

Molecular beam photoelectron spectroscopy: The $C_2D_4^+$ (\tilde{X}^2B_3) ground state

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The He I (584 Å) photoelectron spectrum of $C_2D_4^+$ in its ground electronic state has been measured, using a supersonic molecular beam. The combination of rotational cooling and improved resolution permits new vibrational fine structure to be observed and assigned. In particular, the ν_3 value is accurately determined. A systematic increase in the ν_4 torsional frequency with increasing excitation of the ν_2 C=C stretching vibration is observed, indicating significant coupling between these modes.

I. INTRODUCTION

The He I (584 Å) photoelectron (PE) spectrum of ethylene has been investigated by a number of authors.¹⁻⁷ The $C_2H_4^+$ (\tilde{X}^2B_3) ground state PE spectrum shows vibrational fine structure involving excitation of the C=C stretching mode (ν_2), the CH_2 angle bending mode (ν_3), and the torsional vibrational mode (ν_4). In the past, the interpretation of this state was based on the analogy between the PE spectrum and the 1744 Å Rydberg spectrum of C_2H_4 , with the exception that the ν_3 mode is not active in the Rydberg transition.⁸ In a recent study, Pollard *et al.*⁷ reported a high quality He I PE spectrum of ethylene by using a supersonic molecular beam. Based on the Franck-Condon principle, they retained the traditional assignment of ν_2 as the major vibrational progression in the $C_2H_4^+$ ground state. The ν_2 and ν_3 fundamental vibrational frequencies were obtained as 1264 and 1494 cm^{-1} , respectively.

Cvitaš, Güsten, and Klasinc⁵ measured the ground state PE spectrum of $C_2D_4^+$ and obtained ν_2 and ν_3 as 1340 and 1050 cm^{-1} , respectively. Thus the ordering of the ν_2 and ν_3 vibrational frequencies appears to be reversed from $C_2H_4^+$ to $C_2D_4^+$. Cvitaš *et al.*⁵ explained this by invoking a Fermi resonance between ν_2 and ν_3 in $C_2H_4^+$, as Brundle and Brown³ proposed. However, McDiarmid⁹ questioned the traditional assignment for ν_2 and ν_3 in the $C_2H_4^+$ ground state PE spectrum on the basis of the noncrossing rule and Rayleigh's rule. She proposed to interchange the ν_2 and ν_3 assignments, based on the evidence from studies of the first photoelectron bands of the $C_2H_nD_{4-n}$ series of isotopic molecules by Cvitaš *et al.*⁵ and from studies of $3s$, $3p$, $3d$, $3d'$, $4d'$, and $5s$ Rydberg spectra of these isotopic molecules.¹⁰ Pollard and Trevor¹¹ expressed doubts about the ν_3 value (1050 cm^{-1}) in the $C_2D_4^+$ PE spectrum by Cvitaš *et al.*⁵ since the peak in question was barely above the noise. They felt that a reassignment should await the advent of a high quality measurement or a definitive theoretical prediction of the $C_2D_4^+$ vibrational frequencies.

As a consequence of this controversy, Somasundram and Handy¹² performed an *ab initio* SCF calculation on the ν_2 and ν_3 vibrations in the ground state of ethylene ion. They

predicted that the major vibrational progressions differed, being ν_3 for $C_2H_4^+$, but ν_2 for $C_2D_4^+$. An earlier study of Franck-Condon factors by Botter and Carlier^{13,14} on the ν_2 and ν_3 transitions in the ground states of $C_2H_4^+$ and $C_2D_4^+$ had also suggested that the traditional assignment of ν_2 and ν_3 in $C_2H_4^+$ should be reversed in order for the calculated Franck-Condon factors to agree with the experimental results.

In light of this strong theoretical support for the reassignment, an improved experimental spectrum of $C_2D_4^+$ is clearly needed to provide accurate vibrational frequencies and intensities for comparison with theory. We have now obtained such a spectrum under conditions similar to that used by Pollard *et al.* for $C_2H_4^+$.⁷

II. EXPERIMENTAL

The first band of the $C_2D_4^+$ PE spectrum was recorded on a molecular beam photoelectron spectrometer which has been described in detail before.¹⁵ In brief, a 10% C_2D_4 mixture with He was expanded through a 100 μ nozzle and was skimmed by a 0.9 mm diam conical skimmer. The photon beam crossed the skimmed molecular beam at 90°. The analyzer was an electrostatic hemispherical type with position-sensitive multichannel detection. The entrance to the analyzer was perpendicular to both the molecular beam and the photon beam. The resolution of the spectrometer with which the $C_2D_4^+$ spectrum was taken was 13 meV, as measured for $Ar^+ 2P_{3/2}$. The C_2D_4 sample was supplied by Cambridge Isotope Lab. It had a minimum purity of 99% and was used without further purification.

III. RESULTS AND DISCUSSION

The ground state PE spectrum of $C_2D_4^+$ with its vibrational assignment is shown in Fig. 1. Rotational cooling in the present experiment enables all the vibrational fine structure to be more clearly defined and longer vibrational progressions to be evident than in previous experiments. The general features of the spectrum are regular, with the repetition of a group of four peaks. The principal vibrational progression is ν_2 (C=C stretching), which forms the leading peak in each group of the four peaks with 2 and 4 quanta of ν_4 and 1 quantum of ν_3 . We observe ν_2 up to 5 quanta. One quantum of ν_3 excitation is clearly shown in the current spec-

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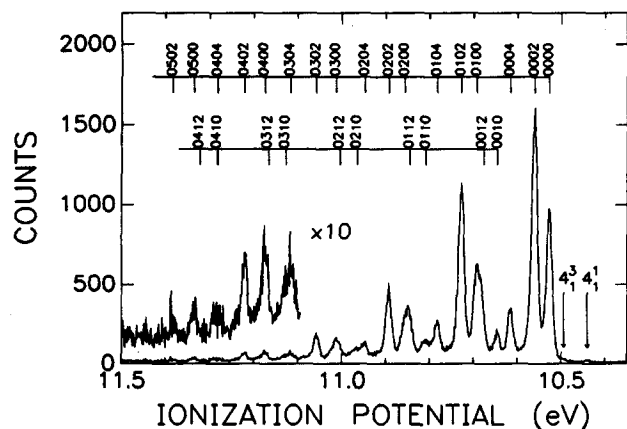


FIG. 1. The He I (584 Å) photoelectron spectrum of $C_2D_4^+$ (\tilde{X}^2B_3) ground state. The vibrational levels are labeled with the ν_1 , ν_2 , ν_3 , and ν_4 vibrational quantum numbers. The symmetry of the state is assumed to be D_2 .

trum, as the fourth peak in each group. Each $0n00$ peak, in the notation of Fig. 1, is overlapped by a $0(n-1)12$ peak. The mean positions of the peaks were determined by a global fitting procedure using Gaussian line shape functions. The overlapping of the $0n00$ peak with the $0(n-1)12$ peak is the major cause of uncertainty in the fitting procedure. The observed splittings and uncertainties are listed in Table I. Least-squares fitting to $\Delta G(\nu_2 + 1/2)$ vs $(\nu_2 + 1/2)$ for $\nu_3 = 0$ yields the following spectroscopic constants: $\omega_e = 1332 \pm 8 \text{ cm}^{-1}$, $\omega_e \chi_e = 5 \pm 4 \text{ cm}^{-1}$. On the high energy side of peak 2 and 4 in each group, there are very weak shoulders present. These are assigned as odd quanta of the torsional mode, $3\nu_4$ and $5\nu_4$, which are vibronically forbidden transitions. These are also observed in the Rydberg transitions.¹⁰ Pollard *et al.*⁷ observed $3\nu_4$ in the $C_2H_4^+$ spectrum. Köppel, Domcke, Cederbaum, and von Niessen¹⁶ discovered that vibronic coupling effects were strong in the ground

TABLE I. Vibrational frequencies in cm^{-1} of the $C_2D_4^+$ (\tilde{X}^2B_3) ground state.^a

ν_3	ν_2	$\Delta G(\nu_2 + \frac{1}{2})$	$\Delta G(\nu_3 + \frac{1}{2})$	$2\nu_4$	$4\nu_4$
0	0	1329(14) ^b		269(7)	714(8)
	1	1322(46) ^b		288(14)	728(15)
	2	1262(45) ^b		294(45)	736(45)
	3	1305(31) ^b		364(31)	859(32)
	4	1295(32) ^b		373(12)	861(18)
1	5			399(22)	
	0	1310(13)	961(8)	266(17)	
	1	1286(17)	941(17)	292(39)	
	2		905(46)		

^a Error limits are given in the parentheses, which combines the uncertainties in the fitting procedure and the energy scale shift during scan ($\pm 0.0005 \text{ eV}$).

^b Values used in least-squares fitting.

state ethylene ion, which accounts for the fact that these forbidden transitions are observed.

Two hot-band transitions can be seen on the low ionization energy side of the spectrum. They are assigned to be 4_1^1 and 4_1^3 . The splittings of these two features from the 0000 peak are 703 ± 10 and $223 \pm 16 \text{ cm}^{-1}$. This is consistent with the temperature-dependence study in the 1744 Å Rydberg spectrum of C_2D_4 by Merer and Schoonveld.⁸ These hot-band transitions were also seen by Stockbauer and Inghram in their threshold PE spectrum.¹⁷ Taking the $1\nu_4$ value of C_2D_4 (726 cm^{-1}),¹⁸ we obtain the $1\nu_4$ and $3\nu_4$ values for $C_2D_4^+$ as 23 ± 10 and $503 \pm 16 \text{ cm}^{-1}$, respectively. The uncertainties are only tentative, since the uncertainty for the $1\nu_4$ value of C_2D_4 is not known. However, these values for the ion are consistent with the calculation of Findley *et al.*¹⁹ and with McDiarmid's values in the Rydberg spectra.¹⁰ Chau²⁰ calculated the torsional energies in $C_2H_4^+$ and $C_2D_4^+$ ground states using a double well potential optimized from earlier experimental results.⁷ In Table II, a comparison is made between the new experimental values and Chau's calculated values for $C_2D_4^+$. The agreement is excellent, implying that Chau's potential is sufficient to account for the observed spectra.

In Table III, the vibrational wave numbers are compared with two previous measurements^{5,17} and with Somasundram and Handy's *ab initio* SCF calculation.¹² Our ν_3 value agrees with Stockbauer and Inghram's measurement, but not with that of Cvitaš *et al.* It agrees reasonably well with the *ab initio* SCF calculation scaled to neutral C_2D_4 . We conclude that Somasundram and Handy's *ab initio* SCF calculation correctly predicted the $C_2D_4^+$ vibrational frequencies.

An interesting observation from Table I is that the values for $2\nu_4$ and $4\nu_4$ exhibit an increase with ν_2 excitation. The values for $2\nu_4$ are plotted in Fig. 2 as a function of the ν_2 vibrational quantum number ν_2 . This shows that the $2\nu_4$ values increase monotonically with the excitation of ν_2 , implying that the C=C stretching vibration (ν_2) is substantially coupled with the torsional vibration (ν_4). Köppel *et al.*¹⁶ calculated the vibrational structure of both the $C_2H_4^+$ and $C_2D_4^+$ ground states in the photoelectron spectra. They found that the mode coupling between the totally symmetric (ν_1 , ν_2 , and ν_3) and the nontotally symmetric (ν_4) vibra-

TABLE II. The observed and calculated torsional energy levels in the $C_2D_4^+$ (\tilde{X}^2B_3) ground state (cm^{-1}).

ν_4	Observed value ^a	Calculated value ^b
0	0	0
1	23(10)	35
2	269(7)	267
3	503(16)	451
4	715(8)	691

^a This work.

^b From Ref. 20.

TABLE III. Comparison of the vibrational wave numbers of $C_2D_4^+$ (\tilde{X}^2B_3) ground state.

	ν_2	ν_3	$2\nu_4$	$4\nu_4$
This work	1332(8) ^a	961(8) ^b	269(7) ^b	714(8) ^b
Stockbauer and Inghram ^c	1315(15)	970(15)	260(15)	680(15)
Cvitas <i>et al.</i> ^d	1340	1050	270	720
Somasundram and Handy ^e	1363	979		

^a Harmonic frequency ω_e . See the text.

^b Observed vibrational splittings from the (000) level.

^c From Ref. 17. Observed vibrational splittings from the (000) level.

^d From Ref. 5. Observed vibrational splittings from the (000) level.

^e From Ref. 12. Scaled harmonic frequencies.

tions was very important. Among the three totally symmetric vibrations, they found that the ν_2 mode was the most important one, which is consistent with our observations. The ν_1 mode is not observable in either isotope. The ν_3 mode is the major vibration in $C_2H_4^+$. By analyzing the $2\nu_4$ values as a function of ν_3 quantum numbers from Ref. 7 (recall that the ν_2 and ν_3 assignment should be interchanged), one finds that the $2\nu_4$ values are constant within the uncertainty. However, the coupling between ν_2 and ν_4 is evident even though only two ν_2 peaks were distinctly observed [$\nu_2 = 0$, $2\nu_4 = 438.4(0.5) \text{ cm}^{-1}$; $\nu_2 = 1$, $2\nu_4 = 442(1) \text{ cm}^{-1}$]. The ν_2 and ν_4 mode coupling manifests itself much more strongly in $C_2D_4^+$ than in $C_2H_4^+$. This is the first observation of such a mode coupling effect for the system. The work of Köppel *et al.*¹⁶ seems to be the only calculation that predicts this behavior. All the ν_4 torsional potential determinations done so far^{7,20,21} are for $\nu_2 = 0$, for which the mode coupling effect would not show up.

IV. CONCLUSION

Our high resolution PES study using a supersonic molecular beam for rotational cooling has revealed additional vibrational fine structure in the ground state of $C_2D_4^+$. Clear assignments are made to all the observed features. The doubtful ν_3 frequency from a previous study is corrected. The ν_2 and ν_3 values are consistent with Somasundram and Handy's *ab initio* SCF calculation of harmonic frequencies, though their calculation gives values that are slightly high. The torsional energy levels measured for both $C_2H_4^+$ and $C_2D_4^+$ are well accounted for by the recent calculation of Chau.²⁰ The significant coupling of C=C stretching vibration (ν_2) with the torsional vibration (ν_4) is observed in $C_2D_4^+$ for the first time.

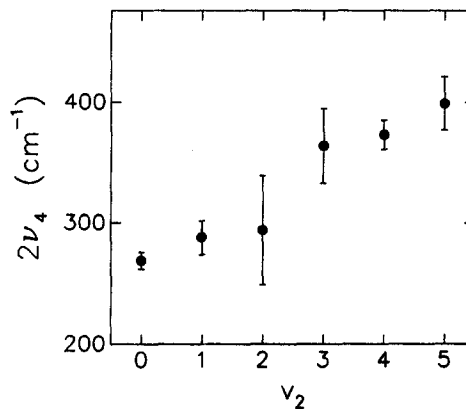


FIG. 2. The $2\nu_4$ values as a function of ν_2 vibrational quantum numbers.

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- ¹A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *Int. J. Mass Spectrosc. Ion Phys.* **1**, 285 (1969).
- ²G. R. Branton, D. C. Frost, T. Makita, C. A. McDowell, and I. A. Stenhouse, *J. Chem. Phys.* **52**, 802 (1970).
- ³C. R. Brundle and D. B. Brown, *Spectrochim. Acta Part A* **27**, 2491 (1971).
- ⁴P. M. Dehmer and J. L. Dehmer, *J. Chem. Phys.* **70**, 4574 (1979).
- ⁵T. Cvitaš, H. Güsten, and L. Klasinc, *J. Chem. Phys.* **70**, 57 (1979).
- ⁶T. Cvitaš, L. Klasinc, and R. McDiarmid, *Int. J. Quantum Chem. Quantum Chem. Symp.* **18**, 537 (1984).
- ⁷J. E. Pollard, D. J. Trevor, J. E. Reutt, Y. T. Lee, and D. A. Shirley, *J. Chem. Phys.* **81**, 5302 (1984).
- ⁸A. J. Merer and L. Schoonveld, *Can. J. Phys.* **47**, 1731 (1969).
- ⁹R. McDiarmid, *J. Chem. Phys.* **83**, 3174 (1985).
- ¹⁰R. McDiarmid, *J. Phys. Chem.* **84**, 64 (1980).
- ¹¹J. E. Pollard and D. J. Trevor, *J. Chem. Phys.* **83**, 3175 (1985).
- ¹²K. Somasundram and N. C. Handy, *J. Chem. Phys.* **84**, 2899 (1986).
- ¹³R. Botter and J. Carlier, in *Ionic Processes In The Gas Phase*, edited by M. A. Almoester Ferreira (Reidel, Dordrecht, 1984), p. 303.
- ¹⁴J. Carlier and R. Botter, *J. Chem. Phys.* **81**, 371 (1984).
- ¹⁵J. E. Pollard, D. J. Trevor, Y. T. Lee, and D. A. Shirley, *Rev. Sci. Instrum.* **52**, 1837 (1981).
- ¹⁶H. Köppel, W. Domcke, L. S. Cederbaum, and W. von Niessen, *J. Chem. Phys.* **69**, 4252 (1978).
- ¹⁷R. Stockbauer and M. G. Inghram, *J. Electron Spectrosc. Relat. Phenom.* **7**, 492 (1974).
- ¹⁸A. J. Merer and R. S. Mulliken, *Chem. Rev.* **69**, 639 (1969).
- ¹⁹G. L. Findley, K. Wittel, W. S. Felps, and S. P. McGlynn, *Int. J. Quantum Chem. Quantum Chem. Symp.* **11**, 229 (1977).
- ²⁰F. T. Chau, *J. Mol. Struct.* **131**, 383 (1985).
- ²¹N. C. Handy, R. H. Nobes, and H.-J. Werner, *Chem. Phys. Lett.* **110**, 459 (1984).