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# The absolute infrared intensities of propyne-$d_0$ and propyne-$d_3$

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The integrated infrared intensities of the fundamental modes of propyne-$d_0$ and propyne-$d_3$ have been measured by the Wilson– Wells–Penner–Weber method, using nitrogen as broadening gas at a pressure of 60 atm. From the measured intensities eight sets of $\partial\mu/\partial S$ values were obtained using an iterative least-squares fitting procedure. The eight sets were left after fixing the signs of six $\partial\mu/\partial S_i$ parameters using CNDO and *ab initio* results and known values for related molecules. Four of the remaining sets were discarded after prediction of the propyne-$d_1$ intensities. Using additional arguments from Coriolis interactions, predictive abilities and further comparison with related molecules one of the remaining four sets could be selected as the more preferable one. The final set $\partial\mu/\partial S_i$ values and the resulting calculated intensities are discussed and compared with the results of Kondo and Koga. The present sign combination is in full agreement with the ones selected by Kondo and Koga. Also the observed intensities, the $\partial\mu/\partial S_i$ values and the calculated intensities are in close accordance.

## INTRODUCTION

Viewing our earlier work on the absolute intensities of methylbromide[1] and acetylene,[2] the measurement of the intensities of propyne is of much interest since it offers the possibility to test the transferability of intensity parameters both for the methyl and ethynyl groups. From a study of the literature data on the infrared vapor spectra of propyne and deuterated derivatives[3–10] it was concluded that measurement of the intensities of propyne-$d_0$ and propyne-$d_3$ would provide sufficient data to obtain a complete set of dipole moment derivative values. The measurement of the propyne intensities is hampered by several overlapping bands, Fermi resonances and Coriolis interactions and thus the evaluation of a complete set of individual intensities with acceptable accuracy from only one member of the propyne family is not possible. Moreover, the availability of isotopic intensity data greatly facilitates the search for the correct sign combination of the dipole moment derivatives. Recently, Kondo and Koga[11] reported the absolute intensities of propyne-$d_0$, propyne-$d_1$, and propyne-$d_3$. They reduced their intensity data to ten dipole moment derivatives with respect to isotope-independent ("primitive") symmetry coordinates. Using the isotopic invariance criterion and additional data from CNDO calculations, Coriolis interaction analyses, and the "CH-bond criterion" they selected one of the $2^{10}$ possible sign combinations for the dipole moment derivatives with respect to the normal coordinates. The results of Kondo and Koga will be compared in detail with the present results.

## EXPERIMENTAL

The sample of propyne was obtained from Matheson Gas Products, Belgium. The purity of this sample was specified to be better than 96%. It was used after fractional distillation from a liquid nitrogen trap. The only detectable impurity in the infrared spectrum was a very weak feature at 852 $cm^{-1}$, indicating the presence of a trace of allene which is known to have the strong $\nu_{10}$ mode at that frequency.

The sample of propyne-$d_3$ was synthesized[12] as follows from ethyne and deuterated methyliodide:

$$3HC{\equiv}CH + 2Li \xrightarrow{\text{liquid } NH_3} 2LiC{\equiv}CH + H_2C{=}CH_2\uparrow$$

(see Ref. 12, p. 22);

$$LiC{\equiv}CH + CD_3I \xrightarrow{\text{liquid } NH_3} CD_3C{\equiv}CH + LiI\ ;$$

$$CD_3CH + LiNH_2 \xrightarrow{\text{liquid } NH_3} CD_3C{\equiv}CLi + NH_3$$

(see Ref. 12, pp. 19 and 23);

$$CD_3C{\equiv}CLi + H_2O \rightarrow CD_3C{\equiv}CH\uparrow + LiOH.$$

In order to ensure that the final product is obtained both in good yield and as pure as possible, the following precautions are important: (i) the acetylene should be acetone free (see Ref. 12, p. 10); (ii) in order to avoid an acetylene impurity in the final product, Li should always be present in excess in the first reaction step; (iii) a small excess of methyliodide-$d_3$ should be added under nitrogen to the acetylide at a temperature of about $-45\,^{\circ}C$; (iv) $LiNH_2$, prepared as described in Ref. 12, p. 19, should be added to a slight excess of $CD_3C{\equiv}CH$ in order to avoid a possible $D \rightarrow H$ exchange; (v) the ammonia should be carefully removed from the $CD_3C{\equiv}CLi$ under introduction of dry nitrogen; (vi) the Li salt should be hydrolyzed with water saturated with NaCl; (vii) the gaseous $CD_3C{\equiv}CH$ is led through a cold water trap to remove impurities and is after drying over $CaCl_2$ catched in a liquid nitrogen trap; (viii) the yield of propyne-$d_3$ is increased by flushing with nitrogen after hydrolysis.

After fractional distillation from the trap, the residual

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TABLE I. Observed absolute intensities of propyne-$d_0$ and propyne-$d_3$.

| | | $\nu_i$ (cm$^{-1}$)[a] | $A_i$ (km/mole) This work[b] | | Ref. 11 |
|---|---|---|---|---|---|
| $d_0$ | $\nu_1$ | 3335.1 | 43.2±1.3 | 43.2±1.3 | 45.1±3.1 |
| | $\nu_2$ | 2910 | 19.5±2.8 | 19.5±2.8 | 14.9±3.6 |
| | $\nu_3$ | 2142 | 5.2±0.2 | 5.2±0.2 | 5.3±0.3 |
| | $\nu_4$ | 1390.6 | 19.2±1.2 | 1.42±0.85 | 1.5±1.0 |
| | $\nu_7$ | 1450.9 | | 17.8±1.8 | 17.9±1.6 |
| | $\nu_5$ | 930.1 | 0.65±0.17 | 0.65±0.17 | 1.0±0.5 |
| | $\nu_6$ | 2980.8 | 15.4±2.2 | 15.4±2.2 | 17.7±3.5 |
| | $\nu_8$ | 1036.0 | 0.25±0.12 | 0.25±0.12 | 0.4±0.3 |
| | $\nu_9$ | 638.6 | 88.5±5.4 | 88.5±5.4 | 87.3±4.5 |
| | $\nu_{10}$ | 329.2 | 15.6±0.6 | 15.6±0.6 | 16.7±1.0 |
| $d_3$ | $\nu_1$ | 3335 | 48.4±2.0 | 48.4±2.0 | 44.8±2.4 |
| | $\nu_2$ | 2110 | 13.1±0.2 | | 12.8±0.7 |
| | $\nu_3$ | 2142 | | | |
| | $\nu_4$ | 1111.2 | 9.8±0.4 | 0.19±0.11 | 0.2±0.3 |
| | $\nu_7$ | 1048.6 | | 9.6±0.5 | 10.6±0.9 |
| | $\nu_5$ | 839.6 | 1.31±0.05 | 0.44±0.25 | 0.4±0.3 |
| | $\nu_8$ | 835.4 | | 0.87±0.15 | 0.8±0.3 |
| | $\nu_6$ | 2234.6 | 8.2±0.5 | 8.2±0.5 | 7.9±0.7 |
| | $\nu_9$ | 636.4 | 92.3±7.6 | 92.3±7.6 | 89.6±5.3 |
| | $\nu_{10}$ | 306.4 | 12.3±0.7 | 12.3±0.7 | 13.6±1.1 |

[a]Reference 10.
[b]First column: observed intensities; second column: individual intensities using intensity ratios from rovibrational analyses (see text).

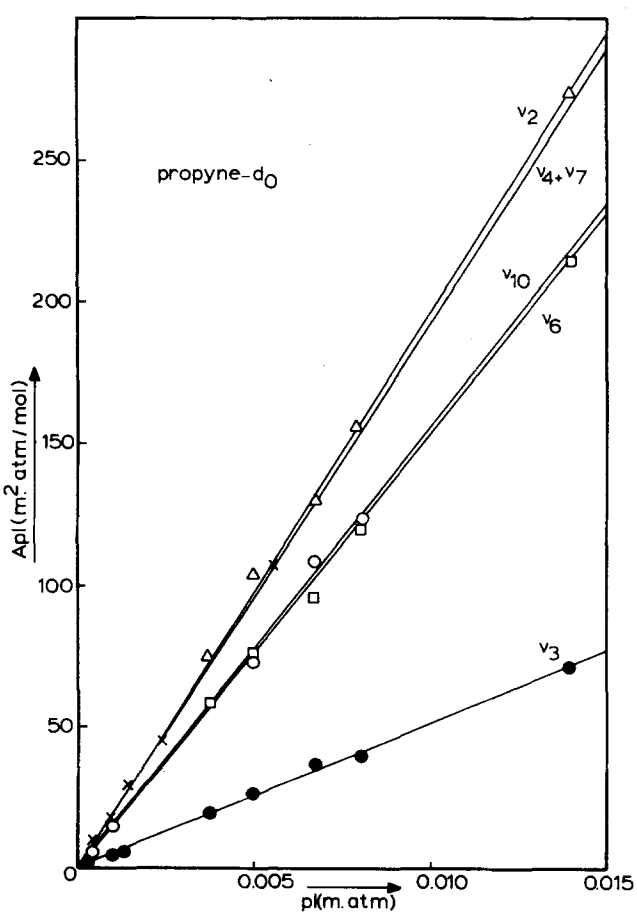


FIG. 1. Beer's law plots for absorption bands of propyne-$d_0$. (△) $\nu_2$; (●) $\nu_3$; (×) $\nu_4+\nu_7$; (□) $\nu_6$; (○) $\nu_{10}$.

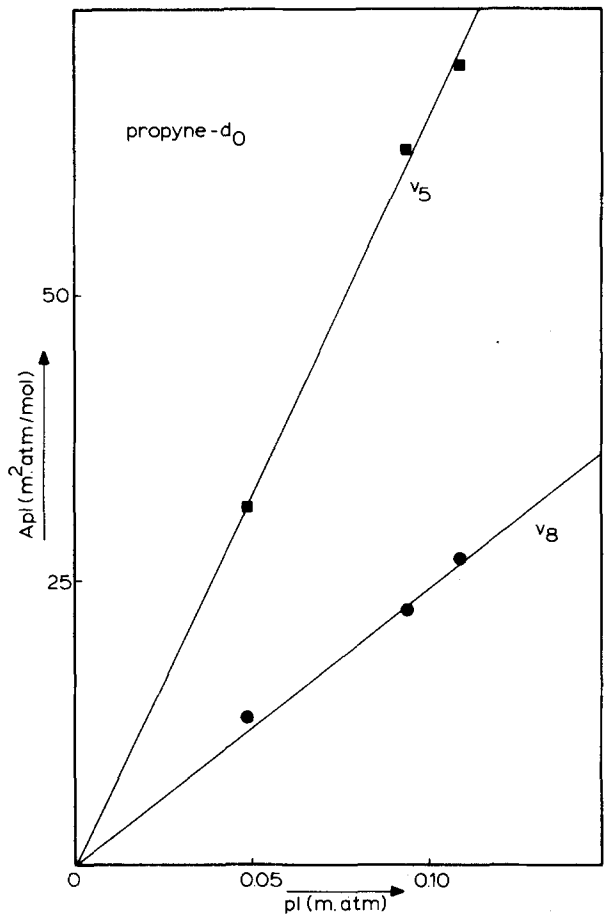


FIG. 2. Beer's law plots for absorption bands of propyne-$d_0$. (■) $\nu_5$; (●) $\nu_8$.

fraction was used. A weak absorption at 739 cm$^{-1}$ due to the very strong $\nu_5$ fundamental of ethyne[2] was the only detectable impurity. No absorption was observed in the $CH_3$ stretching and bending regions.

The intensity measurements were carried out using a Perkin–Elmer Model 180 spectrophotometer equipped with a Data Control interface and a digital magnetic recorder (PE 109). The instrument was flushed with dry and $CO_2$-free air. The spectral slit width was 1.0 cm$^{-1}$ at 3000 cm$^{-1}$. A stainless steel absorption cell with KRS-5 windows and an effective pathlength of 5.15 cm was used. A maximum pressure of 80 atm was allowed.

Sample pressures ranged from 0.5 to 180 cm Hg. Pressures larger than 2 cm Hg were measured with a mercury manometer. Carefully premixed samples of about 10% propyne in nitrogen were used to achieve a good accuracy for the sample pressures lower than 2 cm Hg.

The experimental method used for the determination of the absolute intensities was that of Wilson and Wells[13] and Penner and Weber.[14] The samples were pressurized by adding pure nitrogen up to a pressure of 60 atm. At this pressure and the applied spectral slit width the vibration–rotation lines appear to be sufficiently broadened to give linear Beer's law plots. The spectra were sampled with an interval of 1 cm$^{-1}$ and numerically integrated.



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Apart from a few exceptions as discussed below the errors stated for the observed intensities (see Table I) are standard deviations resulting from the scatter of the data points in the Beer's law plots (see Figs. 1–4). The Beer's law plots are obtained from a linear least-squares procedure. In the error calculation both errors in sample pressure and band areas were taken into account.[15]

The $\nu_6/\nu_2$ region of the propyne-$d_0$ spectrum consists of a number of overlapping bands. In order to facilitate graphical band separations this part of the spectrum has been replotted on a logarithmic frequency scale (see Fig. 5). The weak band at 2760 cm$^{-1}$ may be interpreted as the ternary combination $\nu_{7+8+10}$ being in Fermi resonance with $2\nu_7$.[10] The well established Fermi resonance between $\nu_7$ and $\nu_{8+10}$ (Ref. 8) might favor this assignment over the earlier one of Crawford[3] and, later, also McKean,[16] who assigned this band as $2\nu_4$. However, the possibility that both the $\nu_{7+8+10}$ and $2\nu_4$ levels take part in the resonance with $\nu_2$ and $2\nu_7$ and thus contribute to the 2760 cm$^{-1}$ band can not be excluded.[16] Assuming the unperturbed intensities of $2\nu_7$ and $\nu_{7+8+10}$ (and/or $2\nu_4$) to be zero the observed overtone and combination intensities have been added to the observed $\nu_2$ intensity.[17] The separation of $\nu_6$ from $\nu_2$ has been accomplished by assuming the intensity of $\nu_6$ to be equally distributed at both sides of the $^RQ_0$ subbranch at 2985 cm$^{-1}$.[6] Thus twice the area from 2985 cm$^{-1}$ to the higher integration limit (3200 cm$^{-1}$) has been subtracted from

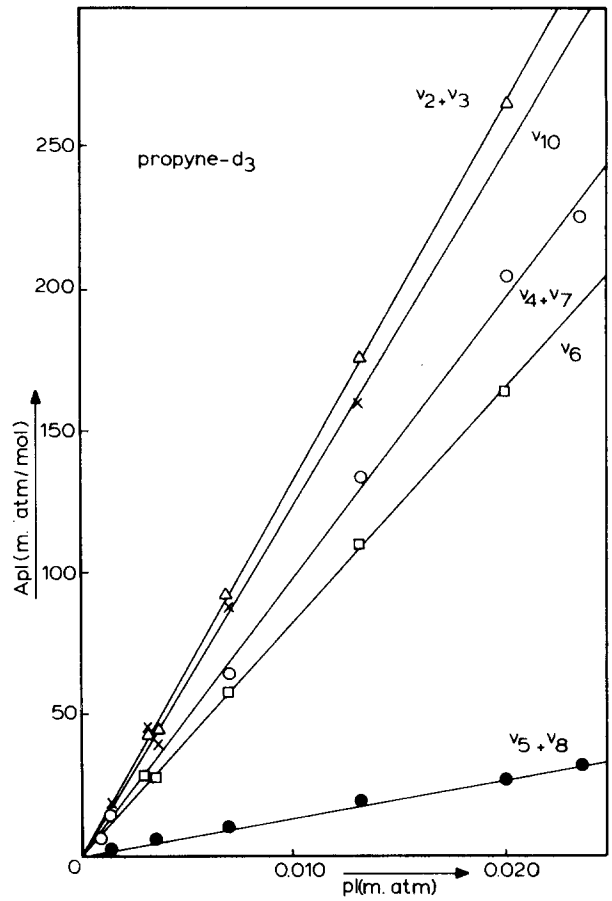


FIG. 4. Beer's law plots for absorption bands of propyne-$d_3$. (Δ) $\nu_2+\nu_3$, (o) $\nu_4+\nu_7$, (●) $\nu_5+\nu_8$, (□) $\nu_6$, (×) $\nu_{10}$.

the total area of the $\nu_6/\nu_2$ band system. In order to account for the uncertainty in this separation procedure the standard errors for the $\nu_6$ and $\nu_2$ intensities have been increased by 10% of the $\nu_6$ band area.

Also the overlapping bands in the $\nu_8/\nu_5$ region of the propyne-$d_0$ spectrum have been replotted on a logarithmic frequency scale (see Fig. 6). The weak band at 971 cm$^{-1}$ has been assigned as $\nu_{9+10}$ (Refs. 3 and 6) and may be assumed to be in Fermi resonance with $\nu_5$. Thus the unperturbed $\nu_5$ intensity is taken as the sum of the observed $\nu_5$ and $\nu_{9+10}$ intensities.[17] However, since Fermi reso-

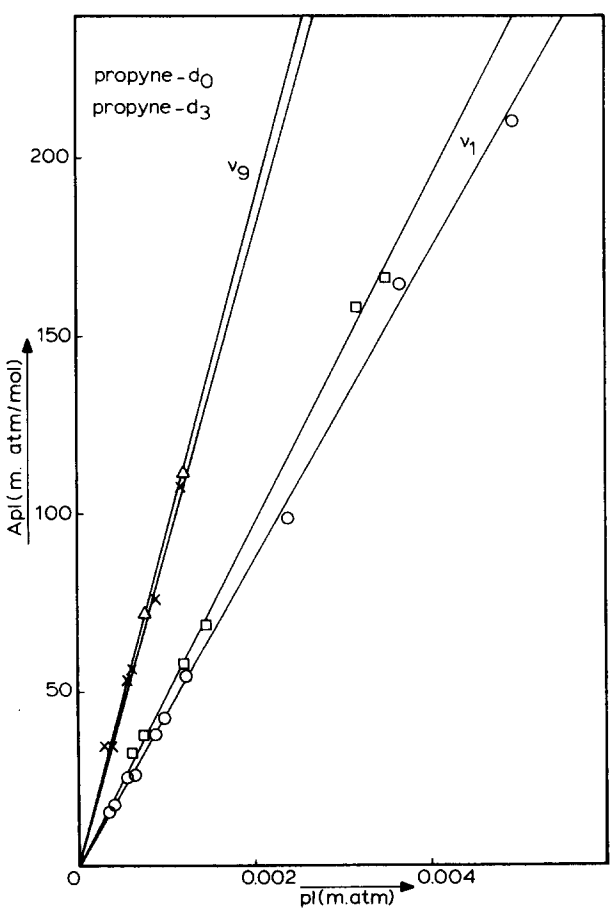


FIG. 3. Beer's law plots for absorption bands of propyne-$d_0$ and propyne-$d_3$. (o) $\nu_1$-$d_0$, (□) $\nu_1$-$d_3$, (×) $\nu_9$ -$d_0$ (Δ) $\nu_9$ -$d_3$.

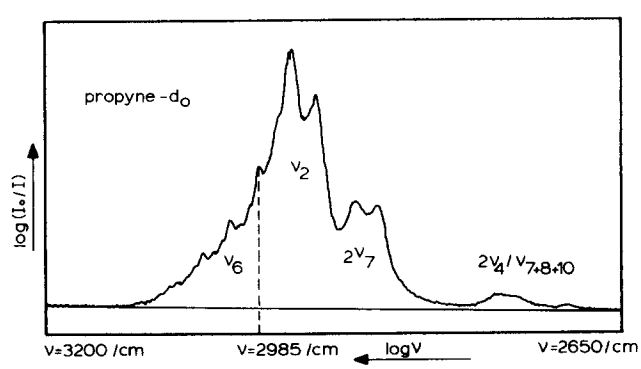


FIG. 5. $\nu_6/\nu_2$ region of the propyne-$d_0$ spectrum on a logarithmic frequency scale.



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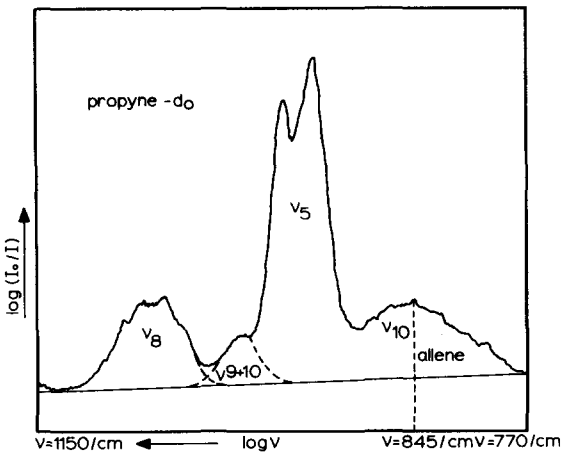


FIG. 6. $\nu_8/\nu_5$ region of the propyne-$d_0$ spectrum on a logarithmic frequency scale.

nance between $\nu_8$ and $\nu_{9+10}$ can not be excluded the standard errors for the $\nu_5$ and $\nu_8$ intensities have been enlarged by the graphically estimated band area of $\nu_{9+10}$. Further, the separation of $\nu_5$ from the allene impurity has been performed similarly as has been done for $\nu_6$ and $\nu_2$. Again it is assumed that the intensity of the band of allene is equally distributed at both sides of the ${}^RQ_0$ subbranch[10] at 845 cm$^{-1}$.[18] Hence twice the area from 845 cm$^{-1}$ to the lower integration limit (770 cm$^{-1}$) has been subtracted from the total $\nu_5/\nu_{10}$ area. The uncertainty involved in this separation procedure has been accounted for by an increase of the $\nu_5$ standard error with 10% of the $\nu_{10}$ band area.

In all other known cases of Fermi resonance [$\nu_1$ with $\nu_3+2\nu_9$,[10] $\nu_3$ with $2\nu_8$,[6] $\nu_7$ with $\nu_{8+10}$,[8] $\nu_7$ with $\nu_{5+9}$ (Ref. 8)] the integration intervals are chosen as to include the observed overtone or combination band intensities in the measured fundamental intensities. The strongly overlapping fundamentals $\nu_4$ and $\nu_7$ could not be separated and thus only the total intensity of the $\nu_4-\nu_7-\nu_{8+10}-\nu_{5+9}$ band complex is given in Table I. The following integration intervals have been used for propyne-$d_0$: $\nu_1$ 3450–3200 cm$^{-1}$, $\nu_6/\nu_2$ 3200–2600 cm$^{-1}$, $\nu_3$ 2200–2010 cm$^{-1}$, $\nu_7/\nu_4$ 1650–1306 cm$^{-1}$, $\nu_8/\nu_5$ 1118–750 cm$^{-1}$, $\nu_9$ 700–560 cm$^{-1}$, and $\nu_{10}$ 400–260 cm$^{-1}$. The integration intervals used for propyne-$d_3$ are $\nu_1$ 3450–3200 cm$^{-1}$, $\nu_6$ 2400–2172 cm$^{-1}$, $\nu_3/\nu_2$ 2172–2000 cm$^{-1}$, $\nu_4/\nu_7$ 1205–890 cm$^{-1}$, $\nu_5/\nu_8$ 900–770 cm$^{-1}$, $\nu_9$ 700–560 cm$^{-1}$, and $\nu_{10}$ 400–260 cm$^{-1}$.

No attempts for band separations have been made in the strongly overlapping $\nu_3/\nu_2$, $\nu_4/\nu_7$, and $\nu_5/\nu_8$ regions of the propyne-$d_3$ spectrum. Since Fermi resonance occurs between the $\nu_2$ and $2\nu_7$ levels,[19] the sum of the observed $\nu_2$ and $2\nu_7$ intensities is considered to represent the unperturbed $\nu_2$ intensity. The same holds for the small contributions of $\nu_{8+10}$ and $\nu_{5+10}$ to the $\nu_4/\nu_7$ band system,[9] which are assumed to be borrowed from $\nu_7$.

The measured intensities for propyne-$d_0$ and propyne-$d_3$ are shown in Table I. In the next column of the same table the individual band intensities are given. The individual intensities for the overlapping pairs could be obtained using the following results of rovibrational band analysis: $A_4/A_7 = 0.08 \pm 0.04$ (Ref. 8) for propyne-$d_0$, $A_4/A_7 = 0.020 \pm 0.010$ (Ref. 9), and $A_5/A_8 = 0.50 \pm 0.20$ (Ref. 9) for propyne-$d_3$. Since no transition moment ratio is known for $\nu_2/\nu_3$ of propyne-$d_3$, no individual intensities for these modes are given in the table. The errors given for the individual intensities of the overlapping pairs include the uncertainties in the transition moment ratios.

The measured intensities reported by Kondo and Koga[11] are given in the last column for comparison.

## DIPOLE MOMENT DERIVATIVES

The internal coordinates, symmetry coordinates and the equilibrium values for the geometry parameters[20] are given in Table II. The normal coordinate analysis was performed with the force field of Duncan *et al.*[10] The internal coordinates and Cartesian axis system are indicated in Fig. 7.

The absolute intensities are related to the dipole moment derivatives with respect to the normal coordinates, according to

$$A_i = \frac{N_0 \pi g_i}{3c^2} \frac{\nu_i}{\omega_i} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_i}\right)^2 , \qquad (1)$$

where $A_i$ is the intensity of $\nu_i$, $N_0$ is Avogadro's number, $g_i$ is the degeneracy, $c$ is the velocity of light, $\nu_i$ and $\omega_i$ are the observed and harmonic frequencies, $\mu$ is the molecular dipole moment, and $Q_i$ is the normal coordinate of the fundamental mode $\nu_i$. The derivatives with respect to the symmetry coordinates are obtained from[21]

$$\mathrm{P}_S = \mathrm{P}_Q \mathrm{L}_S^{-1} , \qquad (2)$$

where $\mathrm{P}_S$ is the $3\times(3N\text{-}6)$ polar tensor with elements $\partial\mu_\xi/\partial S_i$ ($\xi = x$, $y$, or $z$), $\mathrm{P}_Q$ is the polar tensor on normal coordinate basis, and $\mathrm{L}_S^{-1}$ is defined by

TABLE II. Geometrical parameters[a] and symmetry coordinates for propyne.

| | | | |
|---|---|---|---|
| $r_{CH7} = 1.060$ Å | | $r_{CH1} = 1.096$ Å | $\alpha_{HCH} = 108.28°$ |
| $r_{C=C} = 1.2073$ Å | | $r_{C-C} = 1.4596$ Å | |
| $A_1$ | $S_1 = \Delta r_6$ | | |
| | $S_2 = 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)$ | | |
| | $S_3 = \Delta r_5$ | | |
| | $S_4 = \text{Å}[\kappa(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]/[3(1+\kappa^2)]^{1/2}$ | | |
| | $S_5 = \Delta r_4$ | | |
| | $S_{\text{Red}} = \text{Å}[(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) + \kappa(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]/[3(1+\kappa^2)]^{1/2}$ | | |
| | $\kappa = -3 \sin\beta \cos\beta / \sin\alpha$ | | |
| $E$ | $S_{6x} = 6^{-1/2}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$ | $S_{6y} = 2^{-1/2}(\Delta r_2 - \Delta r_3)$ | |
| | $S_{7x} = \text{Å}\, 6^{-1/2}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$ | $S_{7y} = \text{Å}\, 2^{-1/2}(\Delta\alpha_2 - \Delta\alpha_3)$ | |
| | $S_{8x} = \text{Å}\, 6^{-1/2}(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$ | $S_{8y} = \text{Å}\, 2^{-1/2}(\Delta\beta_2 - \Delta\beta_3)$ | |
| | $S_{9x} = \text{Å}\, \Delta\theta_x$ | $S_{9y} = \text{Å}\, \Delta\theta_y$ | |
| | $S_{10x} = \text{Å}\Delta\varphi_x$ | $S_{10y} = \text{Å}\Delta\varphi_y$ | |

[a]Reference 20.



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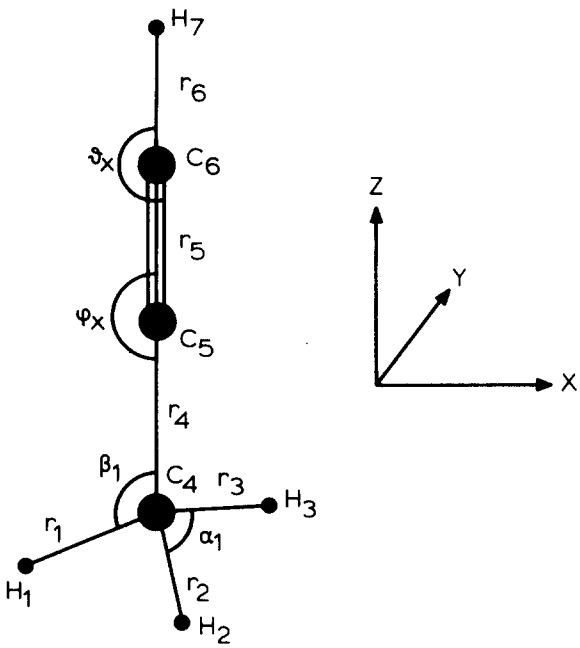


FIG. 7. Definition of internal coordinates and Cartesian axis system for propyne.

$$S = L_S Q \ . \tag{3}$$

In principle, since no information on the sign of the $\partial\mu_\ell/\partial Q_i$ quantities results from Eq. (1), there are $2^{10}$ possible $P_S$ tensors. Since the CNDO method has proven to be rather successful in predicting the signs for $\partial\mu_\ell/\partial S$ quantities (especially for molecules only containing first row elements) our starting point is the CNDO calculated sign combination (see Table III).

TABLE III. CNDO calculated $\partial\mu/\partial S$ values and *ab initio* calculated gross atomic charges[a] and resulting $\partial\mu/\partial S$ values for propyne-$d_0$.[b]

| | |
|---|---|
| CNDO | |
| $\partial\mu_z/\partial S_1 + 0.233$ D Å$^{-1}$ | $\partial\mu_x/\partial S_{6x} + 0.745$ D Å$^{-1}$ |
| $\partial\mu_z/\partial S_2 + 0.724$ | $\partial\mu_x/\partial S_{7x} - 0.186$ |
| $\partial\mu_z/\partial S_3 - 1.083$ | $\partial\mu_x/\partial S_{8x} + 0.468$ |
| $\partial\mu_z/\partial S_4 - 0.016$ | $\partial\mu_x/\partial S_{9x} + 0.729$ |
| $\partial\mu_z/\partial S_4 + 1.004$ | $\partial\mu_x/\partial S_{10x} + 0.366$ |
| *Ab initio*[a] | |
| Gross atomic charges | Dipole moment derivatives[c] |
| $H_1$, $H_2$, $H_3 + 0.163e$ | $\partial\mu_x/\partial S_{9x} + 0.942$ D Å$^{-1}$ |
| $C_4 - 0.220$ | $\partial\mu_x/\partial S_{10x} + 1.013$ |
| $C_5 - 0.040$ | |
| $C_6 - 0.407$ | |
| $H_7 + 0.178$ | |

[a]Reference 22.
[b]Coordinate displacements obtained from the propyne-$d_0$ $A$ matrix have been used and thus the derivatives with respect to the $E$-type symmetry coordinates apply to propyne-$d_0$ only, since the rotational contributions involved in these derivatives are isotope dependent (Ref. 24).
[c]See text.

TABLE IV. Rotational corrections for propyne-$d_0$ and -$d_3$ obtained with heavy isotope reference coordinates.[a]

| | Rotational corrections[b] (D Å$^{-1}$) | | Corrected CNDO derivatives (D Å$^{-1}$) |
|---|---|---|---|
| $S_i$ | $d_0$ | $d_3$ | |
| 6 | +0.0191 | +0.0299 | +0.73 |
| 7 | +0.0196 | +0.0314 | −0.20 |
| 8 | −0.0369 | −0.0610 | +0.49 |
| 9 | +0.0329 | +0.0297 | +0.71 |

[a]Carbon atoms 4 and 5 (see Fig. 7) replaced by heavy isotopes.
[b]Experimental dipole moment, −0.75 D (Ref. 26).

Further, from the *ab initio* calculation on propyne reported by Newton and Lipscomb[22] values for $\partial\mu_x/\partial S_{9x}$ and $\partial\mu_x/\partial S_{10x}$ could be derived. In first order bond moment theory[21] these derivatives are almost completely determined by the equilibrium bond charges. From the gross atomic charges, as given in Table III, values for $\partial\mu_x/\partial S_{9x}$ and $\partial\mu_x/\partial S_{10x}$ have been derived using appropriate coordinate displacements given by the $A$ matrix of propyne-$d_0$. The resulting values, given in Table III, confirm the CNDO calculated signs for these derivatives. Comparison of the predicted propyne-$d_0$ derivatives for the methyl modes with the corresponding observed ones for methylbromide[1] reveals that the calculated propyne values for $\partial\mu_z/\partial S_2$ and $\partial\mu_z/\partial S_4$ have the same sign as the corresponding values for methylbromide, viz., +0.563 and −0.320 D Å$^{-1}$.

Before comparing the $E$-type derivatives of propyne and methylbromide they should both be corrected for the absolute rotational contributions.[23] In this case the heavy isotope displacements[24] are best suited to be used as pure geometrical distortions, since for the asymmetrical stretching and bending modes the heavy isotope displacements turn out to be identical to the geometrical distortions proposed in Ref. 23, while for the rocking mode the heavy isotopes along the $z$-axis result in a pure geometrical mode in which only the hydrogen atoms are displaced. Although the latter mode is not in accordance with the geometrical distortions proposed in Ref. 23, it is the only appropriate mode for the approximate comparison of these two rocking modes. The heavy isotope corrections for the $E$-type methyl modes of propyne are given in Table IV, together with the corrected CNDO dipole moment derivatives. Comparison with the corresponding observed methylbromide values,[1] viz., +0.240, −0.366, and +0.382 D Å$^{-1}$, reveals that all three signs are identical

The derivatives connected with the ethynyl part of propyne may be compared with the corresponding values for ethyne.[2] The derivative with respect to the asymmetrical CH stretching mode of ethyne is recalculated on internal coordinate basis. Using the same position in the axis system as for propyne, $\partial\mu/\partial r_{CH}$ for ethyne has the value +0.937 D Å$^{-1}$. Thus the sign of the corresponding CNDO value for propyne is in accordance



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TABLE V. Eight sets of $\partial\mu/\partial S_i$ values for propyne-$d_0$ and the corresponding signs of the $\partial\mu/\partial Q_i$ values.

| | $\partial\mu/\partial S_i$ values (D Å$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $i$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 1 | +1.105 | +1.096 | +1.075 | +1.067 | +0.901 | +0.893 | +0.871 | +0.864 |
| 2 | +0.620 | +0.573 | +0.597 | +0.549 | +0.651 | +0.607 | +0.618 | +0.575 |
| 3 | +0.670 | +0.572 | +0.311 | +0.222 | −0.870 | −0.969 | −1.228 | −1.315 |
| 4 | −0.028 | −0.125 | +0.105 | +0.001 | −0.044 | −0.142 | +0.089 | −0.016 |
| 5 | +0.150 | +0.014 | −0.406 | −0.527 | +0.504 | +0.365 | −0.052 | −0.171 |
| 6 | +0.399 | +0.400 | +0.400 | +0.398 | +0.399 | +0.400 | +0.400 | +0.398 |
| 7 | −0.405 | −0.404 | −0.405 | −0.405 | −0.405 | −0.404 | −0.404 | −0.405 |
| 8 | +0.209 | +0.213 | +0.212 | +0.207 | +0.210 | +0.213 | +0.212 | +0.207 |
| 9 | +1.108 | +1.107 | +1.107 | +1.109 | +1.108 | +1.106 | +1.107 | +1.110 |
| 10 | +1.130 | +1.127 | +1.127 | +1.132 | +1.229 | +1.127 | +1.128 | +1.132 |
| | $\partial\mu/\partial Q_i$ sign combinations[a] | | | | | | | |
| 3 | + | + | + | + | − | − | − | − |
| 4 | + | − | + | − | + | − | + | − |
| 5 | + | + | − | − | + | + | − | − |
| Res.[b] | 17.8 | 22.6 | 19.6 | 18.1 | 17.7 | 22.4 | 19.3 | 17.9 |

[a]In all cases the signs for $\partial\mu/\partial Q_1$, $\partial\mu/\partial Q_2$, $\partial\mu/\partial Q_6$, $\partial\mu/\partial Q_7$, $\partial\mu/\partial Q_8$, $\partial\mu/\partial Q_9$, and $\partial\mu/\partial Q_{10}$ are +++−+++, respectively. The $\partial\mu/\partial Q_i$ signs for propyne-$d_3$ are the same as those for propyne-$d_0$ except $\partial\mu/\partial Q_8$ which is negative in all cases.

[b]The residuals obtained from the least-squares procedure; see text for definition.

with the observed value for ethyne. The derivative for the active bending mode of ethyne,[2] viz., +1.4918 D Å$^{-1}$, corresponds on internal coordinate basis to a value of +1.0549 D Å$^{-1}$. The corresponding bending mode in propyne becomes comparable to the internal ethyne bending mode by using a heavy isotope reference molecule for propyne (carbon atoms 4 and 5 replaced by heavy isotopes). This leads to a bending mode identical to a pure geometrical distortion in which only the acetylenic hydrogen atom is displaced. The derivative with respect to this reference coordinate corresponds closely to the ethyne bending mode on internal coordinate basis. The corresponding rotational correction or the $S_{9x}$ mode of propyne is given in Table IV, together with the corrected CNDO derivative. As can be seen from the table the CNDO sign for this derivative is confirmed by the sign of the observed value for the corresponding ethyne derivative.

Summarizing the CNDO predicted signs for $\partial\mu_z/\partial S_1$, $\partial\mu_z/\partial S_2$, $\partial\mu_z/\partial S_4$, $\partial\mu_x/\partial S_{6x}$, $\partial\mu_x/\partial S_{7x}$, $\partial\mu_x/\partial S_{8x}$, and $\partial\mu_x/\partial S_{9x}$ have been confirmed by comparison with corresponding modes in methylbromide and acetylene. However, some doubt remains for the signs of $\partial\mu_z/\partial S_4$ and $\partial\mu_x/\partial S_{8x}$, viewing the small predicted value for $\partial\mu_z/\partial S_4$ and the fact that the methyl rocking mode in propyne is not quite comparable to that in methylbromide. Further, the signs for $\partial\mu_x/\partial S_{9x}$ and $\partial\mu_x/\partial S_{10x}$ are confirmed by the *ab initio* results.[22] Thus in the subsequent calculations we have used the following signs for the $\partial\mu/\partial S_i$ quantities: + + +/− +/− +/− + − +/− + +.

With these 16 sign combinations for the $\partial\mu/\partial S_i$ quantieies, we have performed an iterative least-squares fitting procedure[25] using the $\partial\mu/\partial S_i$ values obtained from the individual propyne-$d_0$ intensities (Table I, this work, second column) as starting values. The starting values were fitted to the observed intensities for propyne-$d_0$ and propyne-$d_3$ (Table I, this work, first column) and the intensity ratios mentioned before.[8,9] It appeared to be impossible to obtain a satisfactory fit with a negative value for $\partial\mu_x/\partial S_{8x}$ for any of the corresponding eight possible sign combinations. The possibility of a negative sign for $\partial\mu_x/\partial S_{8x}$ was therefore discarded, leaving only three signs to be fixed. The fitting procedure with a positive sign for $\partial\mu_x/\partial S_{8x}$ resulted in eight different sets of $\partial\mu/\partial S_i$ values which satisfied the constraints on the signs (see Table V). These eight sets only contain five different sign combinations since no fit could be obtained for the + + +, + − −, and − + + sign combinations for $\partial\mu_z/\partial S_3$, $\partial\mu_z/\partial S_4$, and $\partial\mu_z/\partial S_5$, respectively. However, two distinct sets of $\partial\mu/\partial S_i$ values were found for each of the sign combinations + − +, + + −, and − − + for $S_3$, $S_4$, and $S_5$. These eight sets $\partial\mu/\partial S_i$ values correspond to eight different sign combinations of $\partial\mu/\partial Q_i$ values (see Table V). For each of the eight sets the residuals resulting from the least-squares fitting procedure are shown in the table. The residuals ($R$) are defined as

$$R(A_i) = \sum_i [A_i(\text{calc}) - A_i(\text{expt})]^2/\text{err}_i^2 \ , \qquad (4)$$

where $A_i$(expt) include the observed intensities given in Table I (this work, first column) for the $d_0$ and $d_3$ compounds as well as the $A_4/A_7$ ($d_0$),[8] $A_4/A_7$ ($d_3$),[9] and $A_5/A_8$ ($d_3$) (Ref. 9) intensity ratios mentioned before, while the err$_i$ denote the corresponding errors. A criterion for further reduction of the possible sign combinations results from the prediction of the propyne-$d_1$ intensities with each of the eight sets of Table V. The predicted intensities are collected in Table VI together with the experimental data of Kondo and Koga.[11] From the predicted intensities for $A_1$ and $A_3$ it is clear that sets 1 to



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TABLE VI. Predicted and observed intensities for $CH_3CCD$.

| | | Intensities (km/mole) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $A_i$ | $\nu_i$ (cm$^{-1}$)[a] | 1[b] | 2 | 3 | 4 | 5 | 6 | 7 | 8 | obs.[c] |
| $A_1$ | 2616.3 | 15.21 | 15.47 | 16.09 | 16.34 | 33.81 | 34.20 | 35.11 | 35.46 | 32.5±1.2 |
| $A_2$ | 2910 | 15.67 | 14.38 | 15.07 | 13.79 | 15.96 | 14.88 | 14.88 | 13.86 | 15.1±3.2 |
| $A_3$ | 2008.3 | 10.88 | 11.08 | 11.53 | 11.72 | 0.51 | 0.46 | 0.38 | 0.34 | 0.5±0.5 |
| $A_4$ | 1391 | 0.01 | 0.90 | 0.68 | 0.07 | 0.01 | 0.89 | 0.70 | 0.06 | ...[e] |
| $A_5$ | 914[d] | 0.61 | 0.30 | 0.18 | 0.39 | 0.53 | 0.23 | 0.23 | 0.46 | 0.3±0.3 |
| $A_6$ | 2980.2 | 14.55 | 14.57 | 14.57 | 14.52 | 14.55 | 14.58 | 14.57 | 14.51 | 15.9±3.2 |
| $A_7$ | 1450.7 | 18.33 | 18.12 | 18.15 | 18.35 | 18.32 | 18.12 | 18.16 | 18.36 | 17.0±1.4[e] |
| $A_8$ | 1034.8 | 1.18 | 1.24 | 1.24 | 1.13 | 1.19 | 1.24 | 1.23 | 1.12 | 1.0±0.5 |
| $A_9$ | 503.0 | 41.73 | 41.65 | 41.64 | 41.82 | 41.72 | 41.64 | 41.65 | 41.81 | 37.1±2.0 |
| $A_{10}$ | 318 | 20.76 | 20.71 | 20.71 | 20.82 | 20.76 | 20.71 | 20.71 | 20.82 | 21.0±1.2 |
| Res. $(A_i)$[f] | | 646.3 | 656.9 | 681.2 | 691.9 | 8.38 | 9.75 | 12.23 | 13.47 | |

[a]Reference 10.
[b]Numbers refer to the sets of Table V.
[c]Reference 11.
[d]Value taken from Ref. 11.
[e]The sum of $A_4$ and $A_7$ is observed.
[f]The residuals refer to the nine experimental intensity data given in the last column of this table.

4 have to be rejected, also reflected by the large values for the residuals given in Table VI. The residuals for the remaining sets are not very different, although the combined residuals of Tables V and VI are slightly in favor of set 5. It must be kept in mind, however, that the residuals are very sensitive to the arbitrariness in the chosen error limits and thus small differences in the calculated residuals are not very conclusive.

From the analyses of the $\nu_4/\nu_7$ Coriolis interaction in propyne-$d_0$ (Refs. 8 and 11) and the $\nu_4/\nu_7$ and $\nu_5/\nu_8$ Coriolis interactions in propyne-$d_3$ further arguments may be obtained for the selection of the right sign combination. The Coriolis interaction constants obtained from the normal coordinate analysis using the force field of Duncan, McKean, and Nivellini[10] are given in Table VII. The reported signs for the triple products $(\partial\mu_z/\partial Q_i)(\partial\mu_x/\partial Q_j)\zeta_{ij}^y$ determining the intensity perturbation for the above mentioned Coriolis systems are given in the same table. Also the signs for the corresponding $(\partial\mu_z/\partial Q_i)(\partial\mu_x/\partial Q_j)$ products resulting from the remaining sets $\partial\mu/\partial S_i$ values are shown in this table. Inspection of Table VII reveals that set 7 is in full accordance with the Coriolis results, set 5 is in agreement with the $\nu_4/\nu_7$ interactions but in disagreement with the $\nu_5/\nu_8$ interaction, set 8 is only in agreement with the $\nu_5/\nu_8$ interaction, while set 6 is in disagreement with all three interactions. Thus the Coriolis criterion selects set 7 as the more preferable set $\partial\mu/\partial S_i$ values. However, comparison of the sets 5 and 7 with the CNDO calculated $\partial\mu/\partial S_i$ values (see Table III) provides an argument in favor of set 5, viewing the large positive CNDO value for $\partial\mu_z/\partial S_5$, viz., +1.004 D Å$^{-1}$. Although the CNDO predicted $\partial\mu/\partial S_i$ values are known to be not very precise it is hard to believe (but not impossible) that the true value is negative. An argument against set 5 is the very bad prediction of $A_4$ as can be seen from Table VIII. Moreover, the sign of the $\partial\mu_z/\partial S_4$ value of set 5 seems to be in disagreement with the known values for some related molecules as shown in Table XI. The corresponding values for methane, ethane and propane are all positive (provided equivalent positions of the methyl groups in the Cartesian axis system).

In conclusion, viewing the above arguments and the present data, set 7 seems to be the better choice.

TABLE VII. Coriolis interaction constants and signs of the intensity perturbations. The signs of the $(\partial\mu_z/\partial Q_i)(\partial\mu_x/\partial Q_j)$ products for the remaining four sets of $\partial\mu/\partial S_i$ values.

| | | Interacting band systems | | |
|---|---|---|---|---|
| | Set | $\nu_4/\nu_7$ ($d_0$) | $\nu_4/\nu_7$ ($d_3$) | $\nu_5/\nu_8$ ($d_3$) |
| Coriolis interaction constant $\zeta_{ij}^y$ | | −0.565 | −0.499 | +0.246 |
| Sign of the intensity perturbation | | +[a] | + | + |
| Sign of $(\partial\mu_z/\partial Q_i)(\partial\mu_x/\partial Q_j)$ product | 5 | − | − | − |
| | 6 | + | + | − |
| | 7 | − | − | + |
| | 8 | + | + | + |

[a]Duncan *et al.* (Ref. 8) obtain a negative sign for this perturbation. We have adopted the positive sign given by Kondo and Koga (Ref. 11).



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TABLE VIII. Remaining two sets $\partial\mu/\partial S_i$ values and the corresponding calculated intensities for propyne-$d_0$ and propyne-$d_3$.

| | Set 5[a] | | | Set 7[a] | | |
|---|---|---|---|---|---|---|
| | $\partial\mu/\partial S_i$ [b,c] | Calculated intensities | | $\partial\mu/\partial S_i$ [b,c] | Calculated intensities | |
| | $d_0$ | $d_0$ | $d_3$ | $d_0$ | $d_0$ | $d_3$ |
| 1 | +0.901±0.02 | 44.7±1.6 | 44.8±1.6 | +0.871±0.02 | 44.7±1.6 | 44.8±1.6 |
| 2 | +0.651±0.01 | 16.4±0.8 | 0.74±0.19 | +0.618±0.02 | 15.3±0.8 | 0.09±0.19 |
| 3 | −0.870±0.04 | 5.2±0.6 | 12.4±0.7 | −1.228±0.04 | 5.2±0.6 | 12.5±0.7 |
| 4 | −0.044±0.02 | 0.01±0.04 | 0.23±0.14 | +0.089±0.02 | 0.67±0.32 | 0.19±0.13 |
| 5 | +0.504±0.05 | 0.47±0.13 | 0.33±0.10 | −0.052±0.05 | 0.30±0.11 | 0.38±0.11 |
| 6 | +0.399±0.02 | 14.6±1.1 | 8.3±0.6 | +0.400±0.02 | 14.6±1.2 | 8.3±0.7 |
| 7 | −0.405±0.01 | 18.7±0.9 | 9.7±0.5 | −0.404±0.01 | 18.5±0.9 | 9.6±0.5 |
| 8 | +0.210±0.01 | 0.47±0.14 | 1.0±0.2 | +0.212±0.01 | 0.50±0.15 | 0.97±0.19 |
| 9 | +1.108±0.03 | 89.4±6.4 | 87.5±6.3 | +1.107±0.04 | 89.2±6.7 | 87.4±6.6 |
| 10 | +1.129±0.02 | 15.1±0.8 | 12.7±0.6 | +1.128±0.02 | 15.0±0.8 | 12.6±0.7 |

[a]Numbers refer to the sets of Table IV.
[b]$\partial\mu/\partial S_i$ values for propyne-$d_0$; the values for propyne-$d_3$ are obtained from the given values by applying the appropriate rotational corrections.
[c]The stated errors are standard deviations obtained from the least-squares fitting procedure.

## DISCUSSION OF THE RESULTS

The present observed intensities are in pleasing correspondence with the values reported by Kondo and Koga[11] (see Table I). All differences are within the stated error limits. The larger differences occur for $\nu_2$ and $\nu_6$. At one hand this may be due to a difference in the band separation procedure. However, since our sum of $\nu_2$ and $\nu_6$ is larger than that of Kondo and Koga, part of the difference may be due to the integration intervals used. Our integration interval for the $\nu_6/\nu_2$ region includes the weak band at 2760 cm$^{-1}$ while Kondo and Koga only mention the inclusion of $2\nu_7$.

Further, the fact that our band separations are performed with a logarithmic frequency scale while Kondo and Koga have used the linear wavenumber scale may cause small differences in the reported individual band intensities. However, the differences in the measured intensities of free-lying bands ($\nu_1$, $\nu_9$, $\nu_{10}$) emphasize once more that still some problems are involved in the intensity measurements itself. Nevertheless, viewing the $F$-sum[29] results of Table IX the internal consistency of the measured intensities is very good, both for the results of Kondo and Koga and the present data. The differences are never outside the experimental error limits. In some cases no experimental intensity data for the individual modes were available but only the sum of two bands. In such cases, in order to calculate the $F$ sum, the sum intensities have been split up using intensity ratios obtained from the corresponding calculated intensities.

TABLE IX. $F$-sum results for propyne. Units: cm$^3$/mole$^{-1}$.

| | | Kondo and Koga | This work |
|---|---|---|---|
| $A_1$ | $d_0$ | 0.860±0.091 | 0.850±0.058 |
| | $d_3$ | 0.734±0.054 | 0.776±0.040 |
| | $d_1$ | 0.711±0.055 | |
| $E$ | $d_0$ | 37.3±1.4 | 36.5±1.4 |
| | $d_3$ | 37.2±1.7 | 36.4±2.0 |
| | $d_1$ | 36.1±1.4 | |

Since we arrived at the same final sign combination as Kondo and Koga, their $\partial\mu/\partial S_i$ values as shown in Table IX are directly comparable to the present ones. The differences are never outside the error limits. The most serious difference occurs between the $\partial\mu_z/\partial S_1$ values, which directly results from the somewhat different intensities observed for this isolated mode. The differences between the derivatives for $\nu_4$ and $\nu_5$ are not at all significant viewing the large uncertainties for these quantities.

The intensities for propyne-$d_0$, $-d_1$, and $-d_3$ calculated from the final $\partial\mu/\partial S_i$ values of Kondo and Koga are collected in Table X. They compare very well with the intensities calculated from our final set $\partial\mu/\partial S_i$ val-

TABLE X. $\partial\mu/\partial S_i$ values of Kondo and Koga and the resulting calculated intensities for propyne-$d_0$, propyne-$d_1$, and propyne-$d_3$.

| | $\partial\mu/\partial S_i$ (D Å$^{-1}$)[a] | Calculated intensities (km/mole)[b] | | |
|---|---|---|---|---|
| | $d_0$ | $d_0$ | $d_1$ | $d_3$ |
| 1 | +0.824±0.03 | 42.8±2.4 | 33.8±2.2 | 42.8±2.4 |
| 2 | +0.600±0.04 | 15.0±1.8 | 14.7±1.8 | ...[d] |
| 3 | −1.256±0.07 | 5.2±1.2 | 0.4±0.3 | 12.8±1.4[d] |
| 4 | +0.102±0.05 | 0.8±0.8 | ...[c] | 0.2±0.3 |
| 5 | −0.126±0.10 | 0.5±0.2 | 0.4±0.2 | 0.6±0.3 |
| 6 | +0.391±0.02 | 14.6±1.2 | 14.5±1.1 | 8.3±0.7 |
| 7 | −0.401±0.02 | 18.1±1.2 | 18.6±1.3[c] | 9.2±0.6 |
| 8 | +0.226±0.02 | 0.6±0.2 | 1.4±0.3 | 1.0±0.1 |
| 9 | +1.081±0.02 | 85.7±3.0 | 38.9±1.7 | 84.0±3.0 |
| 10 | +1.150±0.03 | 16.2±0.7 | 21.8±0.7 | 13.4±0.6 |

[a]$\partial\mu/\partial S_i$ values pertaining to propyne-$d_0$.
[b]Errors calculated from the errors in the $\partial\mu/\partial S_i$ values as give given by Kondo and Koga (Ref. 11).
[c]Sum of $A_4$ and $A_7$ is given.
[d]Sum of $A_2$ and $A_3$ is given.



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TABLE XI. Final $\partial\mu/\partial S_i$ values for propyne-$d_0$ and corresponding values[a] for a number of related molecules (D Å$^{-1}$).

| | $CH_3CCH$ | $C_2H_2$ [b] | $CH_4$ [c] | $C_2H_6$ [d] | $C_3H_8$ [d] | $CH_3Br$ [e] |
|---|---|---|---|---|---|---|
| 1 | +0.871 | +0.937 | | | | |
| 2 | +0.618 | | +0.372 | +0.736 | +0.746 | +0.563 |
| 3 | −1.228 | 0.0 | | | | |
| 4 | +0.089 | | (+0.375)[f] | +0.356 | +0.045 | (−0.320)[f] |
| 5 | −0.052 | | | | | |
| 6 | +0.400 | | +0.745 | +0.851 | +0.878 | +0.305 |
| 7 | −0.404 | | −0.265 | −0.169 | −0.200 | −0.307 |
| 8 | +0.212 | | +0.265 | +0.130 | +0.126 | +0.282 |
| 9 | +1.107 | +1.055 | | | | |
| 10 | +1.128 | | | | | |

[a]All given values refer to the molecule at the top of each column (thus no rotational corrections are made). All given values are expressed in terms of coordinates similar to those used for propyne.
[b]Reference 2.
[c]Reference 27.
[d]Reference 28.
[e]Reference 1.
[f]Approximate comparable values.

ues (see Tables VII and VIII), once more showing the close correspondence between the results of Kondo and Koga and the present ones. In Table XI a comparison is made between the $\partial\mu/\partial S_i$ values for propyne-$d_0$ and corresponding values for some related molecules.

The ethynyl part of propyne is very much the same as in acetylene as appears from the close correspondence between the mutual $\partial\mu_z/\partial S_1$ and $\partial\mu_x/\partial S_{9x}$ values. The dipole moment derivatives with respect to the methyl modes $S_2$, $S_4$, $S_6$, $S_7$, and $S_8$ compare reasonably well to

TABLE XII. Atomic polar tensors (D Å$^{-1}$) and atomic effective charges ($e$) for propyne and related molecules.

| Ethynyl group | $\mathbf{P}_X^{H7}$ | $\xi_{H7}$ | $\mathbf{P}_X^{C6}$ | $\xi_{C6}$ |
|---|---|---|---|---|
| propyne | $\begin{pmatrix} 0.996 & 0 & 0 \\ 0 & 0.996 & 0 \\ 0 & 0 & 0.871 \end{pmatrix}$ | 0.345 | $\begin{pmatrix} -1.207 & 0 & 0 \\ 0 & -1.207 & 0 \\ 0 & 0 & -2.101 \end{pmatrix}$ | 0.564 |
| acetylene[a] | $\begin{pmatrix} 0.995 & 0 & 0 \\ 0 & 0.995 & 0 \\ 0 & 0 & 0.937 \end{pmatrix}$ | 0.352 | $\begin{pmatrix} -0.995 & 0 & 0 \\ 0 & -0.995 & 0 \\ 0 & 0 & -0.937 \end{pmatrix}$ | 0.352 |
| **Methyl group** | $\mathbf{P}_X^{H1}$ | $\xi_{H1}$ | $\mathbf{P}_X^{C4}$ | $\xi_{C4}$ |
| propyne | $\begin{pmatrix} 0.284 & 0 & -0.128 \\ 0 & 0.467 & 0 \\ -0.358 & 0 & -0.062 \end{pmatrix}$ | 0.139 | $\begin{pmatrix} 0.581 & 0 & 0 \\ 0 & 0.581 & 0 \\ 0 & 0 & 0.241 \end{pmatrix}$ | 0.178 |
| methyl bromide[b] | $\begin{pmatrix} -0.124 & 0 & -0.195 \\ 0 & 0.410 & 0 \\ -0.284 & 0 & -0.319 \end{pmatrix}$ | 0.129 | $\begin{pmatrix} 0.274 & 0 & 0 \\ 0 & 0.274 & 0 \\ 0 & 0 & 2.504 \end{pmatrix}$ | 0.528 |
| ethane[c] | $\begin{pmatrix} -0.591 & 0 & -0.495 \\ 0 & 0.186 & 0 \\ -0.398 & 0 & 0.103 \end{pmatrix}$ | 0.186 | $\begin{pmatrix} 0.608 & 0 & 0 \\ 0 & 0.608 & 0 \\ 0 & 0 & -0.308 \end{pmatrix}$ | 0.190 |
| methane[d] | $\begin{pmatrix} -0.541 & 0 & -0.483 \\ 0 & 0.297 & 0 \\ -0.296 & 0 & 0.192 \end{pmatrix}$ | 0.179 | $\begin{pmatrix} 0.068 & 0 & 0 \\ 0 & 0.068 & 0 \\ 0 & 0 & 0.068 \end{pmatrix}$ | 0.056 |

[a]Calculated from the average $C_2H_2/C_2D_2$ values of Ref. 2.
[b]$C_{3v}$ average values taken from Ref. 1.
[c]Calculated from Ref. 28.
[d]Calculated from Ref. 27.



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the values for methane, ethane and propane. However, the differences make clear that the methyl groups of these molecules by no means may be considered to be identical. Nevertheless, the remarkable difference between the $\partial\mu_z/\partial S_4$ values for ethane and propane is quite surprisingly the more so viewing the close agreement between the remaining derivative values. The derivatives with respect to the internal methyl modes in methyl bromide, viz., $S_2$, $S_6$, and $S_7$ are not very different from the corresponding ones in propyne. However, the negative value for $\partial\mu_z/\partial S_4$ in methyl bromide clearly shows the considerable influence that substituents may have on the values of methyl mode derivatives.

Without any additional assumptions the dipole moment derivatives in terms of symmetry coordinates can be transformed to derivatives with respect to Cartesian displacement coordinates,[30,31] through

$$\mathbf{P}_X = \mathbf{P}_S \mathbf{B} + \mathbf{P}_\rho \beta \ , \tag{5}$$

where B denotes the transformation from the Cartesian to the symmetry coordinates, $\mathbf{S} = \mathbf{BX}$, $\beta$ denotes the transformation from the Cartesian to the Eckart coordinates, $\rho = \beta\mathbf{X}$, and $\mathbf{P}_\rho$ is a $3\times 6$ matrix containing the components of the permanent moment.[24,30]

For an $N$ atomic molecule the $\mathbf{P}_X$ polar tensor can be split up in $N$ atomic polar tensors $\mathbf{P}_X^\alpha$,[30–32] each reflecting the changes in the molecular dipole moment upon the Cartesian displacements of one atom. The atomic polar tensors for propyne and related molecules are collected in Table XII. In the same table also the atomic effective charges $\xi_\alpha$ introduced by King, Mast, and Blanchette[32] and defined by

$$\xi_\alpha = [\mathrm{Tr}(\mathbf{P}_X^\alpha \tilde{\mathbf{P}}_X^\alpha)]^{1/2} \tag{6}$$

are given.

The close correspondence between the $\partial\mu_x/\partial S_{9x}$ values for propyne and acetylene results in almost identical values for the $xx$ and $yy$ elements of the $\mathbf{P}_X^{H7}$ polar tensors, since it can be easily shown that

$$\frac{\partial\mu_x}{\partial x_7} = \frac{\partial\mu_y}{\partial y_7} = \frac{\partial\mu_x/\partial S_{9x}}{r_{CH}} \ . \tag{7}$$

The $zz$ elements of $\mathbf{P}_X^{H7}$ are identical to the $\partial\mu_z/\partial S_1$ values of Table XI. The small difference in the hydrogen effective charge $\xi_{H7}$ results from the small difference between the $zz$ elements and thus from the difference between the $\partial\mu_z/\partial S_1$ values.

The elements of the $\mathbf{P}_X^C$ polar tensor for acetylene have the same magnitude as the elements of the $\mathbf{P}_X^H$ tensor but they have opposite signs. The elements for the $\mathbf{P}_X^C$ tensor of propyne are also negative but with larger magnitude. Clearly, the charge redistribution due to displacements of the C6 carbon atom of propyne differs much from that in acetylene, also reflected by the values for $\partial\mu_z/\partial S_3$ (see Table XI). This leads to strongly different values for $\xi_{C6}$ in propyne and acetylene. Summarizing, the ethynyl groups of propyne and acetylene are very similar as far as the CH bond is concerned, reflected by the pertaining $\partial\mu/\partial S$ values, atomic polar tensors and effective charges. The C≡C bonds are quite different as shown by the values for $\partial\mu_z/\partial S_3$, $\mathbf{P}_X^C$, and $\xi_C$.

The atomic polar tensors for the methyl group are also given in Table XII. The corresponding $\partial\mu/\partial S$ quantities for the methyl group are mixed in the atomic polar tensors. The $xx$ and $zz$ elements of $\mathbf{P}_X^{H1}$ contain contributions from $\partial\mu_x/\partial S_{6x}$, $\partial\mu_x/\partial S_{7x}$, and $\partial\mu_x/\partial S_{8x}$, the $zx$ and $zz$ elements from $\partial\mu_z/\partial S_2$ and $\partial\mu_z/\partial S_4$, while the $yy$ element is completely determined by the value of $\partial\mu_y/\partial S_{7y}$. Although the $\mathbf{P}_X^{H1}$ polar tensors of Table XII are by no means identical there is a rough similarity between the $\mathbf{P}_X^{H1}$ tensors for methane and ethane at one hand and for methylbromide and propyne at the other hand. Also the hydrogen effective charges suggest that the hydrogen atoms in the methyl groups in methane and ethane are rather similar. The same conclusion might be drawn for the hydrogen atoms in the methyl groups of methylbromide and propyne. However, inspection of the $\mathbf{P}_X^{H1}$ polar tensor elements reveals that the extent of correspondence as indicated by the effective charges should be considered with some care. The polar tensors and effective charges for the methyl carbon atoms are very different clearly reflecting the influence of the different substituents to the methyl group.


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