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The excited states of 1, 3-butadiyne determined by electron energy loss spectroscopy

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Dipole forbidden electronic transitions in butadiyne were studied in the range 2–12 eV using a trochoidal electron spectrometer. The lowest observed feature is weak, structureless, with an onset around 2.7 eV, and is probably due to the lowest excited state $^3\Sigma_u^+$. The second triplet state $^3\Delta_u$ is observed at $3.21_6 \pm 0.01$ eV (0_0^0), respectively 4.2 ± 0.2 eV (vertical). It exhibits long progressions in the ν_2' C \equiv C stretch and ν_6' C–H bend vibrations. The latter indicates a bent equilibrium configuration. The UV inactive 0_0^0 transition of the $^1\Delta_u$ state is observed at 5.06 ± 0.01 eV with low electron energies. This value is in excellent agreement with the prediction of Jungen *et al.* based on the interpretation of the UV absorption. At higher electron energies only the UV active vibronic transitions of this state are observed. With low electron energies a number of narrow bands corresponding to dipole forbidden transitions are observed above 7 eV. They are tentatively grouped into three new Rydberg series with $\delta = 0.46, 0.5$, and 0.87 . Finally, three narrow anion states (Feshbach resonances) are observed at 6.71, 6.82, and 7.00 ± 0.04 eV. They decay preferentially by emission of a slow (≤ 0.3 eV) electron.

I. INTRODUCTION

Butadiyne (diacetylene) is the simplest hydrocarbon with conjugated triple bonds and its electronically excited states are thus an important testing ground for theory of electronic structure. Various regions of its UV and VUV absorption spectrum were recorded and analyzed and its electronic structure was calculated a number of times and this Introduction will not attempt to give a comprehensive review of this work.

The lowest very weak UV absorption with an origin at 4.328 eV was analyzed recently by Hardwick and Ramsay¹ and assigned to the *trans*-bent \tilde{A}^1A_u state ($^1\Sigma_u^-$ or $^1\Delta_u$ in the linear configuration). The 4.46–6.2 eV range was studied recently by Haink and Jungen.² They identified two transitions, a weak one leading to the $^1\Sigma_u^-$ (0_0^0 at 4.812 eV) and a somewhat stronger one leading to the $^1\Delta_u$ state (0_0^0 at 5.062 eV). Both transitions are dipole forbidden and only vibronic states containing the degenerate vibrations ν_6^1, ν_7^1 , and ν_8^1 are observed in the UV spectrum. The energies of the origins were determined indirectly from the vibrational analysis. Haink and Jungen propose that the $^1\Sigma_u^-$ state has a barrier to bending and therefore two transitions are observed: linear-to-bent at 4.328 eV and linear-to-linear at 4.812 eV. The $^1\Delta_u$ band was also studied by Lamotte *et al.*³ and a different vibrational assignment was proposed, resulting at 0_0^0 at 5.040 eV. The VUV region was studied by Price and Walsh⁴ and later by Smith.⁵ Smith identified two Rydberg series: $nR-X$ ($n\rho\sigma, ^1\Pi_u$), and $nR'-X$ ($n\rho\pi, ^1\Sigma_u^+$) converging to the first ionization energy and one series ($nR''-X$) converging to the second ionization energy. Gas phase absorption spectrum in the whole region 4.3–10.3 eV was given by Kloster-Jensen *et al.*,⁶ together with a list of λ_{\max} values.

Results of a frozen core calculation of the vertical excitation energies including the triplet states were given by Demoulin and Jungen.⁷

This contribution presents energy loss spectra of butadiyne with the aim of obtaining experimental information on

the symmetry and spin forbidden electronic transitions. Pure vibrational excitation by slow electron impact was described in a previous publication.⁸

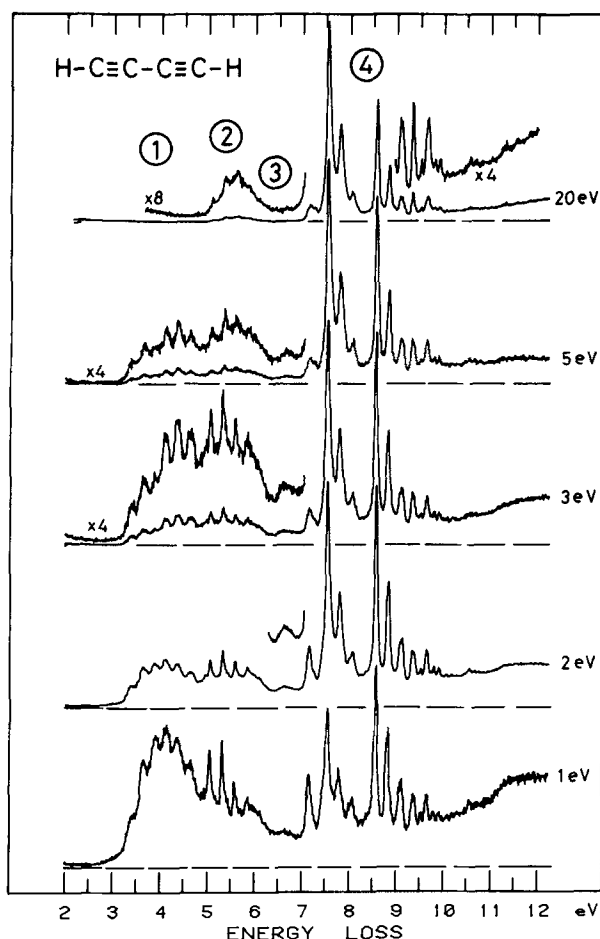


FIG. 1. Electron energy loss spectra of butadiyne recorded with constant residual energies given on the right. The spectrum with $E_r = 20$ eV is essentially identical to the UV–VUV absorption spectrum. At lower E_r , spin and symmetry forbidden transitions also appear. The energy range covered is divided into four regions shown in detail in Figs. 3–6.

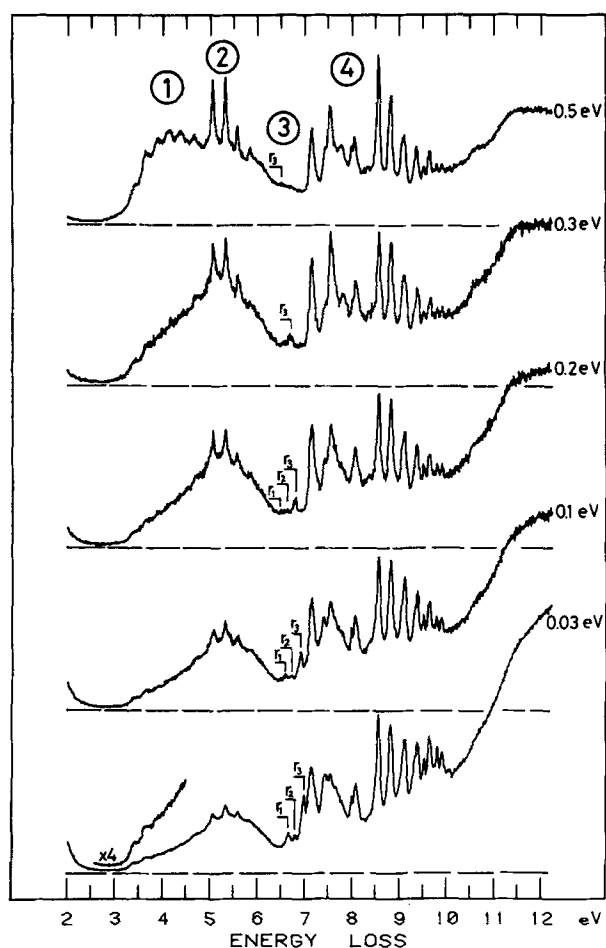


FIG. 2. Continuation of the spectra in Fig. 1 for low residual energies. Three peaks (r_1 – r_3) move on the energy scale as E_r is varied; they are due to anion states (Feshbach resonances). The remaining peaks are fixed and are due to the excited states of the neutral molecule, the role of resonances is limited to changing their relative intensities.

II. EXPERIMENTAL

The trochoidal electron spectrometer and calibration procedures used here were described earlier.^{9,10} A trochoidal monochromator¹¹ is used to generate an electron beam with

TABLE I. New spectral features observed in this work^a (in eV).

Energy	Vibrational spacing	Assignment
2.7 ± 0.1 (onset)	...	$^3\Sigma_u^+$
$3.21_0 \pm 0.01$	0.245, 0.068	$^3\Delta_u$
5.06 ± 0.01	0.265, 0.065	$^1\Delta_u$
6.0 ± 0.2^b	...	Valence
6.7 ± 0.1^b	...	Valence
7.16	0.285	$3R\ 3\ (3s\sigma)$
8.00	0.26	$3R\ 4$
8.07	0.29	$3R\ 5$
8.82	...	$4R\ 3$
9.11	...	$4R\ 4$
9.38	...	$5R\ 3$
9.74	...	$6R\ 4$
10.55	...	(?)

^a 0_0^0 transitions with an error limit of ± 0.02 eV are given except where otherwise noted.

^bBand maximum.

TABLE II. Observed and calculated valence excitation energies (in eV).

State	$^3\Sigma_u^+$	$^3\Delta_u$	$^1\Sigma_u^-$	$^1\Delta_u$
Observed ^a	(3.2 ± 0.5)	4.2 ± 0.2	4.812^b	$5.32(2_0^1)$
Calculated ^c	3.73	4.47	5.16	5.43

^aVertical transition energies.

^bHaink and Jungen, Ref. 2, 0_0^0 transition.

^cDemoulin and Jungen, Ref. 7. The authors predict that these frozen core results will be too high by a few tenths of an eV, in excellent agreement with the experiment.

a narrow energy spread which then collides with a static gaseous sample. Electrons inelastically scattered at 0° and 180° (after a reflection) are energy analyzed by two trochoidal analyzers in series and detected. The spectrometer was used to record energy loss spectra with constant residual energy (E_r). The instrumental resolution was about 0.040 eV (FWHM). The ordinate of all figures is scattered current in arbitrary units, except in Fig. 3 where the derivative of the scattered current is shown. Diacetylene was prepared by the standard method^{12,13} and its purity was checked by UV-photoelectron spectroscopy.

III. RESULTS AND DISCUSSION

In the limit of forward scattering and high electron energies, excitation by electron impact is governed by the dipole selection rules. Previous experiments⁹ have shown that with the present trochoidal spectrometer, predominantly the dipole allowed transitions are observed with residual energies $E_r > 20$ eV. With low residual energies $E_r < 5$ eV, resonant excitation (via intermediate anion state) dominates and many symmetry and spin forbidden transitions also appear.

Figures 1 and 2 show the butadiyne energy loss spectra recorded with a number of residual energies in the range 20–

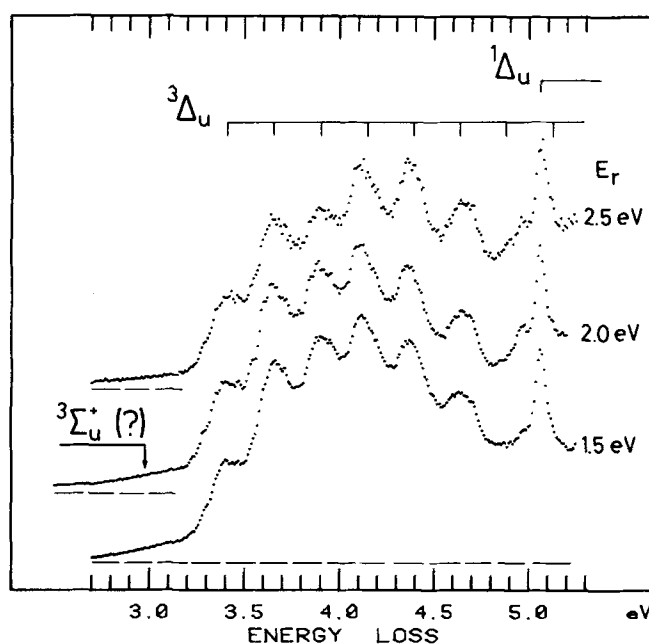


FIG. 3. Expanded view of the spectral region 1 of Fig. 1.

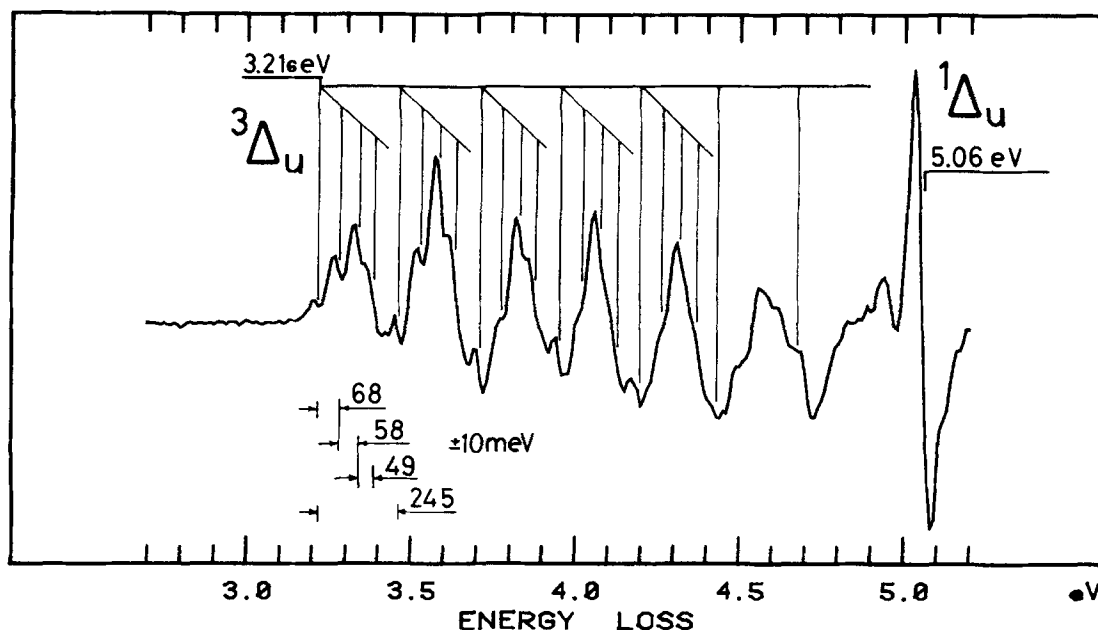


FIG. 4. Digitally calculated derivative of the three curves in Fig. 3. This form of presentation improves the visibility of the finer structure.

0.03 eV. The spectrum with $E_r = 20$ eV is well consistent with the UV spectrum⁶ when the lower resolution of the present experiment is taken into account. At lower residual energies a number of additional bands appear with varying relative intensities.

In principle, band profiles obtained by resonant excitation can deviate from those given by the Franck-Condon principle since the geometry can relax during the lifetime of the anion state. The role of the autodetaching anion state is similar to the role of autoionizing states in resonant photoionization in this respect. In practice, this effect was found to be small, e.g., in benzene where the band profile is largely independent of the residual energy.⁹ In the present case, the effect seems to be more pronounced and the band envelope in the 3–5 eV energy loss region depends to a certain degree upon residual energy, that is upon which resonance is involved in the excitation. The effect introduces some uncertainty into the determination of the vertical transition energy, that is the band maximum. The positions of the individual vibronic peaks remain unaffected.

In the 6–7 eV energy loss region in Fig. 2, there are three sharp peaks whose position depends on E_r , they occur at a constant incident energy. They are assigned to Feshbach resonances, i.e., anion states with doubly occupied Rydberg orbitals. Feshbach resonances were found around 0.5 eV below the respective Rydberg states in many molecules.¹⁴

The spectral range is divided qualitatively into four regions labeled 1–4 in Figs. 1 and 2, and these regions will be discussed separately below. The energies of the previously unreported spectral features are summarized in Table I. Low lying valence transition energies are compared to the results of the frozen core calculation of Ref. 7 in Table II.

A. Region 1, 2.7–5 eV

A weak scattered current is observed in the energy loss range 2.7–3.2 eV in the spectra with $E_r = 0.5$ –2 eV in Figs. 1 and 2 and also in the expanded view in Fig. 3. The feature is not due to hot bands of the higher transition with onset at 3.2

eV since the ratio of the two intensities is not constant for different residual energies. In particular, the 2.73–3.2 eV feature is virtually absent in the $E_r = 5$ eV spectrum where the higher transition is still present. The 2.73–3.2 eV feature could thus be due to the lowest excited state $^3\Sigma_u^+$, predicted in this energy region.⁷

The next band, observed with $E_r = 1.5$ –2.5 eV (Fig. 3), shows a long progression of broadbands in the $\text{C}\equiv\text{C}$ stretch vibration ν_2' . The band maximum (vertical transition) is around 4.2 eV, in good agreement with the value calculated for the second excited state $^3\Delta_u$. To improve the visibility of a narrower structure which is barely seen in Fig. 3, the derivative of the sum of the three curves was calculated. The result after one smoothing cycle¹⁵ is shown in Fig. 4. The

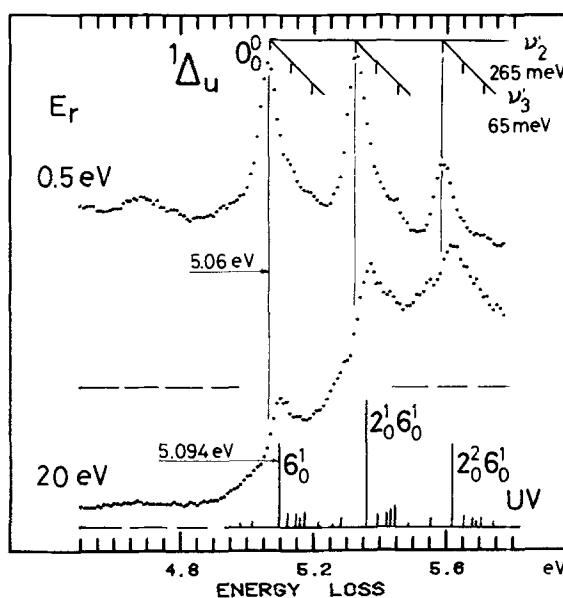


FIG. 5. Expanded view of the spectral region 2, recorded at high and low residual energies. Sharp features of the UV absorption spectrum and their assignment are reproduced schematically from Ref. 2 at the bottom of the figure for comparison.

digital treatment reveals a finer regular structure superimposed on the broadbands, as indicated in Fig. 4. The whole band appears to have a distinct onset and therefore the first structure at $3.21_6 \pm 0.01$ eV was assigned to the O_0^0 transition. The spacing of the finer structure suggests that it is associated with the C-H bend vibration. The large degree of its excitation and the rapidly diminishing spacing suggest a bent equilibrium configuration with a strongly anharmonic potential for this state.

At $E_r = 3\text{--}5$ eV (Fig. 1), the relative intensities of the individual vibronic bands become unregular in this energy loss region. This effect could indicate another electronic transition around 4–4.5 eV, but it could also be due to selective enhancement of excitation of certain vibronic levels via a resonance.

With $E_r < 0.3$ eV, an apparently continuous vibrational structure appears in the 3.5–4.9 eV energy loss region. This feature could also indicate the presence of an additional electronic transition. The \tilde{A}^1A_u state assigned by Hardwick and Ramsay¹ could be responsible for this feature. The experimental evidence has to be taken with caution, however, since

very near threshold energy loss spectra of polyatomic molecules are often distorted by resonances. An arbitrary example for this behavior is *p*-benzoquinone.^{10(b)}

B. Region 2, 5–6 eV

This region is shown expanded in Fig. 5. The energy scales were carefully calibrated at both low and high E_r and are accurate to ± 0.01 eV. The sharp lines in the UV spectrum and their assignment from Ref. 2 are shown schematically for comparison. Apart from the lower resolution the $E_r = 20$ eV spectrum is identical with the UV spectrum. At low residual energies a series of sharp peaks appear, shifted by 35 ± 10 meV to lower energies. These peaks are interpreted as the $n\nu'_2$ progression, i.e., resonant excitation of the dipole forbidden vibronic levels of the $^1\Delta_u$ state, without simultaneous excitation of the degenerate C-H bend vibration ν'_6 . This assignment is based on the observation of the same ν'_2 spacing in the electron impact (265 meV) and UV ($2130\text{cm}^{-1} = 264$ meV²) experiments and the fact that the observed origin at 5.06 ± 0.01 eV is in excellent agreement

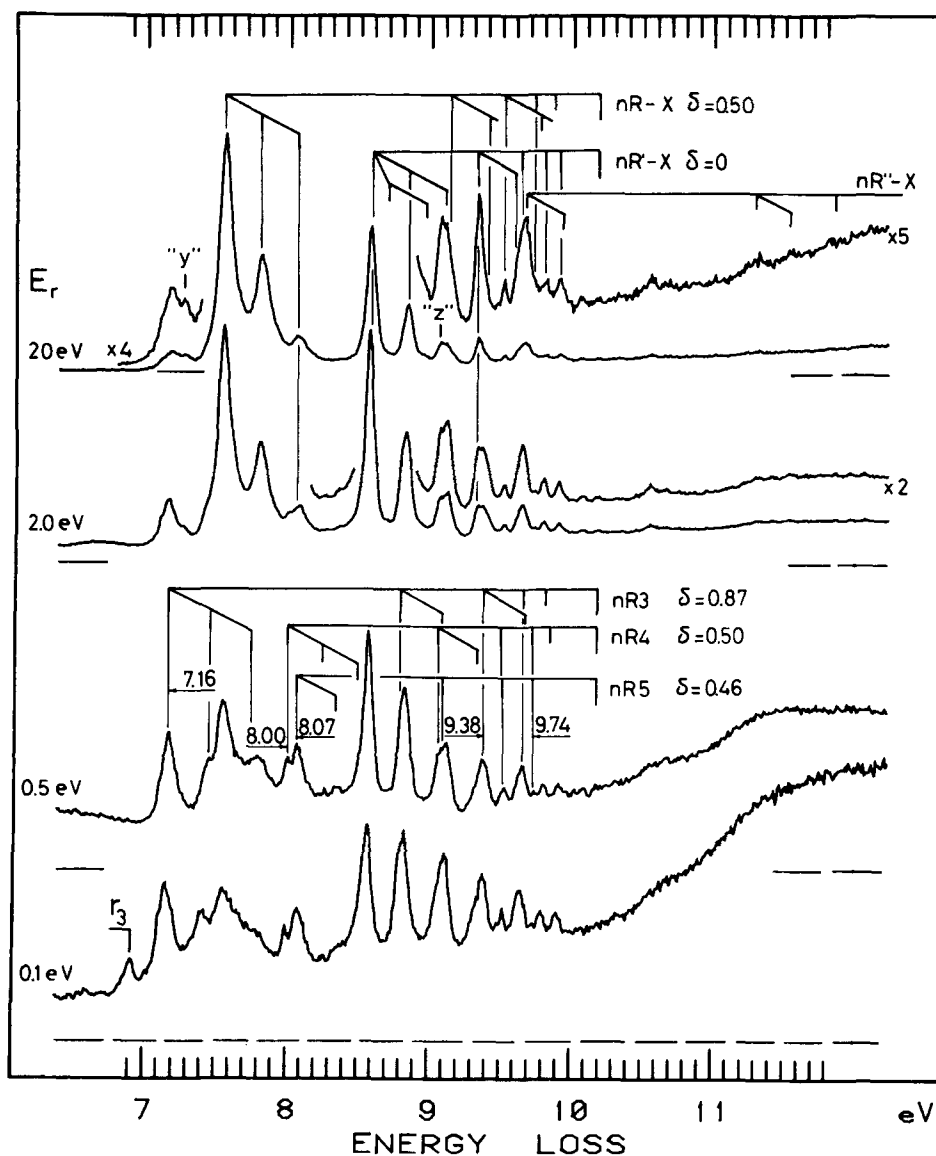


FIG. 6. Expanded view of the spectral region 4. The assignment of the UV active Rydberg series from Ref. 5 is given above the $E_r = 20$ eV spectrum. Additional peaks appearing at low residual energies were tentatively grouped into three new Rydberg series shown above the $E_r = 0.5$ eV curve. The peak labeled r_3 is due to the decay of a Feshbach resonance.

with the value of 5.062 eV predicted from vibrational analysis.² Conversely, the present spectrum favors the vibrational assignment of Ref. 2 over that of Ref. 3 (0_0^0 at 5.040 eV). A weaker structure observed with $E_r = 0.5$ eV could be associated with ν_3 or $2\nu_6'$ excitation (Fig. 4).

C. Region 3, 6–7 eV

In this region a weak structureless band at 6.7 eV is found with $E_r = 1$ –5 eV (Fig. 1). In addition a weak band around 6.0 eV is visible underneath the high energy end of the $^1\Delta_u$ band with $E_r = 0.5$ –3 eV. No well justified assignment of these features appears possible at this point, although higher triplet states were predicted in this energy region by theory.¹⁶

D. Region 4, 7–12 eV

Expanded view of this region is shown in Fig. 6. The $E_r = 20$ eV is again essentially identical with the VUV spectrum.^{5,6} The assignment of Smith⁵ is given above the $E_r = 20$ eV spectrum. Two unassigned bands which were reported and labeled “y” and “z” in Ref. 5 are also marked. At lower residual energies, new features start to appear around $E_r = 2$ eV and become prominent at still lower E_r . These features are new bands at 7.16, 8.00, 8.07, 9.38, and 9.74 eV. In addition, the appearance of new bands at 8.87 and 9.10 eV is indicated by an increase of peak intensities respective to the $3R'-X$ band (8.57 eV) at low E_r . These new features were tentatively grouped into three new Rydberg series labeled nR 3 - nR 5, as indicated in Fig. 6. These series appear to be more regular than the dipole allowed $nR'-X$ and $nR''-X$ series.⁵ This observation could be understood as a result of a larger separation of the valence and Rydberg states in the triplet manifold and thus lesser mutual perturbation.

In view of the large δ , the $3R$ 3 band could be of the s type ($3s\sigma, ^1,^3\Pi_g$). The 7.16 eV feature is broader than the instrumental resolution and probably consists of two bands. These could be the singlet and triplet states, with a splitting of about 0.05 eV. This value of splitting appears reasonable, in acetylene the value of 0.09 eV was found for the corre-

sponding two states.¹⁷ An alternative explanation would involve the $3p\sigma^3\Pi_u$ state. The size of δ suggests that the remaining two series are of the p type. The dipole allowed $np\pi$ ($^1\Sigma_u^+$) series has been assigned as $nR'-X$.⁵ There remain other forbidden $np\pi$ ($^3\Sigma_u^+, ^1,^3\Sigma_u^-,$ and $^1,^3\Delta_u$) series as potential assignments for the nR 4 and nR 5 series. A reinterpretation of the assignment of Smith⁵ and a more detailed assignment of the new Rydberg bands will be presented in a subsequent publication.¹⁶

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