HIGH RESOLUTION RAMAN SPECTROSCOPY AND THE STRUCTURE OF SIMPLE MOLECULES

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THE numerous investigations of the vibrational Raman spectra of molecules have made significant contributions to the development of our present ideas of molecular structures. From the frequencies, relative intensities and depolarization factors of vibrational Raman bands, valuable data on molecular symmetry, force constants and thermodynamic quantities have been obtained for a vast number of simple molecules. Usually, these data have been obtained from the Raman spectra of liquids, photographed at low dispersion.

Additional and much more precise information about the structure of molecules can be obtained from the investigation of the rotational Raman spectra of gases. When the rotational fine structure is resolved, it can lead to the reevaluation of moments of inertia and hence internuclear distances and valence angles.

Immediately after the discovery of the Raman effect in 1928, observations of the rotational Raman spectra of diatomic and simple polyatomic molecules were reported by McLennan and McLeod, Rasetti, Wood, Dickinson, Dillon and Rasetti, Amaldi and Placzek, Lewis and Houston, Bhagavantam, and Teal and McWood. The results were of great significance for the development of the theory of the new effect as well as for a better understanding of molecular physics. In addition, these early experiments and the theory of Placzek and Teller clearly outlined the advantages and potentialities of rotational Raman spectroscopy for the determination of molecular structures. Nevertheless, until recently this experimental technique has not been used for structural determinations to any great extent.

Experimentally, the investigation of the Raman spectra of gases has been a difficult problem because of the low intensity of Raman scattering. The difficulties are further increased if the Raman spectra are to be photographed with sufficient resolution to separate the rotational lines. On the one hand, low gas pressures must be used to prevent excessive line broadening, and this of course reduces the amount of scattered light. On the other hand, it is desirable to use spectrographs of high resolving power, up to 100,000 but unfortunately these are usually of low light-gathering power. Therefore a light source of very high intensity must be used to excite the Raman spectra and the scattered light must be collected and used with the utmost efficiency.

Recent improvements in apparatus have helped to overcome these difficulties to some degree so that Raman spectra of certain gases can now be photographed at high resolution with reasonably short exposure times. The major developments in apparatus include:

(a) a low pressure mercury arc operated at 20 to 30 amperes which emits sharp lines of high intensity with negligible continuum (Welsh, Crawford, Thomas and Love[1] and Stoicheff[2]).

(b) a system of concave mirrors of high reflectance in a long Raman tube which can superimpose about 40 cones of scattered light and therefore increase the efficiency of the Raman tube by almost this factor (Welsh, Cumming and Stansbury[3]). This high increase in efficiency over the conventional single-cone Raman tube arises in the following way. When the gas in the tube is irradiated, the molecules scatter light in all directions. Ordinarily, only a single cone of light enters the spectrograph, but of course there are an infinite number of such cones of light within the tube, any one of which would serve equally well. If some of these cones could be superimposed somehow, an enormous increase in observed light intensity would result. The mirror system achieves this to a limited extent and as already mentioned a factor of about 40 has been gained in this way.

An apparatus built in this laboratory is shown in Fig. 1. The multi-cone Raman tube is illuminated along a length of one metre by four mercury lamps and is completely enclosed in a reflector coated with magnesium oxide. A detailed description of this apparatus is given in reference 2.

With this apparatus it has been possible to photograph the pure rotation spectra and the rotation vibration spectra of several gases, with a 21 ft. grating spectrograph. The spectra are excited by the Hg 4358 line. At this wavelength, the reciprocal linear dispersion in the

second order of the grating is $6 \cdot 7$ cm.$^{-1}$/mm. Gas pressures of 15 cm. to 35 cm. Hg are ordinarily used and exposure times vary from 1 to 20 hours. The slit width used is $0 \cdot 2$ cm.$^{-1}$, equal to the width of the exciting line, and the closest spacing of rotational lines to be resolved to date is $0 \cdot 37$ cm.$^{-1}$ The rotation vibration spectra are considerably fainter than the pure rotation spectra and therefore longer exposure times and higher gas pressures are necessary. The exposure times can be reduced by a factor of about 15, by placing a cylindri-

higher light-gathering power than the 21 ft. grating. With this apparatus, Professor Welsh and his co-workers have obtained some extremely interesting and valuable results on molecular structures. They have shown that high resolution studies of the rotational structure in vibrational Raman bands are now practical, and have recently carried out such investigations with a Raman tube 20 ft. long.

Precise information about the geometrical structure of diatomic and simple polyatomic molecules can also be obtained by a study of
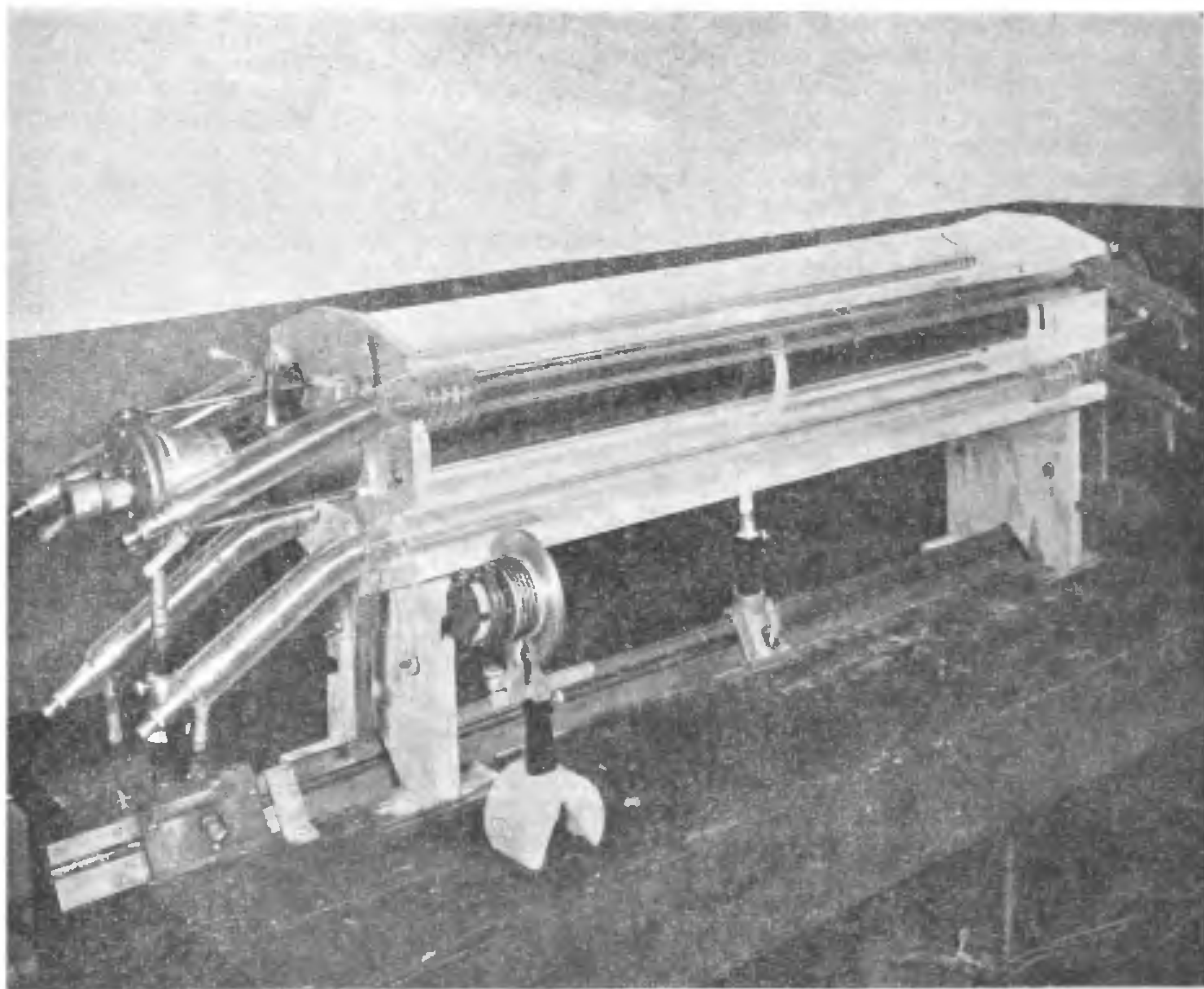

FIG. 1. An apparatus for high resolution Raman spectroscopy of gases. The rear mirrors are shown in the foreground. Electrical leads, water-cooling connections and part of the reflector housing have been removed.

cal lens in the spectrograph in front of the photographic plate.

A similar apparatus built at the University of Toronto[4] has been used primarily for the investigation of rotation vibration spectra. The Raman tube is illuminated along 150 cm., gas pressures up to four atmospheres are sometimes used, together with a prism spectrograph of

the rotational structure observed in their microwave, infrared and electronic spectra. While much valuable information has been obtained from these spectra there are inherent and experimental limitations in such investigations some of which can be overcome by a study of the rotational structure in Raman spectra. These limitations have to some extent dictated

the problems which have been investigated by Raman spectroscopy. It may be worthwhile to discuss briefly some of these limitations, and to show how they may be overcome by investigations of Raman spectra.

All molecules with the exception of those with cubic symmetry have a pure rotational Raman spectrum. In contrast, only polar molecules exhibit rotation spectra in the microwave and far-infrared regions. As is well known, the same information about the ground state can be obtained from rotation-vibrational infrared spectra, but the vibration bands may be perturbed or overlapped by neighbouring bands and sometimes the rotational numbering cannot be ascertained. The pure rotation spectra are unperturbed, simple in appearance and usually easy to analyse. In the Raman effect, the exciting line defines the centre of the rotation spectrum and the rotational numbering can be determined unambiguously. Also, a check on the measurements is provided by a comparison of the Stokes and anti-Stokes lines.

For molecules with elements of symmetry the vibrational Raman spectra are complementary to the vibrational infrared spectra. The rotation-vibration spectra allow one to determine the effect of vibration on the rotational constants. Therefore the Raman and infrared vibration spectra must be investigated at high resolution if one is to eliminate the effect of zero point vibration and to determine the equilibrium structure. In addition, the rotational structure of certain vibrational bands is different in the Raman and infrared spectra. More rotational branches can appear in the Raman band and therefore valuable information can be obtained, which is not available from the infrared spectrum alone. These and other advantages will be illustrated by examples below.

For diatomic and linear polyatomic molecules the rotational energy levels of the ground state are given by the formula

$$\frac{E_r}{hc} = F_0(J) = B_0 J(J+1) - D_0 J^2(J+1)^2 + \ldots, \quad (1)$$

where E_r is the rotational energy in ergs, $F_0(J)$ is the rotational term value in cm.$^{-1}$ and $B_0 = h/(8\pi^2 c I_0)$.

Here B_0 is the rotational constant for the lowest vibrational level and is inversely proportional to the moment of inertia, I_0, for this level. J is the rotational quantum number which represents the total angular momentum of the molecule in units $h/2\pi$. The constant D_0 represents the influence of centrifugal distor-

tion and is very small compared to B_0. For a vibrating molecule B_0 is replaced by B_v where

$$B_v = B_e - \sum_i a_i \left(v_i + \tfrac{1}{2}\right)$$

Here B_e is the rotational constant for the equilibrium position and the a_i are small constants which determine the dependence of B on the different vibrations.

The occurrence of a pure rotational Raman spectrum for linear molecules (non-polar as well as polar), is due to the fact that the polarizability in a fixed direction changes during a rotation of the molecule about an axis perpendicular to its internuclear axis. The selection rules for Raman transitions are $\triangle J = 0, 2$. The rule $\triangle J = 0$ gives the unshifted Rayleigh line which defines the centre of the rotation spectrum and $\triangle J = 2$ gives the Stokes and anti-Stokes rotational lines known as S branches. The displacements of the rotational lines (in units cm.$^{-1}$) from the Rayleigh line are given by the equation

$$|\triangle \nu| = 4 B_0 \left(J + \frac{3}{2}\right) - 8 D_0 \left(J + \frac{3}{2}\right)^3 \quad (2)$$

Therefore we obtain a series of very nearly equidistant lines on either side of the Rayleigh line with the spacing of successive lines being $4 B_0$. The J numbering of the lines is unambiguously obtained from the quotient of the displacement of a given line and the spacing $4 B_0$. Precise values of the constants in equation (2) are then obtained graphically, by plotting $|\triangle \nu|/(J + 3/2)$ against $(J + 3/2)^2$. The intercept gives $4 B_0$ and the slope $8 D_0$.

In Fig. 2, some examples of pure rotational Raman spectra are shown, photographed with the N.R.C. 21 ft. grating. It can be seen that the lines are sharp and well-resolved and therefore accurate measurements can be made. Almost as many anti-Stokes lines are observed as Stokes lines, contrary to vibrational Raman spectra where usually only Stokes lines are observed. This is readily explained by the large number of molecules which are thermally excited into the various rotational levels at room temperature whereas only the lowest vibrational levels (< 500 cm.$^{-1}$) are populated to any appreciable extent.

Values of rotational constants B_0, moments of inertia I_0, and internuclear distances r_0, obtained for various molecules by Raman spectroscopy are collected in Table I.

The most accurate values of the constants for the ground states of H_2 and N_2 are obtained from their Raman spectra. Indeed it is only a

few months ago that the electronic spectrum of N_2 in the vacuum ultraviolet has been photographed with sufficient resolution to determine the molecular constants with an accuracy approaching that of the Raman-effect values. The difficulty has been one of limited resolution and a lack of reliable wavelength standards in the vacuum ultraviolet region : in con-

trast the Raman spectra are photographed in a very favourable wavelength region. The Raman spectra of H_2, HD and D_2[5] have provided precise values of ω_1 and B_0, as well as of the smaller yet significant constants D_0 and H_0 [the coefficient of the term $J^3(J+1)^3$ in equation (1)]. In addition, the Raman results for the $v = 0$ and 1 levels of H_2 and HD were com-
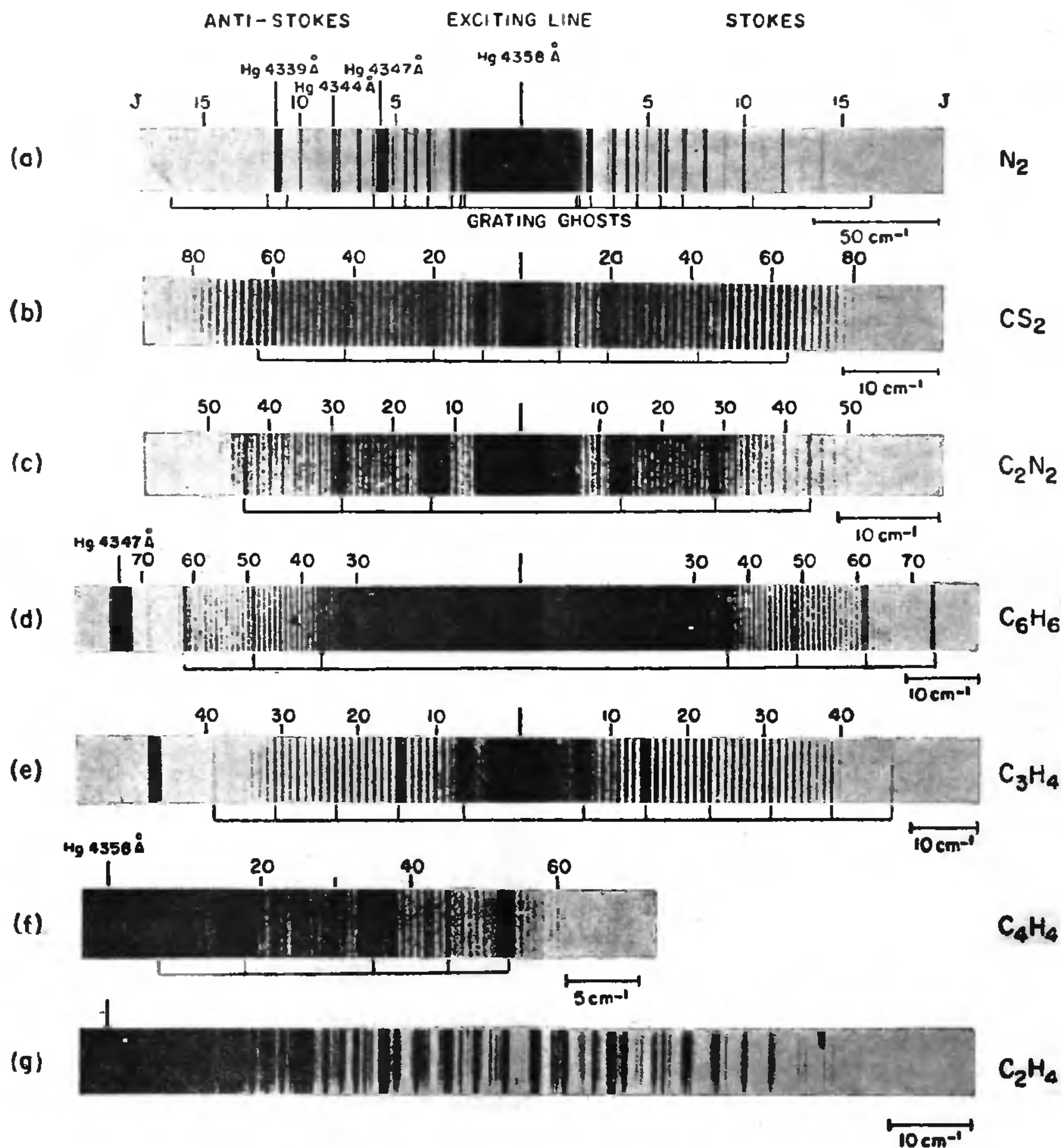

FIG. 2. Pure rotational Raman spectra photographed with a 21 ft. grating. (*a*) spectrum of N_2, (*b, c*) spectra of the linear molecules carbon disulphide and cyanogen, (*d, e*) spectra of the symmetric-top molecules, benzene and allene, (*f, g*) spectra (Stokes branches) of the slightly asymmetric-top molecules butatriene and ethylene.

TABLE I

Rotational constants, moments of inertia, and internuclear distances of molecules obtained from rotational Raman spectra

Molecule		B_0 (cm^{-1})	I_0 (10^{-40} g. cm.^{2})	r_0 (10^{-8} cm.)
Hydrogen	H_2	59.339_2	0.47168	0.75135
	HD	44.667_8	0.62660	0.74973
	D_2	29.910_5	0.93576	0.74820
Fluorine	F_2	0.8828	31.70_5	1.418
Nitrogen	N_2	1.9897_8	14.067	1.1000_6
Carbon Disulphide	CS_2	0.10910	256.54	1.5545
Acetylene	C_2H_2	1.1769_2	23.782	$r(C\equiv C) = 1.207$
Cyanogen	C_2N_2	0.1575_2	177.69	$r(C-C) = 1.380$
Ethylene	C_2H_4	1.008_5	27.75_3	$r(C=C) = 1.344$
	C_3H_4	0.2965_3	94.389	
Allene	$C_3H_2D_2$	0.2619_0	106.88_5	$r(C=C) = 1.309$
	C_3D_4	0.2323_0	120.48_7	$r(C-H) = 1.07\pm.01$
Diacetylene	C_4H_2	0.1468_9	190.54	$r(C-C) = 1.376$
	C_4D_2	0.1276_7	219.40	$r(C-H) = 1.043$
Butatriene	C_4H_4	0.1314_1	210.13	$r(C=C) = 1.284$
Dimethylacetylene	C_4H_6	0.1122	249.4_6	
Butadiene-1, 3 (trans)	C_4H_6	0.1413	198.15	
	C_4D_6	0.11_55	242.33	
Butene-2 (trans)	C_4H_8	0.1206	232.08	
Benzene	C_6H_6	0.1896_0	147.59	$r(C-C) = 1.397$
	$C_6H_3D_3$	0.1716_5	163.06	$r(C-H) = 1.084$
	C_6D_6	0.1568_1	178.45	
s-Triazine	$C_3N_3H_3$	0.2146_0	130.42	$r(C-N) = 1.338$
	$C_3N_3D_3$	0.1935_8	144.59	

bined with Herzberg's data for higher vibrational levels in order to determine a set of equilibrium constants for the ground electronic states of these molecules. It was possible to apply various small corrections for the coupling of electronic and nuclear motions and hence to check the isotopic rules and to determine precisely the interproton distance in the hydrogen molecule.

The rotational Raman spectrum of F_2[6] is of importance since the only known electronic spectrum involving the ground state is continuous and gives no information on the vibrational and rotational constants. Although the Raman spectrum was photographed at low dispersion, a fairly reliable value of the internuclear distance was obtained. In addition the 3 : 1 intensity alternation for odd : even J showed that the F^{19} nuclei obey Fermi statistics and confirmed their spin of 1/2.

The rotation spectra of CS_2, C_2H_2, C_2N_2 and C_4H_2 have led to values of rotational constants and internuclear distances, which are as precise or better than those obtained from infrared or electronic spectra. In the spectrum of CS_2 (Fig. 2 b) only lines of even J appear since the spin of the S^{32} nuclei is zero. Similarly the alternations of intensity observed in the

other spectra are in agreement with the linear symmetric structures of these molecules and with the known spin values and statistics of the nuclei.

For symmetric top molecules the rotational energy levels of a given vibrational level follow the formula

$$F_v(J, K) = B_vJ(J + 1) + (A_v - B_v)K^2$$

where A_v and B_v, apart from a constant, are the reciprocals of the moments of inertia I_a about the top axis and I_b about an axis perpendicular to the top axis. (Centrifugal distortion terms have been omitted.) The quantum number J represents the total angular momentum and K represents the component of J along the figure axis. The Raman selection rules for rotational transitions are $\Delta K = 0$: $\Delta J = 1, 2$. It is readily seen that the lines of the S branch ($\Delta J = 2$, $\Delta K = 0$) are given by the same formula as for linear molecules, and lines of the R branch ($\Delta J = 1$, $\Delta K = 0$) have half the spacing of the S lines and therefore extend only half as far from the exciting line. The rule $\Delta K = 0$ gives rise to a simple appearance of the spectrum although the spectrum really consists of a superposition of several branches, one for each K value. (The exactness of coincidence of the lines depends

on the smallness of the centrifugal distortion terms.) Also, the rule $\triangle K = 0$ accounts for the fact that the displacements of the rotational lines are only dependent on the constant B_0 and not on A_0, that is only one moment of inertia can be determined from the spectrum.

One of the most interesting symmetric-top rotation spectra which has been studied is that of benzene shown in Fig. 2 d. A series of well-resolved lines is observed on each side of the exciting line; these are the S branches with a line spacing of 0·75 cm.$^{-1}$ Close to the exciting line there is a dense continuum partly due to overexposure of the exciting line and to grating ghosts, but mainly due to the R branch lines which are not resolved. The spectra of C_6H_6 and C_6D_6[7] were photographed and analysed, and as a check the spectrum of symmetric $C_6H_3D_3$ was investigated (see Table I). A measurement of these spectra together with the assumption that benzene is planar and hexagonal gave the internuclear distances $r_0(C-C) = 1·397 \pm 0·001$ Å and $r_0(C-H) = 1·084 \pm 0·005$ Å.

At the time of the first announcement of these results, Cox and Smith[8] using modern X-ray methods obtained a value of $1·378 \pm 0·003$ Å for the C-C distance in crystalline benzene at $-3°$ C. Their value differed by 0·02 Å from the Raman-effect value for the free molecule and represented a significant discrepancy. This led to a re-examination of the X-ray data and to the subsequent discovery that the thermal oscillations in the plane of the molecule are markedly anisotropic. Angular oscillations of the whole molecule, about its six-fold axis, with r.m.s. amplitudes as large as 8° were found. As a consequence of such motions the maxima of the time-averaged electron distributions for the carbon atoms appear to be closer to the centre of rotation and hence result in a shorter C-C distance. This correction amounts to about 0·015 Å for the C-C distance which brings the X-ray value to 1·392 Å,[9] very close to the spectroscopic value.

Another molecule for which the effects of such angular motions have led to a discrepancy of 0·02 Å between the Raman-effect and X-ray values of internuclear distances[10] is symmetrical triazine ($C_3H_3N_3$). Corrections of this magnitude may well be significant in other accurate structure determinations.

A recent investigation of infrared bands of allene ($H_2C = C = CH_2$) led to a value of 1·30 Å for the length of the $C = C$ bond, which is significantly shorter than the $C = C$ bond in ethylene (1·344 Å). Since this result is of considerable importance for valence theory an investigation of the rotational Raman spectrum was undertaken and spectra of C_3H_4 (Fig. 2 e) C_3HD_4 and $C_3H_2D_2$ were photographed.[11] Slightly different values of the constants were obtained. Complications in the infrared spectra did not permit clear resolution of the lines and resulted in incorrect rotational numbering. However, the result that the $C = C$ bond length in allene is shorter than that in ethylene was confirmed, the length of the allene bond being $1·309 \pm 0·001$ Å. The Raman data are also consistent with the values $r(C-H) = 1·07 \pm 0·01$ Å and $\angle HCH = 117 \pm 1°$.

One of the most closely-spaced rotation spectra so far resolved by the Raman method is that of dimethylacetylene ($H_3C-C \equiv C-CH_3$). The line spacing is 0·45 cm.$^{-1}$ and leads to the value of the large moment of inertia given in Table I.[12] This single result is of course inadequate for finding the dimensions of this molecule, but when the dimensions of the related molecule methylacetylene ($H_3C-C \equiv CH$) are taken over, $r(C-C) = 1·460$ Å $r(C \equiv C) = 1·207$ Å and $r(C-H) = 1·097$ Å, it can be shown that the calculated moment of inertia is smaller than the experimental value. This would suggest that at least one of the bond lengths is slightly larger than the value found in methylacetylene.

The rotation spectra of several slightly asymmetric top molecules have been investigated including trans 2-butene, 1,3-butadiene, butatriene and ethylene. In appearance, all these spectra (except that of ethylene) resemble those of symmetric tops and indeed this is to be expected since K remains a good quantum number and the selection rules for symmetric tops ($\triangle K = 0$: $\triangle J = 1$, 2) still hold approximately. Therefore the analyses of these spectra can be carried out according to equation (2), but instead of the rotational constant B_0 one obtains $\frac{1}{2}(B_0 + C_0)$. Again, as for symmetric tops, only the one constant is obtained and the lack of other data prevents the determination of the geometrical structures.

The present results for trans 2-butene ($H_3C-CH = CH-CH_3$) are consistent with the following dimensions: $r(C = C) = 1·344$ Å $r(C-C) = 1·500$ Å and $\angle (C = C-C) = 126°$. The observation of a resolved rotation spectrum for 1,3-butadiene ($H_2C = CH - CH = CH_2$) shows that the trans form is the more stable configuration at room temperature: the cis form would give unresolved rotational bands. The results obtained for the normal as well as fully deuterated molecules are in agreement with the dimensions $r(C = C) =$
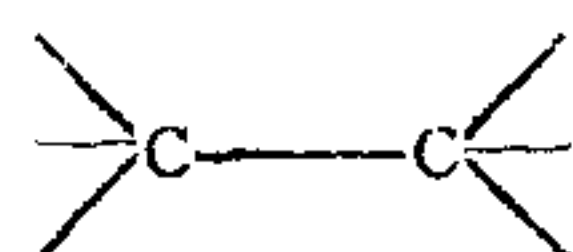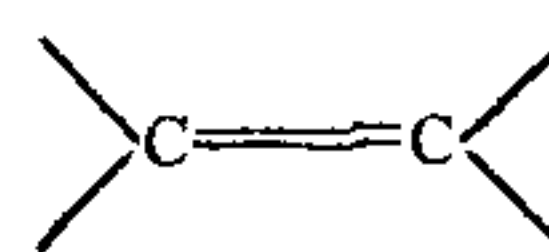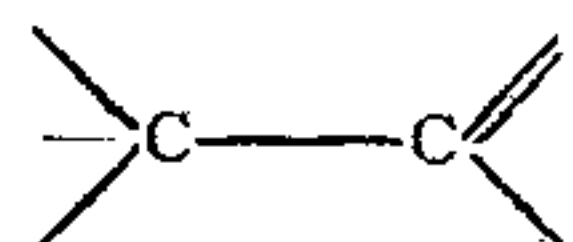
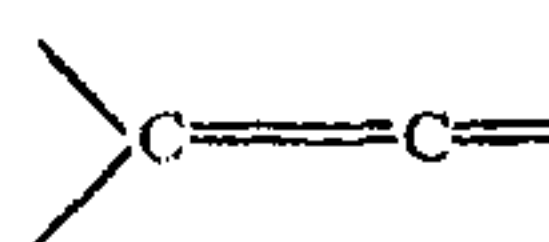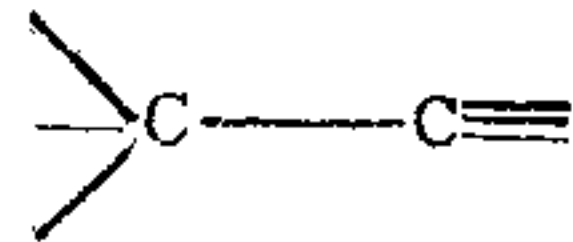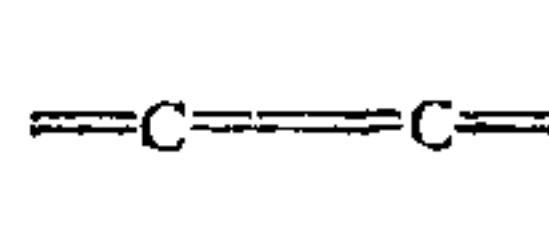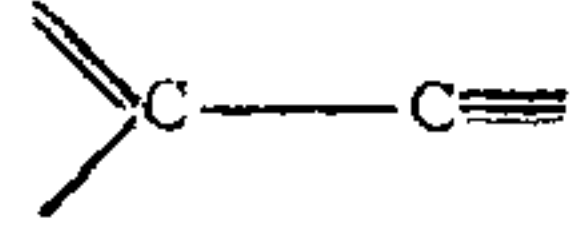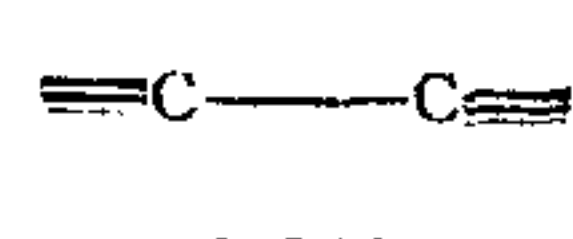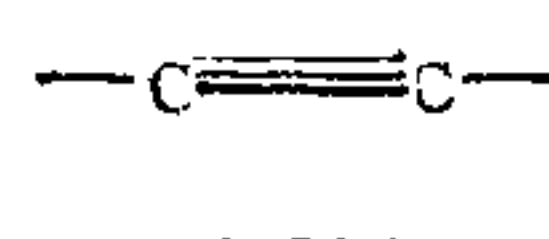1·344 Å r(C-C) = 1·465 Å and $\angle$ (C = C-C) = 123°.

Butatriene (H$_2$C = C = C = CH$_2$) is of interest because the central C = C bond has a different environment to the C = C bonds in ethylene or allene. On the basis of the Raman data[13] and assumed dimensions for the C = CH$_2$ and groups (same dimensions as in allene) a length of 1·284 Å was obtained for the central C = C bond of butatriene. This value is in good agreement with the length found by electron diffraction in carbon suboxide (O = C = C = C = O) where the C = C bonds are similarly adjacent to double bonds, but an independent determination of the central C = C bond in butatriene is desirable.

Only for ethylene does the appearance of the spectrum deviate markedly from the simple rotational structure observed for symmetric top molecules. The ethylene molecule (H$_2$C = CH$_2$) is favourable in this respect since it is relatively light and the main series of lines (R and S branches) therefore have a larger spacing than in the spectra discussed earlier. In addition to the R and S lines ($\triangle$K = 0 : $\triangle$J = 1, 2) which can be interpreted on the symmetric top approximation, a series of lines with smaller spacings than the S lines was observed (Romanko, Feldman, Stansbury and McKellar[14]). It was possible to explain this additional series on the basis of the asymmetric-top theory and to determine a value for the rotational constant C$_0$ = 0·8289 cm.$^{-1}$. As before, the R and S branches were used to evaluate ½(B$_0$ + C$_0$). While an improvement in these values may be possible from the spectrum recently photographed with the 21 ft. grating showing much finer detail (Fig. 2 g), it should be noted that the earlier Raman investigation[14] was the first time that evidence of deviation from the symmetric top structure of ethylene has been obtained from its spectrum, and the results have stimulated a re-examination of the infrared spectrum of ethylene at high-resolution.

The values of carbon-carbon distances obtained from rotational Raman spectra confirm and extend the data obtained by microwave and infrared spectra, and by recent accurate X-ray and electron diffraction investigations of similar molecules. From a compilation of accurate data it has been found[15] that the lengths of carbon-carbon single bonds are dependent on the type of adjacent bonds. A similar dependence is also proposed for carbon-carbon double bonds although not as many accurate data are avail·

able as for the single bonds. A summary of bond lengths (in Å) is given here :

>C——C< 1·544	>C═══C< 1·344
—>C——C< 1·500	>C═══C═ 1·309
—>C——C≡ 1·460	═C═══C═ 1·284
>C——C≡ 1·425	Benzene ring 1·397
═C——C≡ 1·380	—C═══C— 1·207

The above values seem to be surprisingly independent (within ± 0·005 Å) of whether C, H, N, O or S atoms are adjacent to the carbons, and can therefore be used with some assurance in predicting the structure of molecules with these atoms, in the gas phase.

In spite of the difficulties already mentioned in photographing rotation-vibrational Raman bands at high resolution the spectra of C$_2$H$_2$,[16] C$_2$D$_2$,[17] C$_2$H$_4$,[18] C$_2$H$_6$,[19] C$_3$H$_6$,[20] CO$_2$, CS$_2$,[21] CH$_4$[22,23] and NH$_3$[24] have been investigated. Considerable detail has been observed in each spectrum including extensive rotational structure for many of the bands. In a general way, each investigation has yielded new and worthwhile results, in some instances even when no rotational structure was observed.

Although no rotational structure was resolved in the spectrum of cyclopropane, C$_3$H$_6$, the intensity contours of the bands were of great value in making vibrational assignments. In fact the intensity contours of Raman bands of gases are probably better criteria for such assignments than the frequently used depolarization factors. Another example is the spectrum of carbon disulphide CS$_2$ where the sharp Q branches of the Fermi diad ν_1, 2ν_2 were observed as well as those of nine "hot" bands. These data have led to an evaluation of the effects of Fermi resonance and to the determination of a set of vibrational and anharmonic constants for CS$_2$.

For those bands where rotational structure was observed, the vibrational assignments were

unambiguous and the analyses gave band origins and rotational constants. For some bands, particularly in methane and ethane, the analyses also gave values of the Coriolis coupling constants.

The investigation of the ethane spectrum, by Romanko, Feldman and Welsh[19] appears to have solved the long outstanding problem of the equilibrium configuration of ethane. The problem is to determine whether ethane has the eclipsed configuration (point group D_{3h}) or the staggered configuration (point group D_{3d}). An unequivocal decision can be made if the rotational structure in the Raman spectrum of any one of the doubly degenerate bands ν_{10}, ν_{11} or ν_{12} is resolved: For the eclipsed model the selection rules for the quantum number K are $\Delta K = \pm 1$, while for the staggered model $\Delta K = \pm 1$, ± 2. The band ν_{12} has not been observed, and ν_{11} has complications due to Coriolis interactions. However, the band ν_{10} consists of a series of widely spaced lines which are definitely shown to be due to transitions $\Delta K = \pm 2$ and this result establishes the staggered configuration (D_{3d}) for ethane.

The ν_2 and ν_3 Raman and infrared bands of methane are seriously complicated by Coriolis interactions. The Raman spectra have yielded considerably more detail than the infrared spectra and some success in analysing them has been achieved. Values of band origins and rotational constants have been obtained but of more importance is the fact that the Raman results have to some extent helped in the analysis and understanding of some of the complex features in the infrared spectra. In the triply degenerate vibrational level, ν_3, Coriolis coupling splits each rotational level into three. The Raman selection rules are $\Delta J = 0$, ± 1, ± 2 for transitions to each of the three rotational levels and therefore 15 branches are predicted, and all have been observed. The infrared selection rules are $\Delta J = 0$, ± 1, but the transitions are restricted so that only three branches without a common upper level are predicted. These three branches have been observed many times but always accompanied by a series of weak lines which have not been explained. When the frequencies of these extra lines were compared with the Raman frequencies many coincidences were found. There seems to be no doubt that the lines belong to the ν_3 band and that the restricted infrared selection rules are not valid. Similarly, the Raman spectrum of the doubly

degenerate ν_2 vibration[23] shows that Coriolis interaction with the nearby level ν_4 splits the rotational levels of ν_2 into two sets. Transitions with $\Delta J = 0$, ± 1 terminate in one set and transitions with $\Delta J = \pm 2$ terminate in the other. From this analysis it was found that the doublet pattern of the infrared spectrum arises from transitions $\Delta J = 0$, ± 1 to each set of upper levels. Detailed theoretical explanations of these features in the ν_2 and ν_3 bands of methane have not yet been given.

These investigations have shown that valuable information of molecular structures can be obtained from the Raman spectra of gases photographed at high resolution. One may confidently expect that further work in this field will lead to other important results and to a more complete understanding of molecular spectra and molecular structures.

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