion in the  $\tilde{a}^3B_1 \leftarrow \tilde{X}^1A_1$  electronic transition in  $\text{SO}_2$  has been measured previously.<sup>39</sup> Using the experimental values for the bending frequency and the bond angle in these two states, we have calculated FCF's in excellent agreement with those found empirically. It is known<sup>39</sup> that  $\text{SO}_2$  has a ground-state bond angle of  $119.5^\circ$  and an excited-state bond angle of  $126.1 \pm 0.1^\circ$ . Assuming the correct ground-state geometry for  $\text{SO}_2$ , our best match to the experimental Franck-Condon factors yields an excited-state bond angle of  $125.7^\circ$ . The calculated FCF's are quite insensitive to the force constant  $K_{\text{vib}}$  but very sensitive to bending coordinate.

The fact that calculated FCF's are relatively insensitive to bending force constant is important in modeling the geometry of the allylic ion because the bending frequency of the anion has never been measured. The method described above was applied to the transition  $\text{CH}_2\text{CHCH}_2^- \rightarrow \text{CH}_2\text{CHCH}_2$  (and appropriate deuterated isomers). We use as our equilibrium geometry for the neutral molecule the calculated parameters of Takada and Dupuis.<sup>4</sup> Because we only observe excitation in the bend, we believe there is little change in the geometry for the anion except in the

Table V. Photoelectron Franck-Condon Factors<sup>a</sup>

| transition                            | exptl FCF | calcd FCF |
|---------------------------------------|-----------|-----------|
| $\text{CH}_2=\text{CH}-\text{CH}_2^-$ |           |           |
| (0,0)                                 | 0.045     | 0.043     |
| $7_0^1$                               | 0.19      | 0.252     |
| $7_0^2$                               | 0.64      | 0.665     |
| $7_0^3$                               | 1.000     | 1.000     |
| $7_0^4$                               | 0.82      | 0.854     |
| $7_0^5$                               | 0.59      | 0.447     |
| $7_0^6$                               | 0.41      | 0.128     |
| $7_0^7$                               | 0.34      | 0.010     |
| $7_0^8$                               | 0.27      | 0.002     |
| $\text{CH}_2=\text{CD}-\text{CH}_2^-$ |           |           |
| (0,0)                                 | 0.045     | 0.037     |
| $7_0^1$                               | 0.19      | 0.233     |
| $7_0^2$                               | 0.58      | 0.641     |
| $7_0^3$                               | 1.000     | 1.000     |
| $7_0^4$                               | 0.93      | 0.945     |
| $7_0^5$                               | 0.68      | 0.648     |
| $7_0^6$                               | 0.52      | 0.175     |
| $\text{CD}_2=\text{CD}-\text{CD}_2^-$ |           |           |
| (0,0)                                 | 0.065     | 0.036     |
| $7_0^1$                               | 0.23      | 0.223     |
| $7_0^2$                               | 0.59      | 0.612     |
| $7_0^3$                               | 0.96      | 0.981     |
| $7_0^4$                               | 1.000     | 1.000     |
| $7_0^5$                               | 0.82      | 0.658     |
| $7_0^6$                               | 0.67      | 0.265     |

<sup>a</sup> The uncertainty in the experimental FCF values is  $\pm 30\%$ .

bond angle; thus for the anion we use the C-C bond length of the neutral. We approximate allyl as having the structure Y-X-Y with Y being  $\text{CH}_2$  (or  $\text{CD}_2$ ) and X being CH (or CD). Using

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Takada and Dupuis'  $r(\text{C}-\text{C}) = 1.388 \text{ \AA}$  and  $r(\text{C}-\text{H}) = 1.075 \text{ \AA}$ , we calculate effective  $\text{X}-\text{Y}$  bond lengths ( $r_0$ ) of  $1.505 \text{ \AA}$  ( $\text{CH}_2\text{-CHCH}_2$ ),  $1.555 \text{ \AA}$  ( $\text{CH}_2\text{CDCH}_2$ ), and  $1.612 \text{ \AA}$  ( $\text{CD}_2\text{CDCD}_2$ ). The vibrational frequencies in the neutral molecules are the experimental values from this experiment. The frequencies for the anions were varied along with the  $\text{X}-\text{Y}-\text{X}$  angle to obtain the best fit to our fitted FCF's.

Our best fit to the experimental FCF's was for a bond angle change of  $16^\circ$  with a bending frequency in the anion ( $\text{CH}_2\text{CH-CH}_2^-$ ) of about  $500 \text{ cm}^{-1}$ . The optimal fit is insensitive to the ion frequency; the bond angle changes by one degree or less across a large range of frequencies. The calculated results for the three isomers are reported in Table V. We conclude that the bond angle change between allyl anion and allyl is  $16 \pm 4^\circ$ . We feel an uncertainty of  $4^\circ$  is generous even considering that we have assumed a harmonic oscillator and ignored the bond strength contribution to the bend. If one uses the calculated  $\text{C}-\text{C}-\text{C}$  angle for  $\text{CH}_2\text{CHCH}_2$  from Takada and Dupuis of  $124^\circ$ , then the  $\text{C}-\text{C}-\text{C}$  angle is  $140 \pm 4^\circ$  for  $\text{CH}_2\text{CHCH}_2^-$ . Note that this is not a unique answer because a bond angle decrease of  $16^\circ$  works equally well. We believe that the angle increases, however, because the detached electron is from an orbital which is antibonding between the terminal carbons.<sup>33</sup> An increasing angle is consistent with previous calculations.<sup>31-33,40,41</sup>

Synthesized spectra based on our calculated FCF's for the three isotopes are presented in Figure 9. One immediately notices that

we have fit the data (Figures 3-5) quite well in all three cases for the first four or five peaks. For the higher vibrational states this simple model does not fit the data well at all. Note that this is also the spectral region where the peak widths seem to become larger. It is clear that something unexpected is happening in these higher levels. We do not know what this effect is, but we remind the reader that all the peaks in the absorption spectrum of allyl<sup>25</sup> were broadened by predissociation. This phenomenon warrants further study.

### Conclusion

The allyl anion ( $\text{CH}_2\text{CHCH}_2^-$ ) and two isotopically substituted species ( $\text{CH}_2\text{CDCH}_2^-$  and  $\text{CD}_2\text{CDCD}_2^-$ ) have been studied in negative ion photoelectron spectroscopy. The electron affinities of these three radicals as well as the heat of formation of the allyl anion ( $\text{CH}_2\text{CHCH}_2^-$ ) are collected in Table II. The values are in fairly good agreement with previous gas-phase ion chemistry studies.<sup>6-8</sup>

The photoelectron spectra we observe show excitation in only one vibronic mode to be important. We identify this mode as the in-plane skeletal bend of the allyl radical. The vibrational frequencies are reported in Table III. We conclude that the major geometry change occurring when an electron is added to ground-state allyl radical is an opening in the  $\text{C}-\text{C}-\text{C}$  bond angle. A Franck-Condon analysis of our experimental peak intensities is performed. We find this bond angle to increase by about  $16^\circ$ .

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## Resonance Raman Studies of $\text{O}_2$ Stretching Vibrations in Oxygen Adducts of Cobalt Porphyrins. The Importance of Vibrational Coupling

Krzysztof Bajdor, James R. Kincaid,\* and Kazuo Nakamoto\*

Contribution from the Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wisconsin 53233. Received November 17, 1983

**Abstract:** Studies are undertaken to examine the role of vibrational coupling in determining the  $\nu(\text{O}_2)$  frequencies of molecular oxygen adducts of cobalt porphyrin complexes with a number of axial ligands. Specifically, we have carried out strategic isotopic labeling in order to demonstrate that multiple bands and shifts of  $\nu(\text{O}_2)$  may arise from vibrational coupling and thus to distinguish this effect from other, steric or environmental, factors that may give rise to such behavior. Strong evidence is presented for vibrational coupling between  $\nu(\text{O}_2)$  and internal modes of axial ligands that occur at comparable frequencies. The utility of mixed-isotope ( $^{16}\text{O}$ - $^{18}\text{O}$ ) experiments for detecting vibrational coupling is explored. Results, using a limited number of axial ligands (pyridine and imidazole and various substituted analogues) and several different cobalt porphyrins (tetraphenylporphine, octaethylporphine, protoporphyrin IX and diformyl deuteroporphyrin IX dimethyl esters, and picket-fence porphyrin), indicate that axial and (relatively weak) equatorial electronic effects on  $\nu(\text{O}_2)$  are consistent with stabilization of charge separation in the  $\text{Co}^{\delta+}\text{-O}_2^{\delta-}$  formulation. Also, relatively large effects on the  $\nu(\text{O}_2)$  frequency are brought about by interactions of bound  $\text{O}_2$  with solvent molecules (e.g., methylene chloride and methanol).

### Introduction

The nature of dioxygen binding to myoglobin and hemoglobin has been an intensively investigated subject<sup>1-3</sup> during the past decade, and many model systems that reversibly bind molecular

oxygen have been developed in an effort to understand the steric and electronic factors which control oxygen binding in the native proteins. These model systems include the "picket-fence",<sup>4,5</sup> "chelated",<sup>6</sup> "capped",<sup>7,8</sup> "strapped",<sup>9</sup> and "basket-handle"<sup>10</sup> me-

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