

Molecular beam photoelectron spectroscopy of allene

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High-resolution HeI (584 Å) photoelectron spectra of allene rotationally cooled in a seeded supersonic molecular beam were obtained. Vibrational structure was completely resolved in the first band (X^2E), which involved a strong Jahn–Teller effect. A series of ab initio double-zeta multiconfiguration self-consistent field (DZ MCSCF) calculations were carried out for the ground state, and a twist angle of 52° was derived for the ground ionic state. Vibrational fine structure was resolved for the first excited ionic state (A^2E), and assigned to combinations of two symmetric vibrations, $\nu_2(a_1)$ and $\nu_3(a_1)$, with vibrational frequencies of 1320(6) and 1030(6) cm^{-1} , respectively.

1. Introduction

High-resolution photoelectron spectroscopy (PES) of allene is of special interest, both because its unique molecular geometry with two perpendicular π orbitals is a prototype of the D_{2d} molecular point group, and because its ground-state PE spectrum provides a typical example of the Jahn–Teller effect involving nondegenerate vibrations. In spite of this interest, no very-high-resolution PE spectrum has been available until now, especially beyond the first band.

Baker, Turner and Brundle [1] first studied the HeI PE spectrum of allene. They pointed out the involvement of the Jahn–Teller effect in the ground ionic state. Using the MINDO/2 method, Haselbach [2] optimized the equilibrium geometry of the allene cation and found that a D_2 symmetry with a dihedral angle of 38° between the two CH_2 groups was most energetically favorable for the ground ionic state. Thomas and Thompson [3] measured a slightly higher-resolution PE spectrum of allene, and suggested that the complex vibrational structure of the first band involved the Jahn–Teller effect, mainly coupled through the torsional mode $\nu_4(b_1)$. Ce-

derbaum et al. treated the theory of Jahn–Teller effect induced by nondegenerate vibrations [4–6], and applied it to the PE spectrum of allene [4], finding qualitative agreement with the available low-resolution experimental spectrum.

Using a supersonic molecular beam with rotational cooling, we have obtained a very-high-resolution HeI PE spectrum of allene. Vibrational structure was completely resolved for the first band. In addition, vibrational fine structure was resolved in the second band for the first time, allowing us to derive vibrational frequencies for the excited state of the cation. We have also performed a series of ab initio DZ MCSCF calculations to model the diabatic torsional potential energy curves of the ground state, and obtained a twist angle between the two CH_2 groups in the cation.

2. Experimental

The apparatus has been described in detail before [7]. The main feature was the coupling of a supersonic molecular beam source to a high-resolution hemispherical energy analyzer with a multichannel detector. For better rotational cooling, a seeded allene sample (5% allene in He) was used. The allene/He beam, expanded through a 0.10 mm nozzle and

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skimmed by a 0.9 mm diameter conical skimmer, crossed perpendicularly with the photon beam from a He discharge lamp. The photoelectrons were detected at 90° with respect to both the molecular beam and the photon beam. The spectrum is shown in fig. 1. Three separate scans were taken through the known spectral region (one scan from 9.5 to 11.25 eV, two scans from 13.2 to 18.6 eV). Each scan was accomplished within 2 h to minimize the energy scale shift, and was followed by an Ar^+ PE spectrum for calibration. Four complete spectra were collected and added together to achieve better statistical accuracy. The resolution was 12 meV as measured with the $\text{Ar}^+ 2\text{P}_{3/2}$ peak. The energy scale shift was about ± 2 meV within each scan.

3. Computational method

To calculate the torsional potential energy curves of the ground ionic state, we used the ab initio multiconfiguration self-consistent field (MCSCF) method, with a double-zeta (DZ) basis set comparable to Pople's 3-21G set [8]. A total of 210 configurations were obtained by allowing five electrons to be distributed among six orbitals. Geometry optimization was carried out with the HONDO program [9], which included a Newton-Raphson orbital optimization procedure [10].

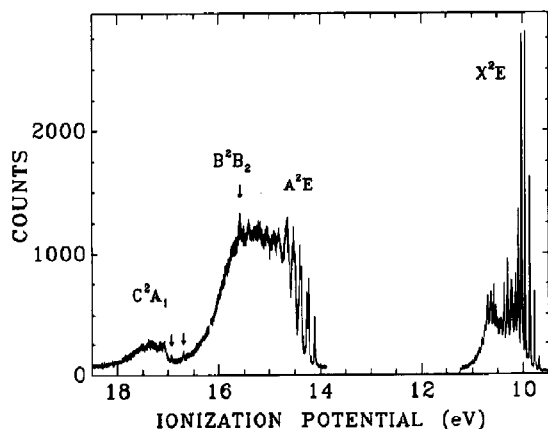


Fig. 1. The HeI photoelectron spectrum of allene. The arrows indicate some background contributions from N_2 .

4. Results and discussion

The $4a_1, 3b_2, 1e, 2e$ molecular orbitals are accessible with the HeI line [11]. The $2e$ orbital is composed of the two perpendicular C-C π orbitals, the $1e$ orbital is mainly from a π -type combination of the C-H σ orbitals with some contribution from the C-C π orbitals, the $3b_2$ orbital is mainly from the C-C σ orbitals, and the $4a_1$ orbital is mainly of C $2s$ character. Fig. 1 shows the PE spectrum with the assignments. Clearly, the X^2E and A^2E bands show well-resolved vibrational structure. The B^2B_2 and C^2A_1 bands involve continuum dissociations, and no fine structure was resolved even under the current high-resolution conditions. In the following, we shall focus mainly on the first two bands.

4.1. The X^2E band

The first band of the allene PE spectrum is displayed in fig. 2. It shows a pronounced progression, with sharp lines in the region from 9.65 to 10.15 eV and then two humps, each with fine structure. The main spectral features are labeled with numbers, and the minor spectral features and small shoulders are labeled with primed or double-primed numbers. The ionization potentials are given in table 1. The X^2E ground state results from ionization of the $2e$ orbital. According to the Jahn-Teller theorem [12], this doubly degenerate state is not stable against certain

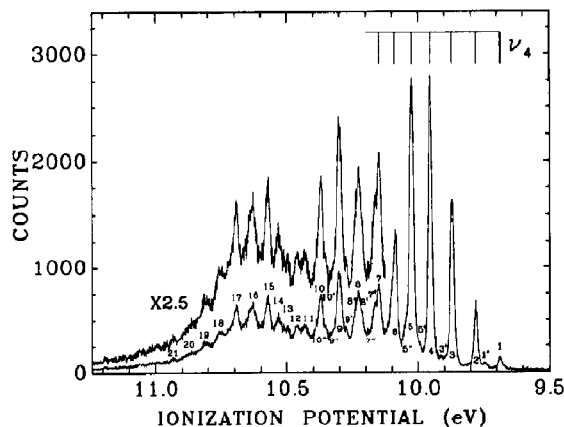


Fig. 2. The Jahn-Teller active X^2E band of the allene photoelectron spectrum.

Table 1
The ionization potentials (IPs) for the X ²E ground state of the allene cation

Peak No.	IP (eV) ^{a)}
1	9.6878
1'	9.7456
2	9.7803
3	9.8700
3'	9.909
4	9.9539
5'	9.9970
5	10.0250
5''	10.0466
6	10.0906
7	10.1494
7'	10.1673
7''	10.1890
8'	10.2146
8	10.2277
8''	10.2408
9'	10.2746
9	10.3004
9''	10.3213
10'	10.3525
10	10.3705
10''	10.3873
11	10.4314
12	10.4620
13	10.495
14	10.533
15	10.572
16	10.633
17	10.692
18	10.755
19	10.810
20	10.866
21	10.934

^{a)} The uncertainty is ± 0.002 eV. The extended accuracy is meaningful only for peak spacings.

asymmetric vibrations and the molecule will consequently be distorted to a lower symmetry in this state. In most cases, degenerate vibrations are coupled in Jahn–Teller distortions. However, it has been shown that only nondegenerate vibrations are active for D_{2d} molecules [4].

Cederbaum et al. [4–6] have studied the theory of the Jahn–Teller effect induced by nondegenerate vibrations and calculated the PE spectra of allene [4]. They found that the Jahn–Teller effect in the ground state of the allene cation was caused by coupling with the torsional mode $\nu_4(b_1)$ and the antisymmetric

stretching mode $\nu_7(b_2)$. They pointed out that the torsional vibration was dominant and that the antisymmetric stretching played an important role in modulating the coupling of the torsional motion. They found that the ground-state allene ion was non-planar with a twist angle of 52°. Their spectral simulation was in qualitative agreement with the then available PE spectrum, and the vibronic coupling was concluded to be responsible for the complex vibrational structure of the first band.

Cederbaum et al. also simulated a high-resolution spectrum with a 5 meV fwhm linewidth. It is remarkable that the calculated spectral features agree with the main features in our high-resolution spectrum very well up to ≈ 10.3 eV, even though they did not use the correct ionic spectroscopic constants. However, above 10.3 eV, it seems that we have resolved more spectral features than the simulation can account for. As pointed out before and shown in fig. 2, the vibrational structure at low energies was dominated by the torsional $\nu_4(b_1)$ mode, while the complicated vibrational structure at higher energies was mainly modulated by the coupling of the antisymmetric $\nu_7(b_2)$ mode. The disagreement at the higher energies implies either that the $\nu_7(b_2)$ coupling was not sufficiently accounted for in the calculation or possibly that more modes are involved. Thus, the current spectrum should provide a better calibration for the theoretical vibronic coupling calculations.

To understand further the nature of the vibronic coupling in the X ²E state, we have performed a series of ab initio DZ MCSCF calculations on the torsional potentials. The results are shown in fig. 3, which plots the potential energy versus the torsional angle relative to planar geometry. The solid curves correspond to the bond lengths C¹–C²=C²–C³=1.35 Å, the optimized value at the potential minimum. The dashed curves are based on unequal bond lengths: C¹–C²=1.32 Å and C²–C³=1.40 Å, that is, by including the coupling of the antisymmetric stretching mode. The following conclusions can be drawn from fig. 3. Firstly, over a large region near the potential minimum, the solid curve is lower than the dashed one. Thus the torsional mode dominates the low energy levels, as shown in fig. 2. Secondly, the potential energy minimum for the solid curve is at 52.2°, which is in excellent agreement with the vibronic calculation [4]. Thirdly, at 90°, the dashed

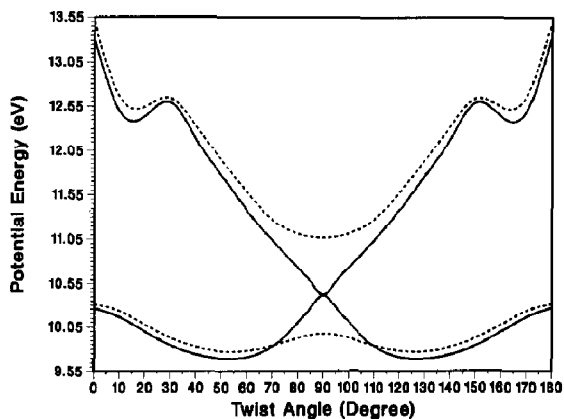


Fig. 3. Potential energy curves for the Jahn-Teller active X^2E ground state of the allene cation versus twist angle. The solid curves represent the two components of the 2E state with $C^1-C^2=C^2-C^3=1.34$ Å. Note the state is degenerate at 90° where the cation has D_{2d} symmetry. The dashed curves represent the two components of the 2E state for the optimized bond lengths at 90° with $C^1-C^2=1.32$ Å and $C^2-C^3=1.40$ Å. Note that the energy gap between the two components at 90° goes to zero as the two C=C bond lengths become equal for D_{2d} symmetry.

curves, which have two unequal C=C bond lengths, are separated, indicating involvement of the $\nu_7(b_2)$ mode in the Jahn-Teller coupling. This supports the earlier vibronic calculation [4]. Finally, two shoulders in the upper potential curves were observed, which have not been reported before. They should be due to avoided curve crossings with the first excited state A^2E , which is also subject to Jahn-Teller distortions.

A previous calculation on neutral allene [13] found a torsional rotation barrier of about 2.3 eV. From fig. 3, we can see that the barrier is reduced to about 0.6 eV in the cation. Thus, the perpendicular π bonding is substantially weakened upon removal of a π electron.

4.2. The A^2E band

This band was not well resolved previously. The current spectrum is shown in fig. 4. More than one vibrational progression is resolved and the assignments are also given in fig. 4. The vibrational structure is basically composed of combinations of the $\nu_2(a_1)$ and $\nu_3(a_1)$ symmetric vibrations. The ν_2 mode is mainly the CH_2 scissoring motion and ν_3 involves

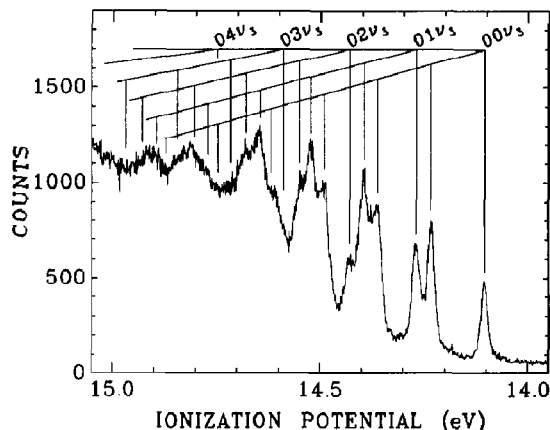


Fig. 4. The fine structure and assignments of the A^2E band of the allene photoelectron spectrum.

mainly the C-H and C=C=C symmetric stretch motions [14].

The A^2E state results from ionization of the $1e$ orbital, which, as stated before, is composed mainly of the π -type combination of the C-H σ bonds plus some contribution from the C=C π bonds. When an electron is ionized from this orbital, the C-H bonds are equally weakened. Thus, it is not surprising that the ν_2 and ν_3 symmetric vibrations are strongly excited. It is important to point out that there is no Jahn-Teller effect in the A^2E state because the two

Table 2

The ionization potentials (IPs) and assignments for the A^2E state of the allene cation

IP (eV) ^{a)}	Assignment (ν_1 ν_2 ν_3)
14.1053	0 0 0
14.2335	0 0 1
14.2689	0 1 0
14.3629	0 0 2
14.3949	0 1 1
14.4300	0 2 0
14.4922	0 0 3
14.5239	0 1 2
14.5511	0 2 1
14.6098	0 0 4
14.6464	0 1 3
14.6805	0 2 2

^{a)} The uncertainty is ± 0.002 eV. The extended accuracy is meaningful only for peak spacings.

Table 3
Spectroscopic constants of the allene cation

State	IP (eV) ^{a)}	ν_2 (cm ⁻¹) ^{b)}	ν_3 (cm ⁻¹) ^{b)}	ν_4 (cm ⁻¹) ^{b)}
X ² E ^{c)}	9.688(2)			745(5)
A ² E	14.105(2)	1320(6)	1030(6)	

^{a)} The adiabatic ionization potential. ^{b)} The fundamental vibrational frequency.

^{c)} For convenience, we maintained the state labeling under the undistorted D_{2d} symmetry.

vibrational modes excited upon photoionization are symmetric and not Jahn–Teller active.

The ionization potentials are given in table 2 with the assignments. The derived vibrational frequencies are 1320(6) and 1030(6) cm⁻¹ for ν_2 and ν_3 , respectively. The spectroscopic constants obtained from this work are summarized in table 3.

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