LBL-27633
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

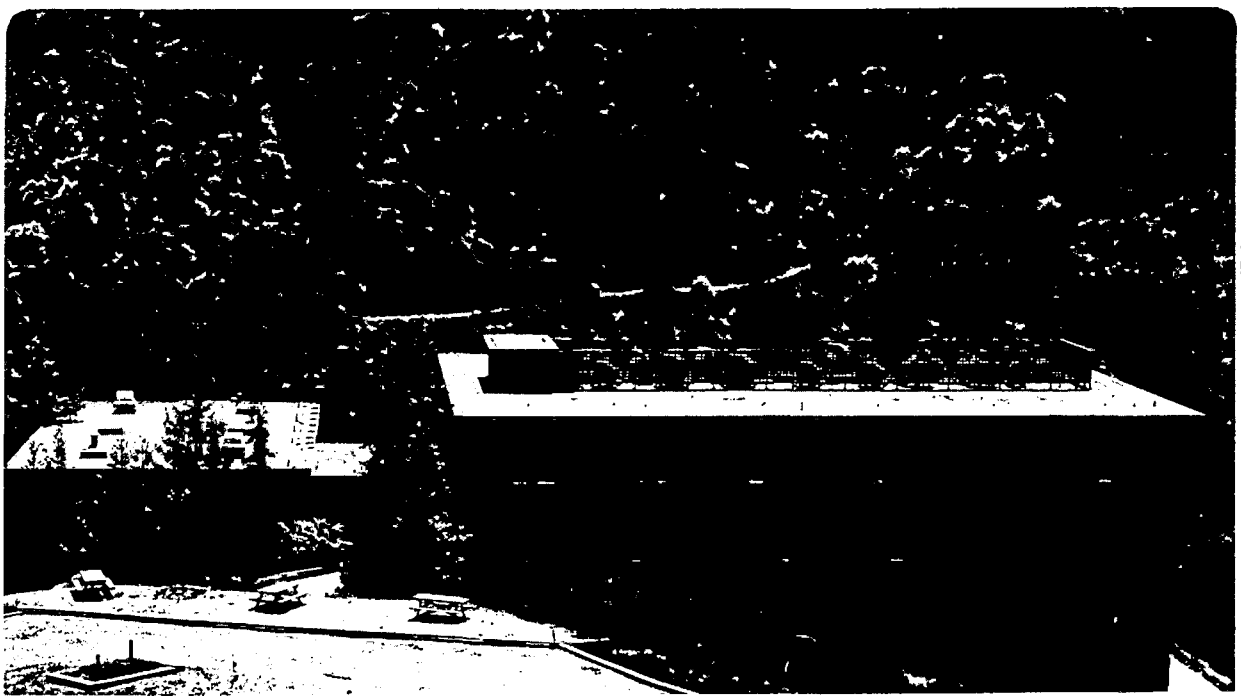
Materials & Chemical Sciences Division

Submitted to Journal of Physical Chemistry

Molecular Beam Photoelectron Spectroscopy of Allene

Z.Z. Yang, L.-S. Wang, Y.T. Lee, D.A. Shirley,
S.Y. Huang, and W.A. Lester, Jr.

August 1989



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

LBL-27633
Copy 2
Bldg. 50 Library.
LOAN COPY
Circulates
for 2 weeks

DISCLAIMER

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

LBL-27633

Molecular Beam Photoelectron Spectroscopy of Allene

Z.Z. Yang*, L.-S. Wang, Y.T. Lee

D.A. Shirley,** S.Y. Huang, W.A. Lester Jr.

Department of Chemistry, University of California

and Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory, 1 Cyclotron Road

Berkeley, California 94720

* Permanent address: Institute of Theoretical Chemistry, Jilin University, Changchun, People's Republic of China.

** To whom correspondence should be forwarded.

Abstract

High resolution photoelectron spectrum of allene rotationally cooled in a supersonic molecular beam has been measured. Analysis of the first part of the 1^2E band based on a simple anharmonic potential model for the torsional vibration near equilibrium geometry yield the force constant $k=16921\pm20$ cm^{-1}, the vibrational frequency $\nu_4(b_1)=806\pm8$ cm^{-1} and the twist angle $\theta=49\pm3^o$ for the ground ionic state. A series of ab initio DZ MCSCF calculations for the two low-lying ionic states of allene gave a good description of the first band. Three vibrational progressions in the second band were resolved and assigned to the three totally symmetric vibrations $\nu_1(a_1)$, $\nu_2(a_1)$ and $\nu_3(a_1)$, with vibrational frequencies 2597 cm^{-1}, 1315 cm^{-1}, and 1024 cm^{-1}, respectively.

I. Introduction

High resolution photoelectron spectroscopy (PES) of allene is of great interest, because, firstly, its peculiar molecular geometry is a prototype of molecular point group D_{2d}, and, secondly, its PE spectrum provides a typical example of the Jahn-Teller effect involving C-C π orbitals in a simple molecule. In spite of its importance, no high resolution PE spectrum has been available.

In 1969, Baker and Turner[1] first studied the PE spectrum of allene in the ionization region 9-21 eV. They pointed out that the Jahn-Teller effect in the ground ionic state resulted from electron ionization of the $2e(\pi)$ orbital in neutral allene. Using the MINDO/2 method, Haselbach[2] optimized the equilibrium geometry of the allene radical cation and found the D_2 symmetry with a dihedral angle of 38° between the two CH_2 groups was most energetically favorable for the ground ionic state of allene. In 1974, Thomas and Thompson[4] measured a PE spectrum of allene with somewhat higher resolution (19 meV), and suggested that the complex vibrational structure of the first band formed by π electron ionization appeared to involve the Jahn-Teller effect mainly coupled with the torsional mode $\nu_4(b_1)$. Heilbronner et al.[3] studied the PE spectrum of allene within the Koopmans' approximation in 1977. Cederbaum et al. discussed the theory of the Jahn-Teller effect induced by non-degenerate vibrational modes,[5,6,7] and applied it to the PE spectrum[5] of allene, finding good agreement with the general features of the experimental spectrum, although they used the vibrational frequencies of neutral allene as parameters.

By using the molecular beam method, we have obtained a high resolution (12 meV FWHM) PE spectrum of allene with HeI 584 Å radiation. We have resolved more vibrational structure than before. We used a simple anharmonic model and a second-order perturbation calculation to analyze the fine structure due to excitation of the torsional vibrational mode in the 9.65-10.15eV range of the first band. From the best fit, we derived new parameters for the ground ionic state of allene, including the vibrational frequency, the force constant for the torsional mode, and the magnitude of the dihedral angle between the planes of the two CH_2 groups. In addition, we did a series of ab initio DZ MCSCF calculations to model the diabatic torsional potential energy curves for both the ground and first excited states.

In Section II, a brief description of the technique used in this paper is presented. Section III gives a brief account of the computational method we used. Section IV contains the results and discussion.

II. Experimental

The apparatus has been described in detail before.[8] The main features involved the combination of a molecular beam source with a high resolution hemispherical energy analyzer and a multichannel detector. The analyzer pass energy was set at 1 eV. For better rotational cooling, a seeded allene sample (5% allene in He) was used in the supersonic expansion. The allene/He beam, expanded through a 0.10 mm nozzle and skimmed by a 0.9 mm diameter conical skimmer, crossed perpendicularly with the photon beam (HeIα, 584Å) from a helium discharge lamp. The photoelectrons were detected at 90° with respect to both the molecular beam and the photon beam. Three separate scans were taken through the known spectral region (1 scan from 9.5

to 11.25 eV, 2 scans from 13.2 to 18.6 eV). Each scan was made within 2 hrs to minimize the energy scale shift, and was followed by a Ar^+ PE spectrum for calibration. Four complete spectra were collected and added together to give better statistics. The resolution was 12 meV FWHM as measured with Ar^+ $^2P_{3/2}$. The energy scale shift was about ±2 meV within each scan.

III. Computational Method

In this study, 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.[11] A total of 210 configurations were obtained by allowing the five π electrons to be distributed among six orbitals. Geometry optimization was carried out with the Hondo program,[12] which included a Newton-Raphson orbital optimization procedure.[13]

IV. Results and Discussion

Figure 1 shows our PE spectrum of allene. The three regions, 9.5-11.5 eV, 13.8-16.8 eV and 16.8-18.0 eV, will be referred to as the first, second and third band, respectively. Clearly, the first band and part of the second band have fine structure. We shall discuss these two bands in order.

For convenience, designations of the ionic states are from the D_{2d} symmetry to which the neutral allene belongs, though the geometry of the allene cation may have different symmetry.

A. First band (1^2E states)

The first band of the allene PE spectrum is expanded in Figure 2. It shows a pronounced progression, with sharp lines in the region 9.65-10.15 eV and then two humps, each of which contains fine structure. Figure 3(a) shows the well-known picture of one of the degenerate 2e(π) orbitals[9] of allene from which an electron is taken out to form the 1^2E states in $C_3H_4^+$. This vertical 2e(π) orbital consists of a dominant $C^{(1)}$-$C^{(2)}$ π bond. The horizontal 2e(π) orbital is entirely equivalent to the vertical one, but in a perpendicular plane. These two π orbitals taken together constitute the basis of the E irreducible representation of the molecular symmetry D_{2d} of allene. When an electron is ionized from either of the 2e(π) orbitals, the resultant ionic state 1^2E would be doubly degenerate if the geometry of allene were unchanged during this process. According to the theory of the Jahn-Teller effect,[10] the molecular framework should distort to remove the electronic degeneracy, if a non-symmetric vibrational mode gets excited.

Cederbaum et al.[5,6,7] have explored the theory of the Jahn-Teller distortion induced by non-degenerate vibrations and calculated the PE spectra of a series of molecules, including allene.[5] They found that the Jahn-Teller distortion is caused by vibronic coupling of the 1^2E degenerate electronic states with the torsional mode b_1 and the antisymmetric mode b_2. They emphasized that the torsional mode is dominant, and that the antisymmetric stretching mode also plays an important role in modulating the coupling between the electronic and vibrational motions. This coupling is responsible for the complex vibrational structure of the first band.

One can give a heuristic interpretation of why the torsional and antisymmetric streching modes are dominantly excited accompanying ionization

of the $2e(\pi)$ electron.[10] From Figure 3, it is evident that removal of an electron from the vertical $2e(\pi)$ orbital mainly weakens the $C^{(1)}$-$C^{(2)}$ bond. The potential barrier to torsional deformation of the $C^{(1)}H_2$ group around the $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ axis is exclusively determined by the vertical π bond, which will now have lost one of its π electrons. Hence the torsional mode is easily excited during this kind of ionization. The antisymmetric stretching mode along the $C^{(1)}$-$C^{(2)}$-$C^{(3)}$ axis is the mode next most easily excited as a result of the inequivalent effect of the $2e(\pi)$ electron on $C^{(1)}$-$C^{(2)}$ and $C^{(2)}$-$C^{(3)}$ bonds.

It has been pointed out that the pronounced progression in the lower energy part of the first band is due to the dominant excitation of the torsional mode.[2,4,5] The supporting evidence is the rapid convergence of the progression.[4] Owing to vibronic coupling, the angle between the planes of the two CH_2 groups in the ground ionic state of allene decreases to be less than 90°. Various values have been given by different authors.[2,5,16,17]

Table 1 lists the PE peaks in the first band. To simulate the torsional vibrational mode near the equilibrium geometry of the ground ionic state, we consider a simple potential energy surface model:

$$U = k\theta^2+k_3\theta^3+k_4\theta^4 \qquad (1)$$

where k is the force constant of the harmonic term and θ is the twist angle from the equilibrium position. With the harmonic term as a basis, we treated $k_3\theta^3+k_4\theta^4$ as a perturbation. We optimized the parameters k, k_3 and k_4 to give the best fit of the calculated vibrational levels with the

pronounced vibrational progression of the first seven peaks the first band, since the torsional mode dominates this region. The fitted peak positions are also given in Table 1. From this fit, we obtained ν_4=806 cm^{-1}, k=16921 cm^{-1}, k_3=543 cm^{-1} and k_4'= -5775 cm^{-1} (with θ in radians). The error limit for these parameters is ±1 percent. The derived value of ν_4 in the cation is smaller than the value 848.59 cm^{-1} for neutral allene,[14] as expected. Figure 4 shows the potential curve based on these parameters. On this curve, the minimum at θ=0°, representing the equilibrium geometry of the cation, lies between two unequal maxima. Assuming that the higher maximum corresponds to a planar geometry of the cation, its twist angle relative to the equilibrium minimum is 49±3°.

To assist the analysis, we have performed ab initio DZ MCSCF calculations of the two low-lying states of allene cation. The results are shown in Figure 5, which plots the potential energy versus the twist angle relative to the planar geometry of the cation. The solid curves correspond to the bond lengths $C^{(1)}$-$C^{(2)}$ = $C^{(2)}$-$C^{(3)}$ = 1.3462 Å, the optimized value at the potential minimum. The dotted curves are based on unequal bond lengths: $C^{(1)}$-$C^{(2)}$ = 1.32 Å and $C^{(2)}$-$C^{(3)}$ = 1.40 Å. The following conclusions can be drawn from Figure 5. Firstly, over a large region near the minimum, the solid curve is lower than the dotted one. Thus the torsional mode dominates the lowest levels of the first band. Secondly, the potential energy minimum for the solid curve is at 52.2°, which is quite close to the value obtained from the simulation of the PE spectrum mentioned above. The twist angles obtained by different methods are listed in Table 2. Thirdly, at θ=90°, the two states (solid curves) are degenerate, but for

the dotted line they are separated, which is a typical Jahn-Teller effect. The two shoulders in the upper potential curve, which have not been reported previously, are not understood.

The region from 10.1 eV to 11.0 eV of the first band corresponds to the strong vibronic interaction area of the two low-lying electronic states with both torsional and antisymmetric vibrations, as Cederbaum et al. have pointed out[5].

B. Second Band (2^2E and 1^2B_2 states)

This band was not well resolved in previous experiments.[1,3,4] The resolved structures in our PE spectrum are shown in Figure 6, where we observed three progressions with nearly the same spacings.

Within Koopmans' approximation, the second band includes ionizations from the $1e(\pi)$ and $3b_2$ molecular orbitals.[3,9] The resolved fine structures in this band should belong entirely to the 2^2E states of the cation. The vertical MO of the $1e(\pi)$ is shown in Figure 3 (b). It is composed of the π-type combination of two $C^{(3)}H$ σ bonds plus a $C^{(1)}$-$C^{(2)}$ π bond, with the former dominant. When an electron is ionized from this orbital, two $C^{(3)}H$ bonds are equally weakened. The three symmetric vibrational modes, ν_1, ν_2 and ν_3, should be strongly excited, since they involve the equal stretching of these two σ bonds.[15] One would not expect a significant Jahn-Teller effect in the 2^2E states of the cation because symmetric modes are not Jahn-Teller active. This agrees with our observation.

The fine structure assignments in this band are given in Table 3 and shown in Figure 6. Indeed, only ν_1, ν_2 and ν_3 were observed. From these assignments, we obtained ν_1=2597 cm^{-1}, ν_2=1315 cm^{-1} and ν_3=1024 cm^{-1} with error limits ±16cm^{-1} for the 2^2E states of the cation (ν_1=3015.51cm^{-1}, ν_2 =1442.55cm^{-1} and ν_3=1072.22cm^{-1} in the neutral allene[14]).

The high energy side of the second band and the entire third band involve continuum dissociation, and no fine structure was resolved even under the high resolution conditions of this experiment.

ACKNOWLEDGMENTS

L.S.W would like to thank Anne-Marie Schmoltner for supplying the allene/He sample. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Departmment of Energy under Contract No. DE-AC03-76SF00098.

TABLE 1. Ionization Potentials of the First Band of Allene.

IP(eV)[a]	Calculated IP(eV)
9.688	9.688
9.781	9.781
9.871	9.869
9.954	9.951
10.026	10.025
10.092	10.092
10.150	10.151
10.169	
10.229	
10.301	
10.372	
10.432	
10.462	
10.497	
10.533	
10.574	
10.633	
10.695	
10.752	
10.812	

a. The uncertainties are ± 0.002eV for the sharp peaks.

TABLE 2. Twist Angles (degree) Corresponding to the Minimum Energy for the C-C-C Linear Structure of Allene Cation.

Twist angle	Methods	Refs.
38.0	MINDO/2	2
52.0	Vibronic Coupling	5
45.0	MNDO	16
44.7	ab initio SCF(UHF)	17
50-60	ESR	18
49±3	PES Fitting	this work
52.2	ab initio MCSCF	this work

TABLE 3. Ionization Potentials for the First Part of the Second Band.

IP(eV)[a]	Assignment[b]
14.104	(0 0 0)
14.231	(0 0 1)
14.267	(0 1 0)
14.362	(0 0 2)
14.392	(0 1 1)
14.426	(1 0 0)
14.489	(0 0 3)
14.520	(0 1 2)
14.548	(1 0 1)
14.612	(0 0 4)
14.650	(0 1 3)
14.681	(1 0 2)

a. See footnote in Table 1.

b. The numbers in parentheses are the respective quantum numbers of the Three a_1 vibrational modes of the cation, ν_1, ν_2 and ν_3.

References

1. (a) C. Baker and D.W. Turner, Chem. Commun., 480 (1969); (b) D.W. Turner, C. Baker, A.D. Baker, and C.R. Brundle, Molecular Photoelectron Spectroscopy (Wiley, New York, 1970).
2. E. Haselbach, Chem. Phys. Lett., 7, 428 (1970).
3. G. Bieri, F. Burger, E. Heibronner, and J.P. Maier Helv. Chim. Acta, 60, 2213 (1977).
4. R.K. Thomas and H. Thompson, Proc. R. Soc. London, A. 339, 29 (1974).
5. L.S. Cederbaum, W. Domcke and H. Koppel, Chem. Phys., 33, 319 (1978).
6. L.S. Cederbaum, W. Domcke , H. Koppel and W. von Nissen, Chem. Phys., 26, 169 (1977).
7. L.S. Cederbaum, H. Koppel and W. Domcke, Int. J. Quantum Chem.: Quantum Chemistry Symposium, 15, 251 (1981).
8. J.E .Pollard, D.J. Trevor, J.E .Reutt, Y.T. Lee and D.A. Shirley, J. Chem. Phys., 77, 34 (1982).
9. K. Kimura et al., Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules (Halsted Press, New York, 1981).
10. (a) J.H.D. Eland, Photoelectron Spectroscopy, p142 (Butteworths, London, 1984); (b) J.W. Rabelais, Principles of Ultraviolet Photoelectron Spectroscopy (Wiley, New York, 1977).
11. J.S. Binkley, J.A. Pople and W.J. Hehre, J. Am. Chem. Soc, 102, 939 (1980).
12. M. Dupuis, J. Rys and H.F. King, J. Chem. Phys., 65, 111 (1976).
13. L. Yaffe and W.A. Goddard III , Phys. Rev. A13, 1682 (1958).
14. F. Hegelund, J.L. Duncan and D.C. McKean, J. Mol. Spectros. 65, 366 (1977).

15. (a) R.C. Herman and W.H. Shaffer, J. Chem. Phys.,17, 30 (1949). (b) G.Herzberg, Infrared and Raman Spectra (VNR company, New York, p339,1945).

16. G. Frenking and H. Schrarz, Int. J. Mass Spectrom Ion Phys., 52, 131 (1983).

17. K. Haddaway, et al., J. Org. Chem. 52, 4239 (1987).

18 Y. Takemura, T. Shida, J. Chem. Phys., 73, 4133 (1980).

Figure Caption

Figure 1. HeI PE spectrum of allene.

Figure 2. The first band of the allene PE spectrum.

Figure 3. The vertical molecular orbitals: (a) for $2e(\pi)$; (b) for $1e(\pi)$.

Figure 4. The potential curve of the torsional mode in the ground ionic state of allene following Eq. (1). Note that here the potential minimum is set at o degree twist angle.

Figure 5. Potential curves for the two lowest-lying states of allene cation vs. twist angle: o and ● curves represent the 1^2E ground state and 2^2E excited state of $C_3H_4^+$, respectively, when $C^{(1)}$-$C^{(2)}$ = $C^{(2)}$-$C^{(3)}$ = 1.3242Å. Note the two curves cross at 90° where the cation has D_{2d} symmetry. □ and ■ represent the 1^2E ground state and the 2^2E excited state for the optimized bond lengths at 90°, with $C^{(1)}$-$C^{(2)}$ = 1.32Å and $C^{(2)}$-$C^{(3)}$ = 1.40Å. Note that the energy gap between the two lowest-lying states at 90° goes to zero as the two C-C bond lengths become equal for the D_{2d} symmetry.

Figure 6. Fine structure and assignments of the second band.

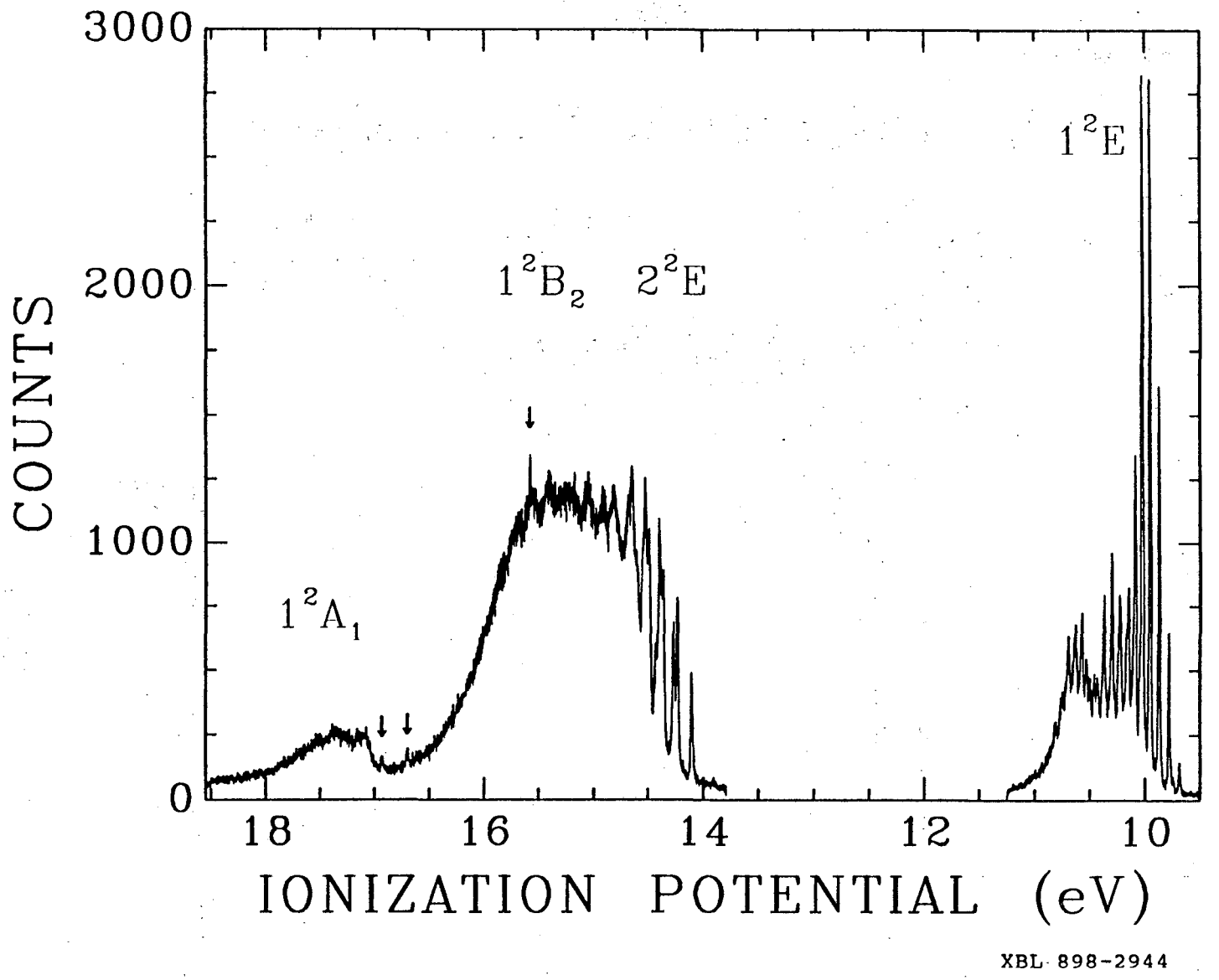
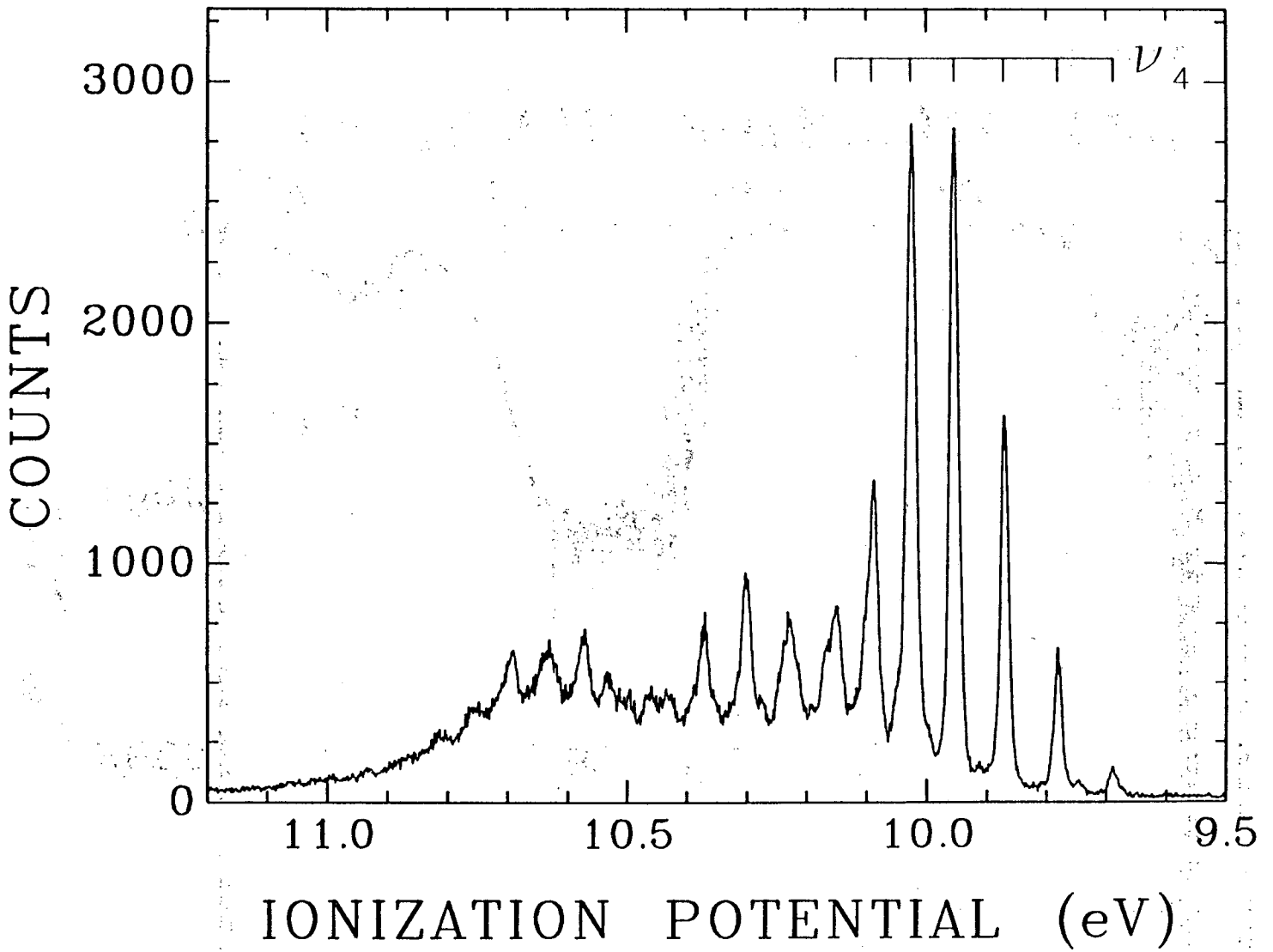
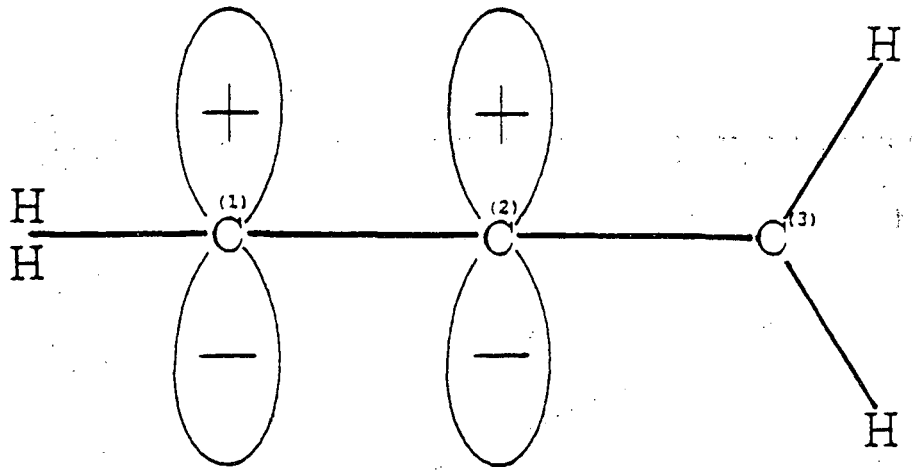

3000
2000
1000
0
COUNTS
1^2A_1
1^2B_2 2^2E
1^2E
18
16
14
12
10
IONIZATION POTENTIAL (eV)
XBL 898-2944

Figure 1

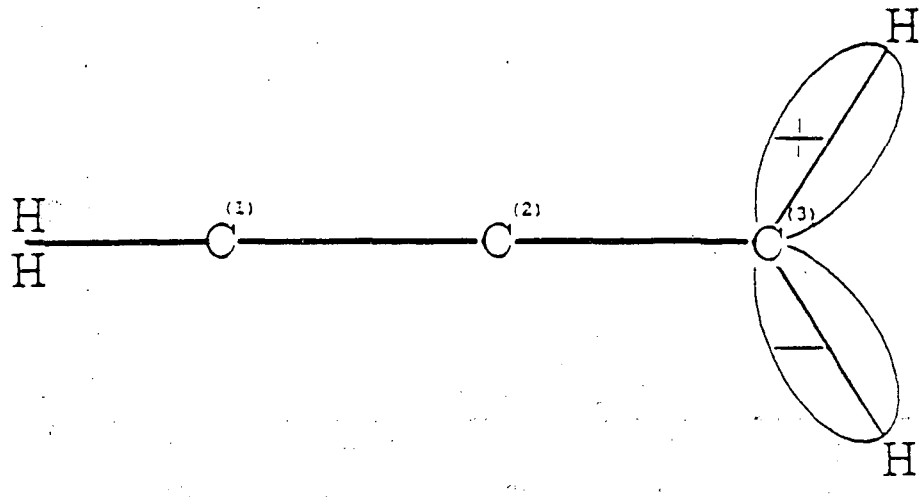


XBL 898-2945

Figure 2



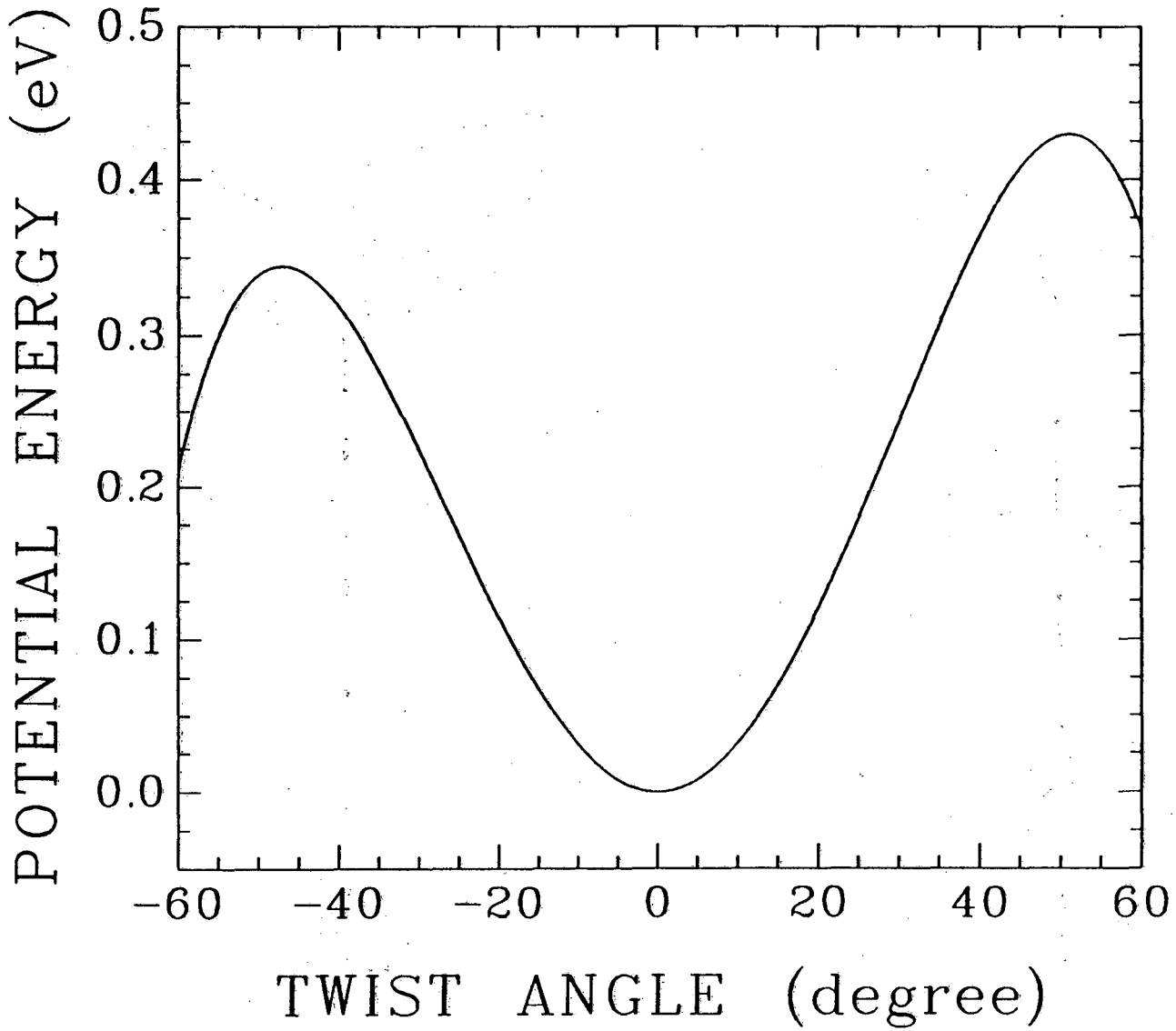
(a)



(b)

XBL 898-2947

Figure 3



XBL 898-2946

Figure 4

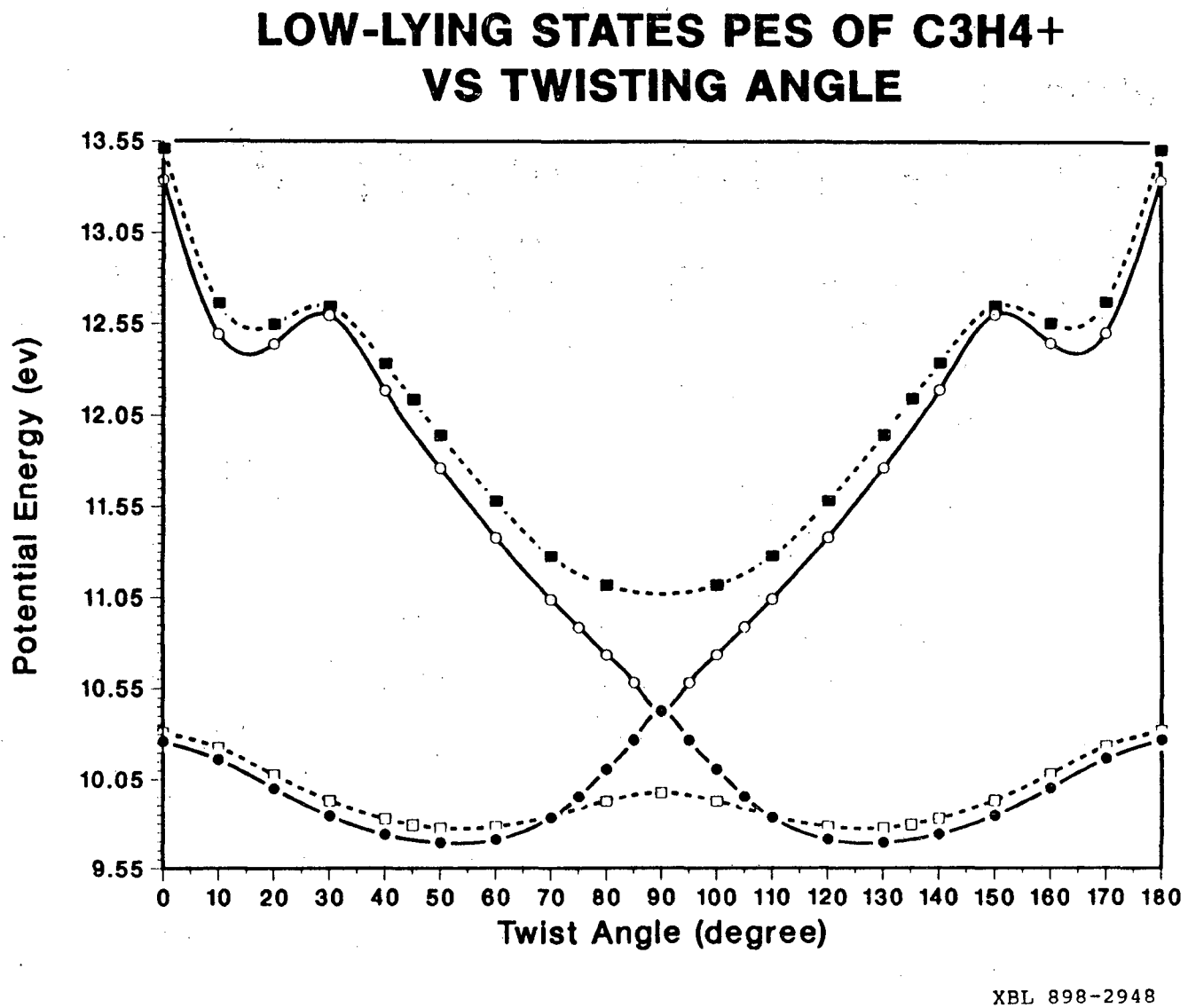

LOW-LYING STATES PES OF C3H4+
VS TWISTING ANGLE
Potential Energy (ev)
13.55
13.05
12.55
12.05
11.55
11.05
10.55
10.05
9.55
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
Twist Angle (degree)
XBL 898-2948

Figure 5

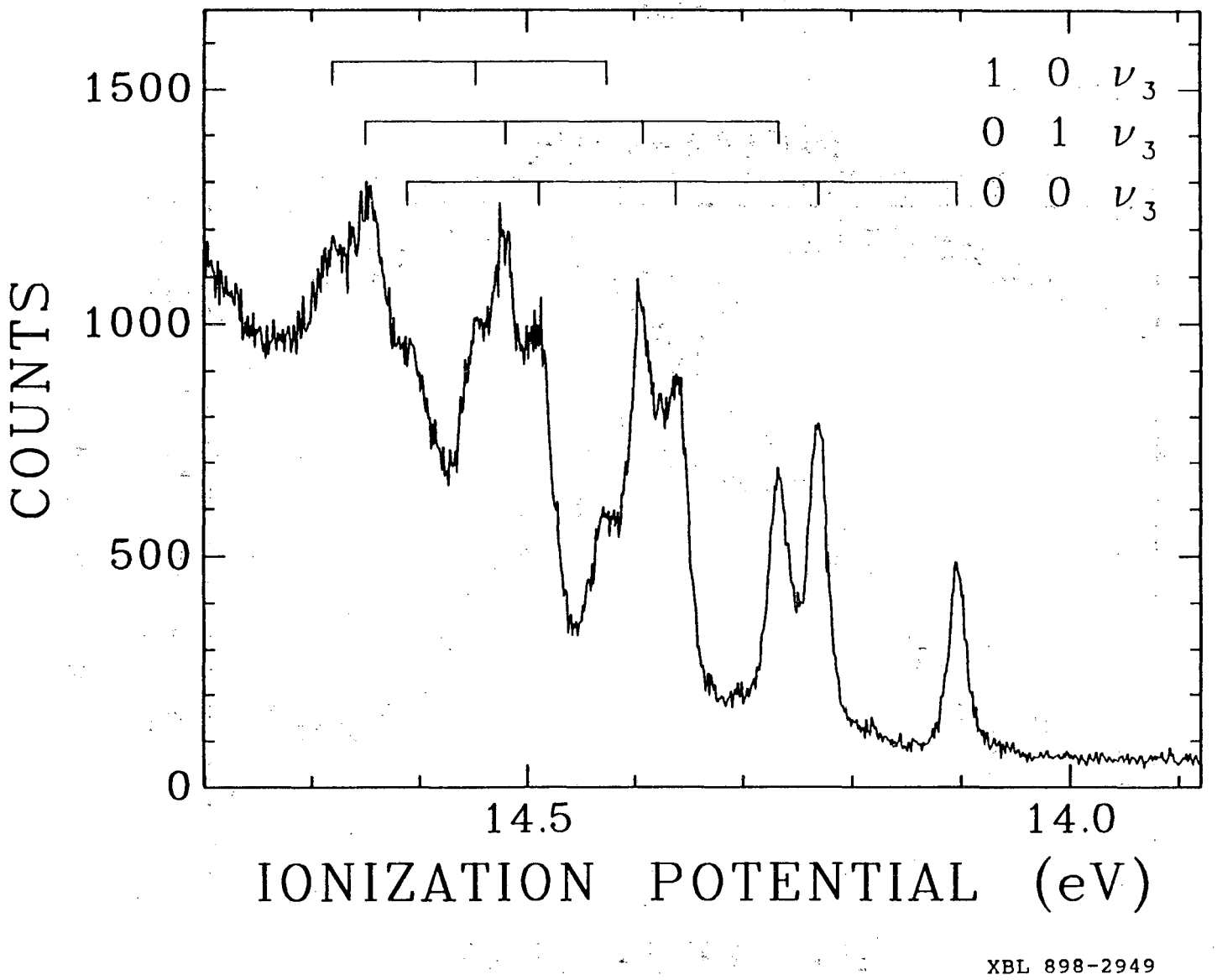

1500
1000
500
0
COUNTS
14.5
14.0
IONIZATION POTENTIAL (eV)
1 0 ν_3
0 1 ν_3
0 0 ν_3
XBL 898-2949

Figure 6

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720