

Electron-impact spectroscopy of the alkynes: A comparison of propyne and 1-butyne with acetylene^{a)}

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The electronic excitation spectra of propyne and 1-butyne have been investigated by the method of variable angle electron-impact spectroscopy. In both molecules, two singlet-triplet transitions were observed with maximum intensities at 5.2 and 5.8 eV. No evidence was found for the existence of any transitions with vertical excitation energy below 5 eV. A number of previously unreported transitions to superexcited states in both propyne and 1-butyne were detected. The relationship of these spectra to those of acetylene is discussed, and the different behavior of valence and Rydberg transition energies in response to alkyl substitution is explained qualitatively in terms of the different excited state charge distributions.

I. INTRODUCTION

The triply-bonded hydrocarbon molecules, of which acetylene is the prototype, are among the least well understood of the systems traditionally investigated by molecular spectroscopists. Acetylene itself continues to be the subject of much experimental¹⁻⁶ and theoretical⁷⁻¹⁰ research. However, as Robin¹¹ has noted, it seems likely that part of the reason for the lack of an unambiguous interpretation of the acetylene spectrum is that so few derivatives of acetylene have been studied for purposes of comparison. In an attempt to correct this deficiency, we have investigated the variable angle electron-impact energy-loss spectra of propyne (methylacetylene) and 1-butyne (ethylacetylene). These data supplement those reported previously in a similar study of acetylene.^{1,2}

II. PREVIOUS EXPERIMENTS

The ultraviolet absorption spectrum of propyne was first reported by Price and Walsh,¹² who observed two weak features peaking at 6.45 and 7.51 eV (Herzberg's $\bar{X} \rightarrow \bar{A}$ and $\bar{X} \rightarrow \bar{B}$ transitions,¹³ respectively), as well as two Rydberg series converging toward an apparent ionization potential (I. P.) of 11.30 eV. However, subsequent investigations by Watanabe and co-workers^{14,15} failed to confirm the existence of the \bar{A} and \bar{B} states, or the validity of the previous¹² Rydberg series interpretation. Instead, Nakayama and Watanabe,¹⁵ on the basis of their spectral analysis, identified three Rydberg series in propyne which converged to an I. P. of 10.36 eV. This value agreed with that determined from photoionization studies.¹⁴ Nakayama and Watanabe¹⁵ also

studied the uv absorption of 1-butyne. They identified three Rydberg series in this molecule as well and determined the corresponding I. P. to be 10.18 eV.

More recently, a number of electron-impact studies^{3,4(b),6,16,17} have been performed on these molecules. Three different threshold excitation investigations^{3,4(b),16} of propyne have been reported, and two such studies^{4(b),16} of 1-butyne have appeared. The threshold excitation methods have the advantage of exciting strongly those transitions which are forbidden by optical electric dipole and spin selection rules.¹⁸ Frequently, spin- and/or symmetry-forbidden transitions will be among the most prominent features of a threshold excitation spectrum.¹⁸ Unfortunately, these techniques cannot be used, by themselves, to differentiate spin-allowed transitions from spin-forbidden ones,¹⁹ and this characteristic is one of the chief limitations of the threshold methods.²⁰ In contrast, the variable angle, variable impact energy method² employed in the present study provides an easy means of differentiating spin-allowed from spin-forbidden transitions.

In 1965, Bowman and Miller¹⁶ reported the trapped electron (TE) threshold spectrum of propyne. They detected four features, one of which peaked near 6.1 eV but was not identified. Using the double retarding potential difference (DRPD) threshold method, Knoop³ observed a broad feature in propyne between 5 and 6 eV, with a maximum at 5.6 eV, and also detected a peak at 6.3 eV. From the 5.6 eV peak, he inferred the presence of two excited states at 5.2 and 5.8 eV. By analogy with similar features that had been previously detected by electron impact in acetylene,^{1,2} he identified the 5.2 and 5.8 eV features as the $\bar{X} \rightarrow \bar{a}$ and $\bar{X} \rightarrow \bar{b}$ singlet-triplet transitions in propyne. He also suggested that the 6.3 eV peak might be due to the third singlet-triplet transition. Dance and Walker,^{4(b)} using a TE spectrometer with considerably better resolution than that of Bowman and Miller,¹⁶ confirmed the existence in propyne of optically forbidden transitions (presumably singlet-triplet excitations) at 5.2 and 5.8 eV, but they observed no transition at either 6.1 or 6.3 eV.

Two other electron-impact investigations^{6,17} of propyne have been reported. Wei and Kuppermann¹⁷ used

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a fixed scattering angle ($\theta = 90^\circ$) spectrometer to study the energy-loss spectrum of propyne at a number of incident electron energies between 30 and 50 eV. These studies indicated the presence of a transition at 5.9 eV, which had an intensity with a dependence on impact energy characteristic of singlet-triplet transitions. The feature observed by Wei apparently corresponds to the $\bar{X} \rightarrow \bar{b}$ transition observed in threshold excitation experiments.^{3,4(b)} More recently, Stradling *et al.*⁶ have used a fixed scattering angle ($\theta = 0^\circ$) spectrometer to study the energy-loss spectrum of propyne at 70 eV incident electron energy. The spectrum they obtained was relatively similar to the uv spectrum of Nakayama and Watanabe.¹⁵

The first electron-impact investigation of 1-butyne was the TE study of Bowman and Miller.¹⁶ The spectrum they observed was quite similar to that of propyne, and had an unidentified feature with a maximum intensity near 6.3 eV. Dance and Walker^{4(b)} identified two transitions at 5.3 and 5.8 eV in their TE spectra of 1-butyne as the $\bar{X} \rightarrow \bar{a}$ and $\bar{X} \rightarrow \bar{b}$ singlet-triplet excitations. However, they found no peak at 6.3 eV. Stradling *et al.*⁶ obtained the 70 eV, $\theta = 0^\circ$ energy-loss spectrum of 1-butyne, and confirmed the uv data of Nakayama and Watanabe.¹⁵

An issue that has been of considerable interest in the spectra of all the alkynes is whether there are any singlet-triplet excitations below the $\bar{X} \rightarrow \bar{a}$ transition. Bowman and Miller¹⁶ reported a feature peaking at 2.0 eV in a TE investigation of acetylene, and assigned the peak tentatively to a singlet-triplet transition. Similar features were observed¹⁶ at 2.8 eV in propyne and at 2.4 eV in 1-butyne. In 1970, Trajmar, Rice, and Kuppermann^{2(b)} interpreted the results of the variable angle electron-impact spectra of acetylene, which they had reported previously,¹ in a manner that left open the possibility that there might be a low-lying triplet state in acetylene which they could not detect. The lowest energy feature they did observe was the $\bar{X} \rightarrow \bar{a}$ transition, which extended from 4.5 eV to beyond 5.5 eV, with a maximum intensity at 5.2 eV energy loss. Trajmar *et al.*^{2(b)} interpreted the DCS ratio behavior of this feature to indicate that it was a $\Delta\Lambda = 1$ transition, consistent with a ${}^1\Sigma \rightarrow {}^3\Pi$ assignment. Such a transition could be produced by $\pi \rightarrow \sigma^*$ or $\sigma \rightarrow \pi^*$ electron promotions. However, available theoretical calculations^{21,22} indicated that the lowest singlet-triplet transition in acetylene is the $\pi \rightarrow \pi^*$, $\bar{X} {}^1\Sigma_g^+ \rightarrow 1 {}^3\Sigma_u^+$ excitation. As a result of this analysis, Trajmar *et al.*^{2(b)} concluded that the existence of a triplet state below the \bar{a} state was not incompatible with their results.

In recent years, three additional groups of researchers³⁻⁵ investigating the threshold spectra of the alkynes have detected a low-lying feature with a maximum in the range 1.7-3.0 eV. However, Knoop,³ Dance and Walker,⁴ and van Veen and Plantenga⁵ have all assigned this feature to vibrational excitation of the ground electronic state via temporary negative ion formation.

In 1972, Burton and Hunziker²³ interpreted their photosensitized emission experiments to signify that a low-

lying acetylene triplet state exists, and has an excitation energy that is greater than 2.6 eV but less than 4.7 eV. They implied that this triplet state was not the previously identified \bar{a} state. In their experiments, they observed that biacetyl phosphoresces when acetylene is added to a flowing mixture of mercury, biacetyl, and nitrogen, in the presence of 2537 Å light. The mechanism suggested involves triplet-triplet energy transfer from $\text{Hg } {}^3P_0$ to acetylene, forming a metastable, vibrationally excited triplet state of acetylene. Subsequently, the triplet acetylene, in another triplet-triplet energy transfer process, produces triplet biacetyl, which then phosphoresces. In Sec. IV.C, we attempt to explain these results in terms of the experimentally observed acetylene triplet states.

III. EXPERIMENTAL

The apparatus employed in these experiments has been described in detail in a number of earlier publications.^{2,24,25} To obtain a typical energy-loss spectrum, the incident electron energy (E_0) is set in the normal operating range (20-100 eV), the flexible bellows scattering chamber is bent so as to give the desired scattering angle ($\theta = -20^\circ$ to $+80^\circ$), and the lens potentials and ramp generator are adjusted to sweep repeatedly over any given region of the energy-loss spectrum, extending from the infrared to the extreme vacuum ultraviolet excitation regions. A molecule is usually studied at about ten scattering angles between 0° and 80° , and at two or three impact energies. The relative intensities of various features at different scattering angles are then used to determine relative differential cross sections (DCS) for both elastic and inelastic scattering. It is these DCS values which are most useful in distinguishing spin-allowed from spin-forbidden features.²

In the present study, propyne and 1-butyne were investigated at scattering angles from 0° to 80° , in the 0-15 eV energy-loss range. In addition, a number of acetylene spectra were obtained for purposes of comparison with propyne and 1-butyne. The principal incident electron energies employed for propyne were 20, 35, and 50 eV, while 1-butyne was studied at incident energies of 30 and 50 eV. Both molecules were also studied briefly at low scattering angles ($\theta < 5^\circ$), at an impact energy of 75 eV. The acetylene spectra were obtained at impact energies of 15, 25, and 40 eV. Typical sample pressures in the collision chamber were 4-10 mtorr, as indicated by an uncalibrated Schulz-Phelps ionization gauge. Electron beam intensities entering the scattering chamber were approximately 50-100 namp. The energy resolution, as measured from the full width at half maximum (FWHM) of the elastic peak, was set between 0.10 and 0.16 eV for most spectra.

The samples of acetylene and propyne were obtained from Matheson Gas Products, and had stated purities of 99.6% and 96.0%, respectively. The 1-butyne was obtained from Air Products and Chemicals, Inc., and had a stated purity of 95%. Samples were vacuum degassed from a liquid nitrogen trap prior to use. Other than that, they were used without further purification, and no evidence of impurity absorptions was found.

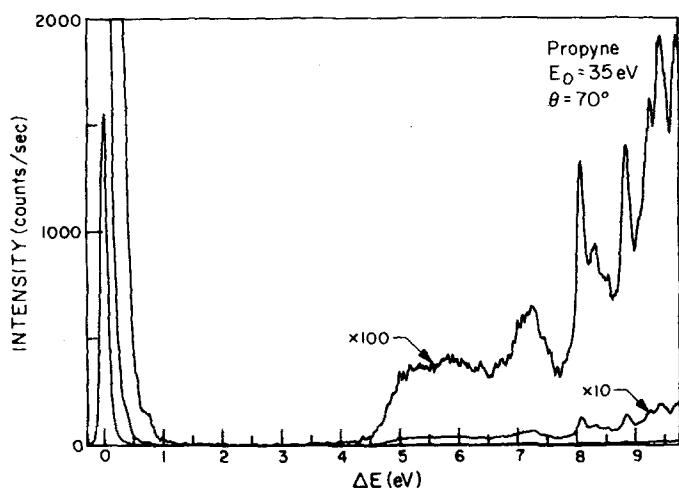


FIG. 1. Electron energy-loss spectrum of propyne at an incident electron energy (E_0) of 35 eV and a scattering angle (θ) of 70° ; 8.0 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 54 namp incident electron current; 0.13 eV energy resolution (FWHM). The narrow peak near 6.4 eV energy loss was not a reproducible feature (see discussion in text).

In the following section, the maximum intensity transition energies listed are estimated to have uncertainties of 0.05 eV, except where indicated. The limits of the observed Franck-Condon envelopes are estimated to within 0.1 eV. The relative DCS values and intensity ratios were obtained by methods described previously.²⁴

IV. RESULTS AND DISCUSSION

A. Propyne

Table I contains a list of the transition energies obtained for propyne. It also lists the values reported in previous studies of the uv spectra,^{12,15} and electron-impact spectra.^{3,4(b),6,16,17}

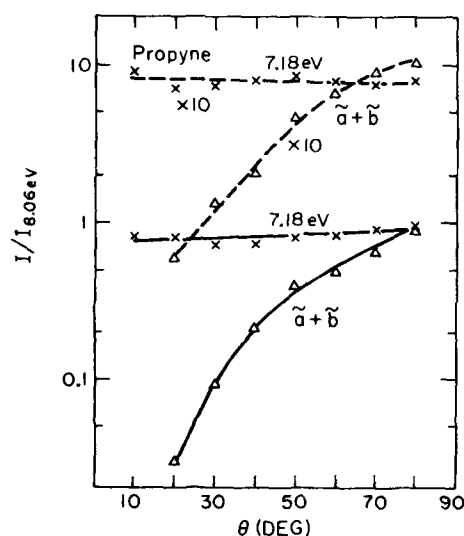


FIG. 2. Ratio of the intensities (I) of various transitions in propyne to that of the 8.06 eV transition at incident electron energies of 35 eV (dashed lines) and 50 eV (solid lines). The excited states for the curves shown are the sum of the \tilde{a} and \tilde{b} states (Δ) and the 7.18 eV \tilde{B} singlet state (x). The intensity ratio curves at 35 eV have been multiplied by a factor of 10.

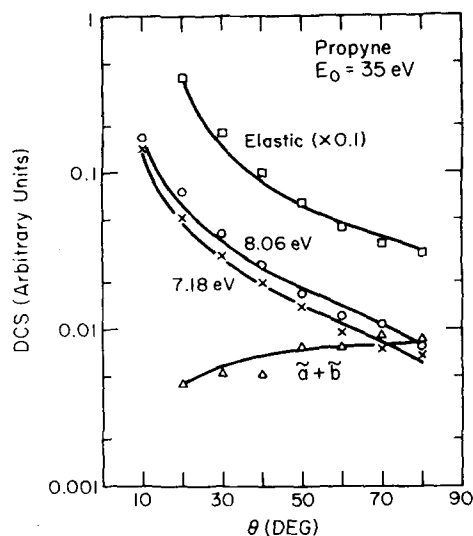


FIG. 3. Relative differential cross sections (DCS) in propyne at an incident electron energy (E_0) of 35 eV, for elastic scattering (\square) and transitions to the following excited states: the sum of the a and b states (Δ); the 7.18 eV \tilde{B} singlet state (x); and the 8.06 eV singlet state (\circ). The curve for elastic scattering has been multiplied by 0.1. The arbitrary units for the DCS curves were determined by setting the value for elastic scattering at $\theta = 40^\circ$ to 1.0, and therefore the units in this graph cannot be compared with those in any other graph.

1. Triplet states

Two poorly resolved transitions can be observed in the 4.5–6.5 eV energy-loss region of propyne (Fig. 1). The maximum intensities of these features occur at 5.2 ± 0.1 and $5.8_5 \pm 0.1$ eV. The ratio of the combined intensity of these two features to that of the optically allowed transition at 8.06 eV is displayed as a function of scattering angle in Fig. 2. The rapid increase of this ratio with increasing scattering angle, as well as the relatively isotropic nature of the corresponding DCS curves (Figs. 3 and 4), indicate that both the 5.2 and the 5.8₅ eV transitions are spin forbidden. Further-

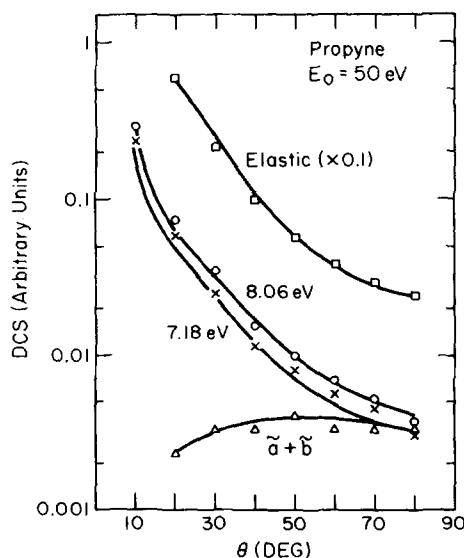


FIG. 4. Same as Fig. 3 for $E_0 = 50$ eV.

TABLE I. Excited electronic states of propyne.

State ^a	Vertical transition energy (eV)			
	Optical ^b	Threshold electron impact	Other electron impact ^c	Present research ^d
\tilde{a}	...	5.2 ^{e,f}	...	5.2 ± 0.1
\tilde{b}	...	5.8 ^{e,f}	5.9	5.8 ₅ ± 0.1
...	...	6.1, ^g 6.3 ^e
\tilde{A}	6.45, 6.7	6.7 ^f	...	6.7 ± 0.1
...	7.04	7.0, ^f 7.1 ^{e,g}
\tilde{B}	7.2	7.2 ^f	(7.2 ₅ , 7.4 ₄) ^{h,i}	(7.18, 7.38) ^h
...	7.51
\tilde{C}	7.86	...	7.87	7.88
3R'	8.04, 8.05	8.1 ^f	8.05	8.06
3R' + ν_5	8.17	8.2 ^e
3R' + ν_3	8.29	8.3, ^g 8.35 ^f	8.28	8.30
3R''	8.45	...	8.43	8.47
4R	8.83		8.81	8.84
3R'' + 2 ν_3	8.93	8.9 ^f
4R + ν_3	9.07, 9.12	...	9.08	9.08
4R'	9.21	9.23 ^f	9.21	9.25
4R''	9.36	...	9.39	9.36
4R' + ν_3	9.45	9.44
5R	9.51	9.5 ^f
5R'	9.66	...	9.66	...
4R' + 2 ν_3	9.69	9.71
5R''	9.75
6R'	9.91	...	9.93	9.96
7R	9.99	...	10.01	...
7R'	10.03
7R''	10.10	...	10.10	...
9R'	10.17	...	10.16	...
9R''	10.18	10.19
10R''	10.22	...	10.24	...
Rydberg	10.28
Superexcited state (SES)	10.57
SES	10.72
SES	12.7 ± 0.1
SES	14.7 ± 0.1

^aRydberg state assignments are taken from Ref. 15.

^bAll excitation energies are from Ref. 15, except for four values (6.45, 7.51, 8.04, and 9.12 eV) which are from Ref. 12. As noted in the text, the 6.45 and 7.51 eV features are of suspect validity.

^cAll values are from Ref. 6, except for the \tilde{b} state transition energy (5.9 eV), which is from Ref. 17.

^dEstimated uncertainties are ± 0.05 eV unless otherwise indicated.

^eReference 3.

^fReference 4(b).

^gReference 16.

^hValues enclosed in parentheses may be vibrational bands of a single electronic band system.

See discussion in text.

ⁱThese values were obtained from measurements on Fig. 3 of Ref. 6.

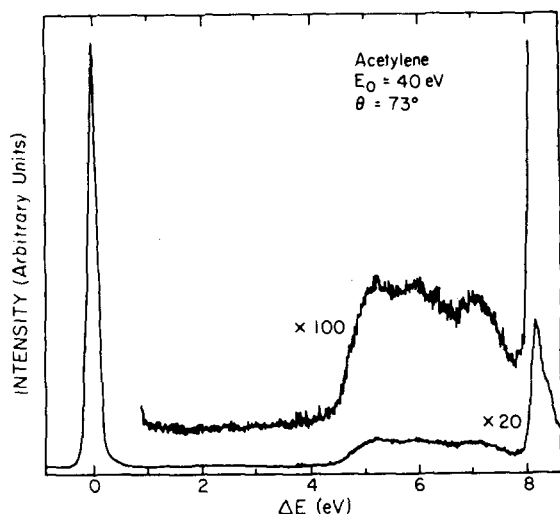


FIG. 5. Electron energy-loss spectrum of acetylene at an incident electron energy (E_0) of 40 eV, and a scattering angle (θ) of 73° ; 0.20 eV energy resolution (FWHM). As in Fig. 1 the narrow peak near 6.4 eV energy loss was not a reproducible feature. (See discussion in text.)

more, both transitions have a greater relative intensity at lower impact energies than at higher ones. This characteristic behavior^{2, 20, 24-27} confirms the spin-forbidden nature of these two features, which are clearly the first and second singlet-triplet excitations, $\bar{X} - \bar{a}$ and $\bar{X} - \bar{b}$, of propyne.

For comparison with propyne, we display an energy-loss spectrum of acetylene in Fig. 5, in which the 5.2 eV peak of the $\bar{X} - \bar{a}$ transition and the 6.0 eV peak of the $\bar{X} - \bar{b}$ transition are clearly resolved. Theoretical calculations^{8-10, 21, 22} on acetylene indicate that the two lowest triplet states in that molecule are the $1^3\Sigma_u^+$ and the $1^3\Delta_u$ states, respectively, and that both are produced by $\pi - \pi^*$ valence transitions. In propyne, the corresponding features are similar in location, profile, and scattering characteristics to those in acetylene. We can therefore infer that they are also due to $\pi - \pi^*$ excitations. The relative insensitivity of valence transition energies to substitution in the σ framework of the molecule is easily explained. Since the charge distribution of a valence excited state is localized and not too different from that of the ground state, we might expect the effects of substituents on the absolute energies of these states to be nearly equal, leaving their energy difference (i. e., transition energy) almost unchanged. In fact, this behavior is observed in the simple alkynes for transitions to all the experimentally observed $\pi - \pi^*$ valence states, \bar{a} , \bar{b} , \bar{A} , and \bar{B} . (See discussion in Sec. IV. B.)

We found no direct evidence in propyne of any spin-forbidden transitions at energy losses greater than that of the $\bar{X} - \bar{b}$ excitation. Specifically, we did not detect a reproducible feature near 6.3 eV, in contrast to the DRPD results of Knoop,³ but in agreement with the TE spectrum of Dance and Walker.^{4(b)} However, in an occasional spectrum of both acetylene (Fig. 5) and propyne (Fig. 1), a narrow peak appears near 6.4 eV energy loss, but these features were not regularly repro-

ducible under the present low signal-to-noise ratio experimental conditions. Furthermore, the energy width of this sporadic feature is of the order of the FWHM, or narrower than it. In addition, this part of the spectrum is overlapped by the neighboring $\bar{X} - \bar{b}$, $\bar{X} - \bar{A}$, and $\bar{X} - \bar{B}$ transitions. As a result, we cannot use our spectra to suggest the existence of another weak transition in this region.

Although we observed no features in propyne which could be correlated with a third singlet-triplet transition, we did obtain some indirect evidence that seems consistent with the existence of an underlying transition, possibly spin forbidden, at an excitation energy near 8.3 eV. The basis for this inference is an unexpected difference in the angular dependence of the scattering intensity of the peaks at 8.06 and 8.30 eV. If the only transitions occurring in this region were the two vibrational bands of the $\bar{X} - 3R'$ transition, we would expect that the two peaks would show essentially the same dependence on scattering angle. This conclusion follows from the Franck-Condon principle and has been amply confirmed in electron impact.^{2(b), 26-28} Instead, we observe at 35 and 50 eV impact energies that the ratio of the height of the 8.30 eV peak to that of the 8.06 eV peak increases by about 30%-35% as the scattering angle increases from 0° to 80° . At 20 eV incident energy, the same ratio increases by approximately 60%, as θ increases from 10° to 80° . Such increases are far larger than the maximum expected variation due to instrumental effects, which is about 10%.

In view of this ratio variation with scattering angle and impact energy, it seems likely that there is an underlying transition which could be spin forbidden in the vicinity of the 8.30 eV peak. Similar results were found in this region of the acetylene spectrum.^{2(b)} However, in this case, the analogy with acetylene may be misleading, because the underlying state in the acetylene spectrum^{4, 5} appears to be the $1^3\Pi_u$ state, which has partial Rydberg character.⁹ Rydberg states, in contrast to most valence states, have diffuse charge distributions, which differ significantly from that of the ground state. As a result, the variation of a Rydberg state energy in a series of related compounds resembles that of the corresponding ionic state more than that of the ground state. Therefore, the excitation energy of the $1^3\Pi_u$ state in acetylene should be significantly higher than that of the corresponding state in propyne, as is the case for the first I. P., but in contrast to the behavior of the \bar{a} and \bar{b} state transition energies. Since no theoretical calculations on the excited electronic states of propyne are available, it is difficult to suggest an assignment for the transition that may underlie the 8.3 eV region.

2. Singlet states

The propyne singlet-singlet transition energies listed in Table I agree in essential aspects with those reported in most previous optical¹⁵ and electron-impact^{4(b), 6} spectra. The first prominent feature in the spectrum that is due to a spin-allowed transition occurs in the 6.5-7.7 eV energy-loss region, with a maximum

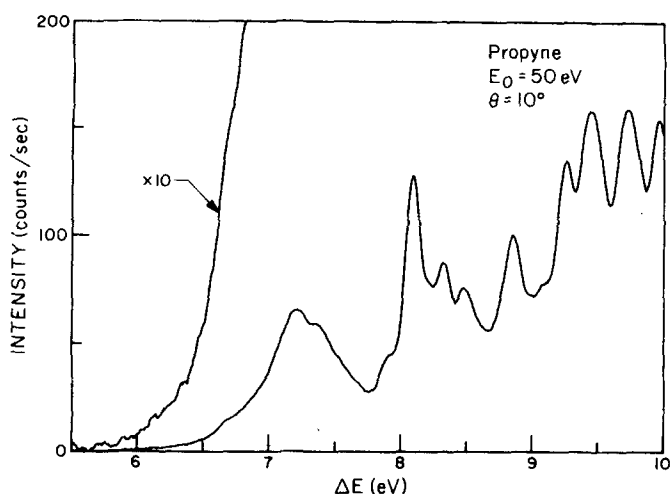


FIG. 6. Electron energy-loss spectrum of propyne at an incident electron energy (E_0) of 50 eV and a scattering angle (θ) of 10° ; 3.0 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge.

intensity at 7.18 eV (Fig. 1). In some spectra, a second peak is observed at 7.38 eV (Fig. 6), and this may represent either vibrational excitation of the same electronic band system or excitation of the $\pi-3s$ Rydberg transition. (See discussion in next paragraph.) A similar peak can be seen in the propyne spectrum reported by Stradling *et al.*⁶ The angular dependence of the scattering intensity in the 6.5–7.7 eV region (Figs. 2–4) indicates that this is an allowed excitation, since its DCS is forward peaked, and its relative intensity, with respect to the optically allowed $\bar{X}-3R'$ singlet-singlet transition at 8.06 eV, is independent of angle. The analogous $\bar{X}-\bar{B}$ transition in the electron-impact spectrum of acetylene peaks near 7.1 eV (Fig. 5). This band system in acetylene has been assigned²⁹ to the valence shell $\pi-\pi^*$ excitation $\bar{X}^1\Sigma_g^+ \rightarrow 1^1B_u(1^1\Delta_u)$. Accurate *ab initio* calculations⁹ show that this feature is the second lowest energy singlet-singlet transition in acetylene. It is interesting to note that the $\bar{X}-\bar{B}$ transition in acetylene is symmetry forbidden, whereas in propyne it is symmetry allowed, due to the lower molecular symmetry. This difference is clearly reflected in the differing intensity ratio curves, as can be seen by a comparison of Fig. 2 of the present paper with Fig. 2 of Ref. 1.

The excitation energy region near the peak of the $\bar{X}-\bar{B}$ transition in propyne quite likely also contains the $\pi-3s$ Rydberg transition.¹¹ This transition is expected to occur near the 7.18 eV peak, since the term value of the \bar{B} state is 3.18 eV, a value similar to that of the ($\pi, 3s$) state in acetylene (3.25 eV), and appropriate for a 3s Rydberg state.¹¹ It is possible that the peak observed at 7.38 eV in some low angle spectra (Fig. 6) is due to such a $\pi-3s$ transition. However, higher resolution spectra at a number of impact energies and scattering angles would be required to confirm this suggestion. The $\pi-3s$ transition ($\bar{X}-\bar{C}$) in acetylene occurs at a considerably higher energy loss, 8.16 eV,^{2(b)} due to the higher first I. P. (11.41 eV).³⁰

One difference between our results in this energy-loss region of propyne and those of some earlier experiments^{4(b),15} is that we do not resolve a separate peak at 7.0 eV, as has been observed in TE^{4(b)} and uv¹⁵ absorption experiments. Dance and Walker^{4(b)} assigned this peak to an electronic transition different from the one at 7.2 eV, although it also seems possible that these peaks (as well as the one at 7.38 eV) are simply vibrational bands of a single electronic transition.

In some of our propyne spectra (see Fig. 6), particularly at low scattering angles, there is evidence of a shoulder at 6.7 eV on the low energy-loss tail of the 7.18 eV transition. A similar feature was observed at this excitation energy in the TE spectra of Dance and Walker,^{4(b)} who suggested that the transition is probably a valence singlet-singlet excitation, although they could not rule out the possibility that it represents a third singlet-triplet transition. The appearance of this feature in our spectra, particularly at low scattering angles, is consistent with the singlet-singlet assignment.

The identity of the 6.7 eV feature in propyne can be inferred from a comparison with acetylene. A weak series of well-resolved bands between 6.35 and 6.79 eV energy loss in the spectrum of the latter molecule was observed in the 40 and 50 eV low scattering angle, high resolution, electron-impact studies of Lassetre *et al.*²⁸ At lower excitation energies, a well-known, weak ($f \approx 10^{-4}$) transition ($\bar{X}-\bar{A}$) occurs in the 5.23–5.90 eV region of the uv absorption spectrum³¹ of acetylene, and this feature has been identified as the $\pi-\pi^*$ valence transition $\bar{X}^1\Sigma_g^+ \rightarrow 1^1A_u(1^1\Sigma_u^-)$.^{9,32} Although for years the maximum intensity of the $\bar{X}-\bar{A}$ transition was believed to occur near 6 eV,³¹ more recent experimental²⁹ and theoretical⁹ evidence indicates that this absorption band system peaks at considerably higher energies. In fact, the vertical transition energy may occur in the 6.6–6.7 eV region.^{9,11,29} In retrospect, it seems possible that the 6.35–6.79 eV acetylene bands observed by Lassetre *et al.*²⁸ may belong to the $\bar{X}-\bar{A}$ transition. Such an assignment could explain the previous failure to identify this transition.²⁸ In view of these results for acetylene, it seems reasonable to assign the 6.7 eV feature in propyne to the lowest-lying singlet-singlet transition, $\bar{X}-\bar{A}$.

A puzzling discrepancy exists between our 75 eV, 2° spectrum (Fig. 7) of the 6–7 eV energy-loss region in propyne, and the 70 eV, 0° spectrum of this same region obtained by Stradling *et al.*⁶ In our spectrum, we observe measurable scattering intensity at excitation energies as low as 6 eV, while in the spectrum of Stradling *et al.*⁶ no appreciable scattering occurs below 7.1 eV, at which point there is a sharp rise in the scattering intensity. We are unable to account for this difference.

The remaining transitions that we have detected in propyne below the first I. P. can plausibly be assigned as Rydberg excitations (Figs. 6 and 7 and Table I). Of course, this Rydberg structure is not nearly so well resolved as in the uv spectra. Indeed, it seems likely that several transitions contribute to each peak we ob-

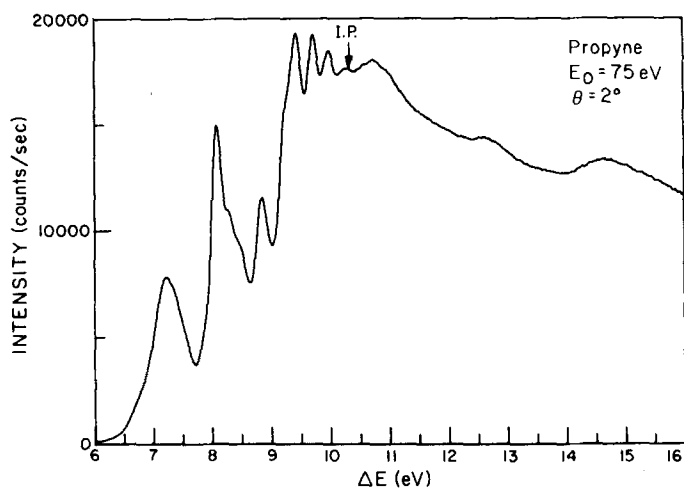


FIG. 7. Electron energy-loss spectrum of propyne at an incident electron energy (E_0) of 75 eV and a scattering angle (θ) of 2° ; 10 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 70 namp incident electron current. The lowest molecular ionization potential (I. P.) is indicated.

serve between 9.7 and 10.2 eV. We have also observed transitions to four superexcited states at 10.57, 10.72, 12.7, and 14.7 eV. Although the first two of these peaks have not been explicitly mentioned before, they do seem to appear in the published spectra of both Nakayama and Watanabe¹⁵ and Stradling *et al.*⁸ These bands probably represent Rydberg transitions converging to vibrationally excited states of the ground electronic state of the positive ion. If the 12.7 and 14.7 eV features are also due to Rydberg states, we can employ the term value method^{33,34} to assign them as $4\sigma - 3p$ and $3\sigma - 3p$ Rydberg excitations, respectively. The 12.7 eV feature has a term value of 2.5 eV with respect to the third I. P. at 15.2 eV, and the 14.7 eV feature has an identical term value with respect to the fourth I. P. at 17.2 eV.³⁵ Term values of this magnitude are com-

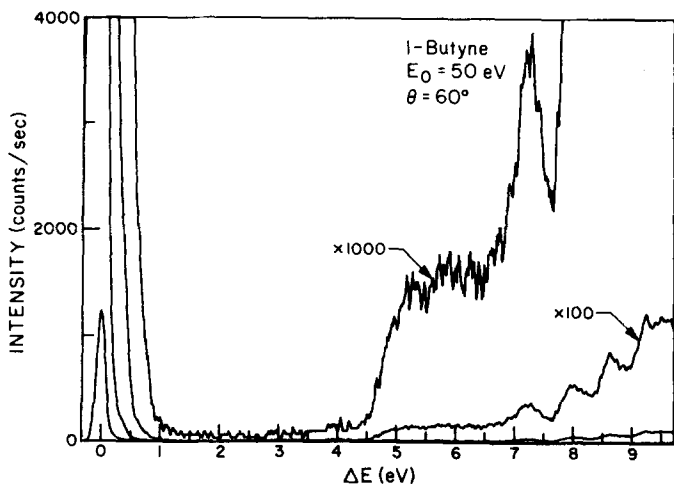


FIG. 8. Electron energy-loss spectrum of 1-butyne at an incident electron energy (E_0) of 50 eV and a scattering angle (θ) of 60° ; 4.5 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 92 namp incident electron current; 0.16 eV energy resolution (FWHM).

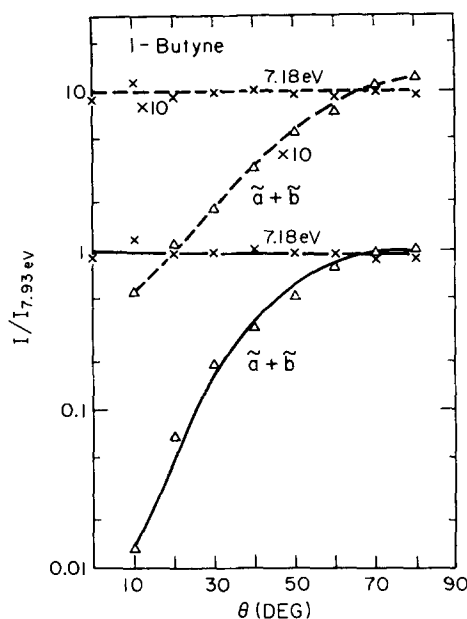


FIG. 9. Same as Fig. 2 for 1-butyne, with the 7.93 eV transition as the reference.

monly associated with transitions terminating in $3p$ Rydberg orbitals in the alkynes.¹¹

B. 1-Butyne

The low energy-loss part of the spectrum of 1-butyne (Fig. 8) is quite similar to that of propyne. In particular, no transitions are observed to peak below 5 eV energy loss. Measured transition energies are listed in Table II. It is interesting to note that transitions to the \tilde{a} , \tilde{b} , \tilde{A} , and \tilde{B} excited valence states occur at excitation energies indistinguishable from the corresponding energies in propyne, and very similar to those in acetylene. The intensity ratio curves (Fig. 9) and DCS plots (Figs. 10 and 11) confirm the spin-forbidden

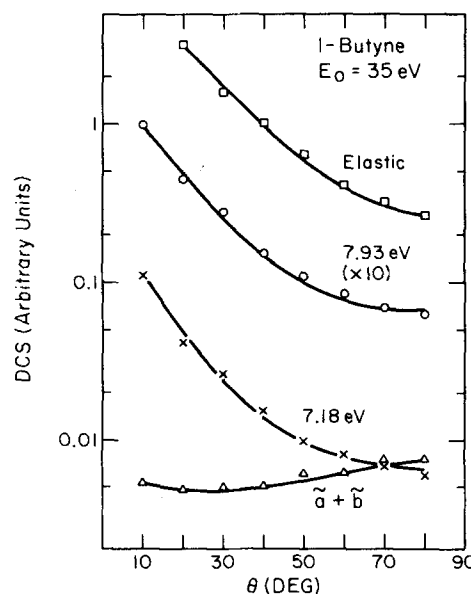


FIG. 10. Same as Fig. 3 for 1-butyne, except that the 7.93 eV singlet state curve has been multiplied by a factor of 10, and the elastic scattering curve is drawn to scale.

TABLE II. Excited electronic states of 1-butyne.

State ^a	Vertical transition energy (eV)			Present Research ^g
	Optical ^b	Threshold electron impact ^c	Other electron impact ^d	
\tilde{a}	...	5.3	...	5.2 ± 0.1
\tilde{b}	...	5.8	...	5.8 ₅ ± 0.1
...	...	6.3
\tilde{A}	...	6.7	6.79	6.7 ± 0.1
...	6.98	6.9
\tilde{B}	7.2	7.2, 7.3	(7.27, 7.33, 7.44) ^f	7.18
3R'	7.78	7.78
3R' + ν_2	7.89	...	7.93	7.93
3R' + ?	8.00	8.0	8.07	...
3R' + ?	8.14	8.11
...	8.26	8.2	8.20	...
3R''	8.37	8.37
4R	8.57	8.7	8.62	8.57
4R + ν_1	8.81	8.78
4R'	9.03	...	8.97	9.02
4R''	9.16	...	9.23	9.20
5R	9.35	9.3
5R'	9.46	9.45
6R''	9.72	9.70
7R''	9.86	9.91
Superexcited state (SES)	10.24
SES	10.43
SES	10.68
SES	10.90
SES	12.3 ± 0.1
SES	14.7 ± 0.1

^aRydberg state assignments are taken from Ref. 15.

^bReference 15.

^cAll values are from Ref. 4(b), except for the states at 6.3 and 7.3 eV, which are from Ref. 16.

^dReference 6.

^eEstimated uncertainties are ± 0.05 eV unless otherwise indicated.

^fThese peaks may be vibrational bands of the $\tilde{X} \rightarrow \tilde{B}$ transition.

nature of the $\tilde{X} - \tilde{a}$ and $\tilde{X} - \tilde{b}$ transitions, which were first reported in the TE spectra of Dance and Walker.^{4(b)}

As in propyne, the behavior of the DCS curves of Figs. 10 and 11 shows that the $\tilde{X} \rightarrow \tilde{B}$ transition in 1-butyne at 7.18 eV is fully allowed. In contrast with propyne, the scattering intensity profile we observe in the 6–7 eV region (Figs. 8, 12, and 13) agrees well with that observed by Stradling *et al.*⁶ In neither study have any peaks been detected near 7.0 eV energy loss, in disagreement with both TE^{4(b)} and uv absorption spectra.¹⁵

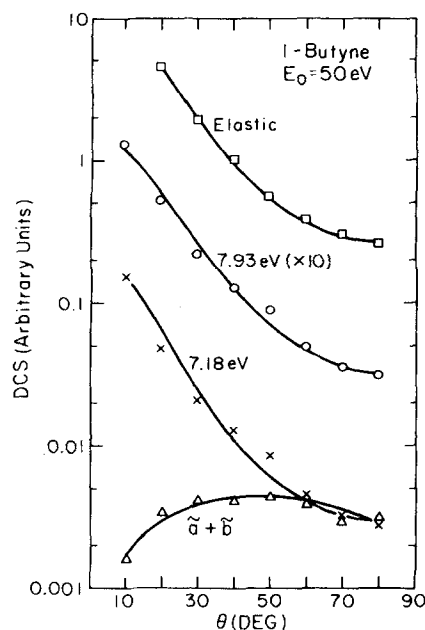


FIG. 11. Same as Fig. 10 for $E_0 = 50$ eV.

The region of the 1-butyne spectrum from about 7.7 to 8.3 eV is also a source of disagreement among the various reported results. Our higher resolution spectra (Figs. 12 and 13) show three peaks at 7.78, 7.93, and 8.11 eV. As indicated in Table II, four prominent bands are found in this region of the uv absorption spectrum. Nakayama and Watanabe¹⁵ assigned these features as vibrational bands of the $\tilde{X} - 3R'$ Rydberg transition. Our results are compatible with the optical data since, under our resolution conditions, the band we detect at 7.93 eV should be the unresolved summation of the uv¹⁵ bands at 7.89 and 8.00 eV.³⁶ In contrast, our band system profile in this region is considerably different from that reported by Stradling *et al.*,⁶ who detected an in-

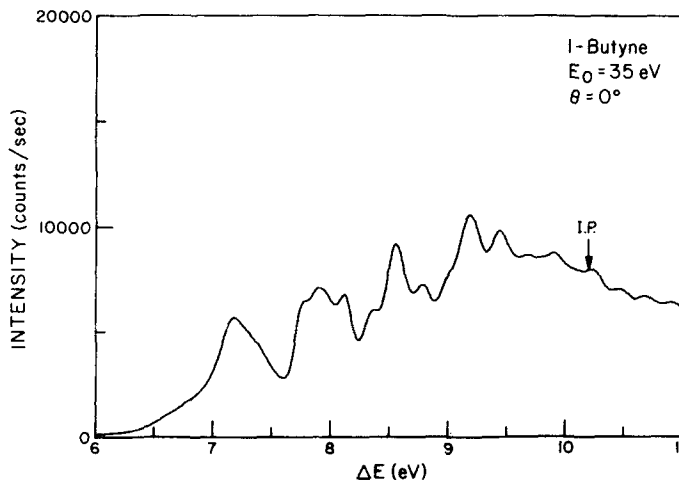


FIG. 12. Electron energy-loss spectrum of 1-butyne at an incident electron energy (E_0) of 35 eV and a scattering angle (θ) of 0°; 7.0 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 78 namp incident electron current. The lowest molecular ionization potential (I.P.) is indicated.

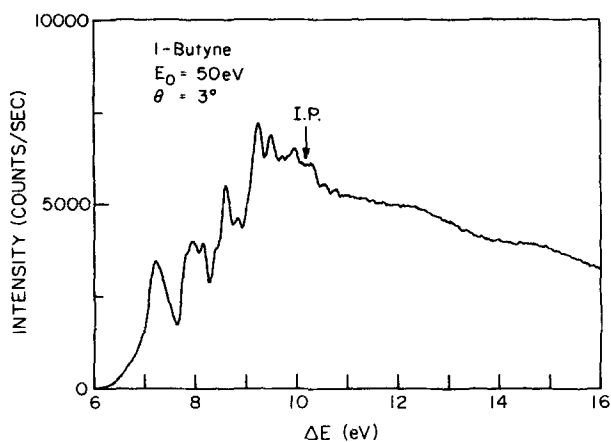


FIG. 13. Electron energy-loss spectrum of 1-butyne at an incident energy (E_0) of 50 eV and a scattering angle (θ) of 3° ; 5.4 mtorr sample pressure; 103 namp incident electron current. The lowest molecular ionization potential (I. P.) is indicated.

tense peak at 7.93 eV, and weak shoulders at 8.07 and 8.20 eV.

The other Rydberg transitions in 1-butyne observed in these experiments agree fairly well with the available uv and electron-impact data. Superexcited states detected at 10.24, 10.43, 10.68, and 10.90 eV (Fig. 12) probably correspond to Rydberg series converging to vibrationally excited states of the ionic ground electronic state. Broad features occur at 12.3 and 14.7 eV (Fig. 13), and these seem to be analogous to similar features in propyne. It is reasonable to infer that these transitions in 1-butyne are also members of Rydberg series converging to electronically excited ionic states.

C. Low-lying triplet states in the alkynes and photosensitized emission studies

As mentioned in Sec. II, the existence of a triplet state in the alkynes below the \bar{a} state has been debated for a number of years. In order to learn whether such a state exists in acetylene, propyne, or 1-butyne, we conducted a careful search for any excited states that might lie below the \bar{a} state. In many of the spectra, the background noise was extremely low, and signal-to-background ratios of 10:1–20:1 were obtained on the peaks of the $\bar{X} \rightarrow \bar{a}$ and $\bar{X} \rightarrow \bar{b}$ transitions (Figs. 1 and 8). Nevertheless, no features were detected at energy losses below the $\bar{X} \rightarrow \bar{a}$ transition. The sensitivity of the apparatus was such that we estimate that peak intensities 20 times weaker than those of the $\bar{X} \rightarrow \bar{a}$ or $\bar{X} \rightarrow \bar{b}$ excitations could have been detected.

The results of the present experiments indicate strongly that no electronic excitations occur in the alkynes below the $\bar{X} \rightarrow \bar{a}$ transition. Moreover, in our view, there is no convincing evidence, experimental or theoretical, that contradicts this assertion. The low-lying features observed by Bowman and Miller¹⁶ almost certainly represent temporary negative ion formation.^{3–5} As mentioned in Sec. II, Trajmar *et al.*^{2(b)} stated that they could not rule out the existence of a

triplet state at a lower energy than the \bar{a} state. This statement was based on the assumption that the $\bar{X} \rightarrow \bar{a}$ transition was due to a $\Delta\Lambda = 1$ excitation. That assumption, in turn, was based on a tentative empirical selection rule for electron impact which resulted from observations of a small number of diatomic molecules. However, the generality of this rule has never been established.^{26,27} In addition, a high quality *ab initio* calculation of the vertical excitation energies has since been made.⁹ These energies agree with the ones we observe experimentally to within 0.3 eV or better. The two lowest acetylene triplet states in that calculation occur at 5.02 eV ($\bar{X} \ ^1\Sigma_g^+ \rightarrow 1 \ ^3\Sigma_g^+$) and 5.87 eV ($\bar{X} \ ^1\Sigma_g^+ \rightarrow 1 \ ^3\Delta_u$), in very satisfactory agreement with our values of 5.2 and 6.0 eV, respectively. This is strong evidence that there are no additional electronic states below the 5.2 eV \bar{a} state.

Finally, we show that the results of the photosensitized emission studies of Burton and Hunziker²³ are consistent with this interpretation of the acetylene spectrum. Inspection of the onset of excitation of the \bar{a} state (Fig. 5) indicates that it occurs at about 4.5 eV. This is sufficiently low to permit energy transfer from $\text{Hg } ^3P_0$ (4.67 eV) to acetylene to form the \bar{a} state. However, in order to have energy transfer occur from this state to biacetyl, there must be a finite overlap^{37,38} of the phosphorescence spectrum of acetylene and a singlet–triplet absorption band system of biacetyl. The $S_0 \rightarrow T_1$ absorption of biacetyl is known to occur between 2.6 and 3.65 eV.³⁹ Unfortunately, the phosphorescence spectrum of acetylene is unknown. Nevertheless, we can make the reasonable assumption that acetylene in its \bar{a} state can donate at least 2.6 eV to an acceptor molecule. With this assumption, a sufficient condition (although not a necessary one) for acetylene \rightarrow biacetyl energy transfer is that the 0–0 band of the $\bar{X} \rightarrow \bar{a}$ transition lie below 3.65 eV, which is the high energy limit of the biacetyl $S_0 \rightarrow T_1$ absorption. Although the apparent onset of the $\bar{X} \rightarrow \bar{a}$ transition is appreciably greater than 3.65 eV, this onset does not necessarily correspond to the 0–0 band of the transition, which could easily lie at a much lower energy. Indeed, the *ab initio* calculation of Demoulin and Jungen⁹ places the 0–0 band at 3.14 eV.

This analysis supports the suggestion that the acetylene \bar{a} state can transfer its excitation energy to biacetyl, producing the T_1 state observed in phosphorescence. Alternatively, the energy transfer process may produce a higher triplet state of biacetyl. Such a state could rapidly undergo internal conversion to the phosphorescent T_1 state. Either mechanism implies that the acetylene triplet state postulated by Burton and Hunziker²³ to photosensitize biacetyl phosphorescence is the \bar{a} state. It is therefore not necessary to invoke the existence of a triplet below that state to explain their observations.

V. CONCLUSIONS

In this investigation we have used the method of variable angle, variable impact energy, electron-impact spectroscopy to confirm the existence of singlet \rightarrow trip-

let transitions at 5.2 and 5.8₅ eV in both propyne and 1-butyne. It is argued that no lower energy electronic transitions exist, in accord with recent electron-impact studies of these molecules, and high-quality *ab initio* calculations on the parent compound, acetylene. These results are shown to be consistent with the findings of photosensitized emission studies of acetylene. The vertical transition energies of the two triplet states in propyne and 1-butyne are quite similar to those observed in acetylene, and this result is consistent with the $\pi \rightarrow \pi^*$ valence nature of these transitions. Since the charge distribution in the ground electronic state differs little from that of the valence excited states, it is not surprising that methyl or ethyl substituents affect the singlet-triplet valence shell transition energies very little.

On the other hand, transitions to the Rydberg states of both propyne and 1-butyne occur at energies approximately 1-1.5 eV lower than their counterparts in acetylene. Unlike a valence excitation, a Rydberg transition involves an excited state charge distribution which is diffuse and significantly different from that in the ground state. Substitution in the σ framework of the molecule affects the ground state differently than it does the excited states, and this in turn can lead to a pronounced shift in the transition energies.

In both propyne and 1-butyne, several previously unreported or unidentified superexcited states have been observed. These are believed to represent Rydberg transitions to vibrationally or electronically excited states of the positive ions.

- ¹S. Trajmar, J. K. Rice, P. S. P. Wei, and A. Kuppermann, *Chem. Phys. Lett.* **1**, 703 (1968).
- ²(a) A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.* **72**, 3894 (1968); (b) S. Trajmar, J. K. Rice, and A. Kuppermann, *Adv. Chem. Phys.* **18**, 15 (1970).
- ³F. W. S. Knoop, Ph.D. thesis, University of Leiden, Leiden, The Netherlands, 1972.
- ⁴(a) D. F. Dance and I. C. Walker, *Chem. Phys. Lett.* **18**, 601 (1973); (b) D. F. Dance and I. C. Walker, *J. Chem. Soc. (London) Faraday Trans. II* **70**, 1426 (1974).
- ⁵E. H. van Veen and F. L. Plantenga, *Chem. Phys. Lett.* **38**, 493 (1976).
- ⁶R. S. Stradling, M. A. Baldwin, A. G. Loudon, and A. Maccoll, *J. Chem. Soc. (London) Faraday Trans. II* **72**, 871 (1976).
- ⁷W. E. Kammer, *Chem. Phys. Lett.* **6**, 529 (1970).
- ⁸M. Jungen, *Chem. Phys.* **2**, 367 (1973).
- ⁹D. Demoulin and M. Jungen, *Theor. Chim. Acta* **34**, 1 (1974).
- ¹⁰W. E. Kammer, *Chem. Phys.* **5**, 408 (1974).
- ¹¹M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1975), Vol. II, p. 106.
- ¹²W. C. Price and A. D. Walsh, *Trans. Faraday Soc.* **41**, 381 (1945).
- ¹³G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966), p. 641.
- ¹⁴K. Watanabe and T. Namioka, *J. Chem. Phys.* **24**, 915 (1956).
- ¹⁵T. Nakayama and K. Watanabe, *J. Chem. Phys.* **40**, 558 (1964).
- ¹⁶C. R. Bowman and W. D. Miller, *J. Chem. Phys.* **42**, 681 (1965).
- ¹⁷(a) P. S. P. Wei and A. Kuppermann (unpublished); (b) P. S. P. Wei, Ph.D. thesis, California Institute of Technology, Pasadena, California, 1968.
- ¹⁸H. H. Brongersma and L. J. Oosterhoff, *Chem. Phys. Lett.* **1**, 169 (1967).
- ¹⁹J. T. Dowell and T. E. Sharp, *J. Chem. Phys.* **47**, 5068 (1967).
- ²⁰O. A. Mosher, M. S. Foster, W. M. Flicker, J. L. Beauchamp, and A. Kuppermann, *J. Chem. Phys.* **62**, 3424 (1975).
- ²¹I. G. Ross, *Trans. Faraday Soc.* **48**, 973 (1952).
- ²²R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.* **48**, 354 (1968).
- ²³C. S. Burton and H. E. Hunziker, *J. Chem. Phys.* **57**, 339 (1972).
- ²⁴O. A. Mosher, W. M. Flicker, and A. Kuppermann, *J. Chem. Phys.* **62**, 2600 (1975).
- ²⁵W. M. Flicker, O. A. Mosher, and A. Kuppermann, *J. Chem. Phys.* **64**, 1315 (1976).
- ²⁶O. A. Mosher, Ph.D. thesis, California Institute of Technology, Pasadena, California, 1975.
- ²⁷W. M. Flicker, Ph.D. thesis, California Institute of Technology, Pasadena, California, 1976.
- ²⁸E. N. Lassette, A. Skerbele, M. A. Dillon, and K. J. Ross, *J. Chem. Phys.* **48**, 5066 (1968).
- ²⁹P. D. Foo and K. K. Innes, *Chem. Phys. Lett.* **22**, 439 (1973).
- ³⁰W. C. Price, *Phys. Rev.* **47**, 444 (1935).
- ³¹G. W. King and C. K. Ingold, *Nature* **169**, 1101 (1952).
- ³²C. K. Ingold and G. W. King, *J. Chem. Soc.* **1953**, 2725.
- ³³(a) W. R. Harshbarger, M. B. Robin, and E. N. Lassette, *J. Electron Spectrosc.* **1**, 319 (1972/1973); (b) W. R. Harshbarger, N. A. Kuebler, and M. B. Robin, *J. Chem. Phys.* **60**, 345 (1974).
- ³⁴M. J. Coggiola, W. M. Flicker, O. A. Mosher, and A. Kuppermann, *J. Chem. Phys.* **65**, 2655 (1976).
- ³⁵The third and fourth ionization potentials were obtained from D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, London, 1970), p. 171.
- ³⁶Transition energies for these bands were measured from Fig. 4 of Ref. 15.
- ³⁷D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).
- ³⁸(a) M. W. Schmidt and E. K. C. Lee, *J. Am. Chem. Soc.* **90**, 5919 (1968); (b) **92**, 3579 (1970).
- ³⁹These limits were derived from a spectrum obtained by V. McMillan and displayed as Fig. 5-5 in J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (John Wiley and Sons, New York, 1966), p. 422.