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The difficulty of making bubble-free, strain-free, and crack-free glasses plus the hygroscopic nature of the glass, prevented taking spectroscopic data that were reproducible.

The similarity of the solubility and the color change under irradiation of inorganic iodides and bromides in both the metaphosphates and water, make for a comparison on the similarity of the mode of reaction. However, it is difficult to demonstrate that H and PO₃ or NaO and PO₂ radicals are formed as a result of irradiation in the solid state in the same way as O and OH radicals² are formed in the liquid water state.

It is more likely that the color effect results from electrons ejected from the iodide to form the iodine atom, and the electrons caught in traps to form color centers.³

The assistance of Douglas Wordie and Joe Ross is gratefully acknowledged.

* Deceased, March 2, 1955.

¹ Produced by a Picker x-ray using 200 kev, 10 ma, with a 0.01-in. copper filter.

² A. O. Allen, *J. Phys. Chem.* **52**, 479 (1948).

³ Shelne, Sharp, and Kriner, *J. Chem. Phys.* **19**, 1422 (1951).

Ionization Potential of Propyne*

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THE spectroscopic ionization potential of propyne at 11.30 ev obtained by Price and Walsh¹ from two Rydberg series appears to be too high in comparison to recent electron impact value of 10.48±0.06 ev by Franklin and Field² and 10.3±0.1 ev by Coates and Anderson.³ Very recently Darby and Walsh⁴ have reported that new spectra of propyne support the previous spectroscopic value. In view of this discrepancy we have applied the photo-ionization method⁵ to determine the ionization potential of acetylene, propyne, and 1-butyne using samples² kindly furnished by Dr. F. H. Field.

Figure 1 shows the yield curve of propyne in semilog scale. The yield increases rapidly from an undetectable value at about 1210 Å to 38% at 1196 Å, and from there on it increases gradually to about 80% at 1166 Å. The break in the curve at 10.36±0.01

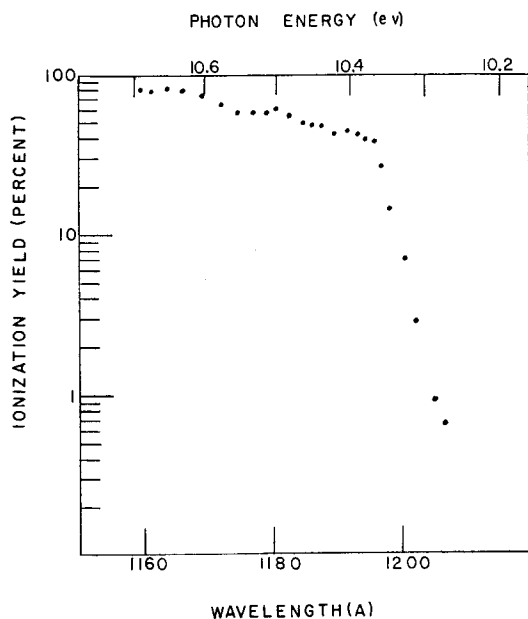


FIG. 1. Ionization yield curve of propyne.

TABLE I. Rydberg series for propyne in cm⁻¹.

n	Series I		Series II	
	ν obs.	ν calc.	ν obs.	ν calc.
2	64 910	64 996	68 140	68 217
3	74 290	74 253	75 500	75 463
4	77 940	77 989	78 620	78 578
5	79 870	79 858	80 160	80 197
6	80 940	80 926	81 170	81 153
7	81 600	81 592	81 730	81 745
8	82 030?	82 036	82 140?	82 150

ev (1196±1 Å) represents⁵ the first ionization potential of propyne.

The total absorption coefficient in the region 1166–1196 Å was found to be about 1800 cm⁻¹. To ascribe both this absorption and the high ionization yield to a small amount of impurity, it would be necessary for this impurity to have an improbable *f*-value.

The absorption spectrum of propyne obtained by a photoelectric method⁶ showed a number of strong diffuse bands in the region 1600–1200 Å but mainly continuous absorption below 1200 Å. Some of these bands can be arranged into two series as shown in Table I and they approximately fit the following equations:

$$\text{Series I } \nu = 83\,580 - \frac{R}{(n+0.43)^2} \quad n=2,3,4,\dots$$

$$\text{Series II } \nu = 83\,600 - \frac{R}{(n+0.67)^2} \quad n=2,3,4,\dots$$

The mean series limit corresponds to an ionization potential of 10.36 which agrees with the photo-ionization measurement. Thus there appear to be Rydberg series other than those reported by Price and Walsh.

The effect of alkyl substitution does not seem to be abnormal in the case of acetylene. Its ionization potential was found to be 11.41±0.01 ev (in agreement with the spectroscopic value⁷) so that there is a lowering of 1.05 ev with methyl substitution. Furthermore, the ionization potential of 1-butyne was found to be 10.18±0.01 ev or 0.18 ev lower than that of propyne.

Thus our results support the electron impact value.

We wish to thank Professor R. S. Mulliken, Dr. F. H. Field, and Professor W. C. Price for their interest in these measurements.

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¹ W. C. Price and A. D. Walsh, *Trans. Faraday Soc.* **41**, 381 (1945).

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³ F. H. Coates and R. C. Anderson, *J. Am. Chem. Soc.* **77**, 895 (1955).

⁴ Reported at the European Molecular Spectroscopy Group Conference, Oxford, July, 1955.

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Hopfield's Emission Bands of O₂ in the Region 1900–2350 Å

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BY using a condensed discharge through a mixture of (He+O₂), Hopfield¹ found five emission bands in the region 2032–2218 Å, and he suggested that they were due to the normal oxygen molecule. In his book, Herzberg² suggested that the lower state of the bands is possibly the H-state.³

We repeated Hopfield's experiment using two vacuum spectrographs, one a one-meter normal incidence type at MIT, and the other the spectrograph described in a previous paper.⁴ Besides the five bands observed by Hopfield, we found several additional

TABLE I.

v', v''	λ (in vac.)	ν (cm ⁻¹)	$\Delta\nu$	$\Delta_2\nu$	I^a	Hopfield's λ (in vac.)
0 0	1940.3	51 538			0.02	
0 1	1985.0	50 378	1160		0.17	
0 2	2030.5	49 249	1129	31	0.50	2031.5
0 3	2076.6	48 156	1093	36	0.90	2077.3
0 4	2123.4	47 094	1062	31	0.66	2123.8
0 5	2170.6	46 070	1024	38	0.46	2170.7
0 6	2218.3	45 080	990	34	0.37	2218.2
0 7	2266.4	44 123	957	33	0.25	
0 8	2314.8	43 200	923	34	0.17	
0 9	2363.1	42 317	883	40	0.15	

^a Densitometer reading in logarithmic scale.

bands belonging to the same progression, two of which appeared on the shorter wavelength side. The measured data are shown in Table I together with Hopfield's data. As one can see in the table, the present data agree well with Hopfield's except for his two shortest λ 's at 2031.5 and 2077.3 Å. Hopfield mentioned that the band at 2077.3 Å was masked by second-order atomic lines, while in our case we were not troubled by the superposition problem. As for the 2031.5 Å band, we are unable to explain the disagreement between the two measurements.

All the bands have a single head shading toward the shorter wavelengths and no Q -branch was observed. They were excited only in a condensed discharge of (He+O₂). In general, they are weaker than the second negative bands of O₂⁺, $A^2\Pi_u-X^2\Pi_g$, which appear in the same region. However, by reducing the partial pressure of O₂ to less than about five percent of the total pressure (1~20 mm Hg), the Hopfield bands can be obtained without any serious interference caused by the superposition of the O₂⁺ bands.

The appearance of their fine structure seems to indicate that the transition is $\Sigma-\Sigma$. Therefore, the lower state of the bands is probably not the H-state² because, according to Price and Collins,³ the upper state of the H-bands in absorption is very probably a $^3\Pi$. The $\Delta G:v$ curve of the lower state shows a fairly good straight line which is shown in Fig. 1. If we assume that the shortest band

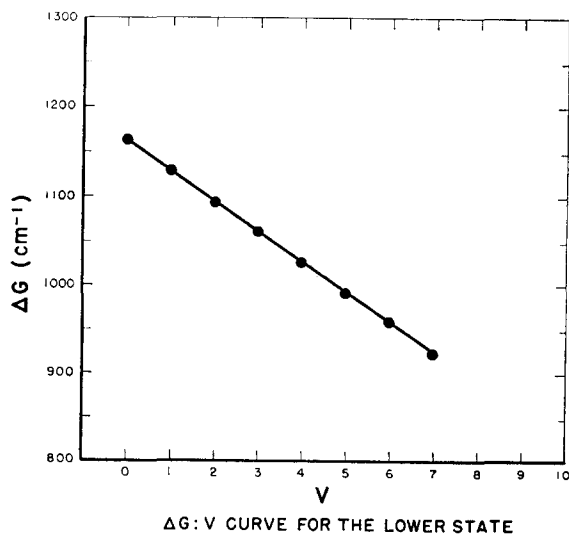


FIG. 1.

at 1940.3 Å is the (0,0) band, the vibrational constants of the lower state can be calculated as: $\omega_0''=1180$ cm⁻¹, and $\omega_0''x_0''=17.2$ cm⁻¹.

In absorption, Tanaka and Takamine⁵ picked up four new progressions in the vacuum region. One of them, progression II, shows a good agreement in the $\Delta\nu$ values with those of the present progression.⁶ Furthermore, the structure of the absorption bands appears to be simpler than that of the H-bands. Accordingly, the upper state of the progression II is possibly the lower state of the present bands. If the suggestion is accepted, the excitation energy of the upper state of the present bands turns out to be 20.58 eV, which is very close to the energy, 20.61 eV, of the metastable helium atom, $1s2s^1S_0$. It is interesting to note that when argon was used instead of helium, these bands could not be observed at all. This would suggest that the excitation is due to collisions of the second kind with the metastable helium atom or the helium molecule in a metastable state.⁷ The proposed excitation energy, 20.58 eV, of the upper state is also close to one of the ionization potentials, 20.21 eV, of O₂,⁸ and consequently, there may result preionization in the upper state.

Part of the present work has been carried out in the Spectroscopy Laboratory at Massachusetts Institute of Technology, and the authors wish to express their thanks to Professor G. R. Harrison and Professor R. C. Lord for the use of one of their spectrographs.

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Infrared Spectra of T₂O, THO, and TDO†

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WE have studied the vapor phase infrared spectra of T₂O, THO, and TDO in the region 700 to 7000 cm⁻¹ with resolutions up to 1 cm⁻¹. The spectrometer used was a Perkin-Elmer Model 12-B single beam instrument, modified for double-pass operation, and equipped with NaCl and LiF prisms. The gas cell, fitted with AgCl windows, had a path length of approximately 10 cm and was heated to 80°C to allow the observation of spectra at pressures up to 225 mm. Quantities of T₂O were synthesized by oxidizing tritium gas of greater than 95% purity with heated CuO. The THO and TDO observed were produced in low concentration in the T₂O by exchange. The experimental data are presented in Table I.

Although the two relatively weak bands corresponding to ν_1 for THO and TDO were observed in the region 2200 to 2300 cm⁻¹, they could not be extricated with the available resolution from each other and from the stronger band ν_2 of T₂O. The low concentrations of THO and TDO limited the number of bands of these molecules which could be measured.

All of the tabulated bands, with the exception of the ν_2 fundamentals, exhibited Q -branches which were displaced to the low-frequency side of the band centers. Since it was not possible, with the resolution of our instrument, to obtain the band-center frequencies by rotational analysis, they were estimated visually. However, a simplified analysis, involving only levels of low J was applied to ν_2 of T₂O and gave a frequency within 1 cm⁻¹ of the visually estimated center.

To obtain the zero-order frequencies, ω_i from the experimental data, anharmonicity corrections were applied using the x_{ij} values obtained by Libby.¹ In the last two columns of Table I, the