The Microwave Spectrum of Bromoacetylene; r_s-Structure, Dipole Moment, Quadrupole Coupling Constants and Excited Vibration States

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The microwave spectrum of bromoacetylene has been investigated in the frequency range from 7 GHz to 35 GHz. From Stark effect measurements the dipole moment has been determined as $\mu = 0.23 \pm 0.01$ D, and the r_s-structure has been derived in four independent ways from twelve isotopic species: C−H = 1.0553 Å, C≡C = 1.2038 Å, C−Br = 1.7913 Å (internal consistency better than ±0.0003 Å). Quadrupole coupling constants have been determined for eleven isotopic forms and are $e\,q\,Q = 541.4_7$ MHz and 648.0_0 MHz for $HCCBr^{81}$ and $HCCBr^{79}$, respectively.

Rotation spectra have also been observed for excited states of the three lowest normal modes and for several isotopic forms. For the Br^{81} (Br^{79}) species the rotation-vibration coefficients are $\alpha_5 = -10.98$ (-11.02) MHz, $\alpha_4 = -1.57$ (-1.61) MHz and $\alpha_3 = +12.88$ ($+13.40$) MHz. For the bending vibrations, ν_5 and ν_4, l-type doubling constants are obtained as $q_{l5} = 4.14$ (4.17) MHz and $q_{l4} = 2.6$ MHz. Analysis of the Fermi resonance between the first excited state of ν_3 and the $l = 0$ component of the second excited state of ν_5 gives the mixing ratio of these two states as $a/b = 1.45$ (1.51) and the interaction energy as $W_{3,5} = 1.313$ (1.181) $\delta_{3,5}$ for the Br^{81} (Br^{79}) species. With an approximate value of $\delta_{3,5} \cong 25\ \text{cm}^{-1}$, the cubic force constant is obtained as $k_{3,55} \cong 44\ \text{cm}^{-1}$.

The results are discussed in relation to the molecular properties of other halogen acetylenes and halogen cyanides.

I. Introduction

In the many structural studies of mono-halogen acetylenes by rotational and vibrational spectroscopy, microwave data on bromoacetylene have remained unavailable for a long time, possibly because the extremely small dipole moment indicated by dielectric measurements [1] suggested a very weak rotational spectrum. Repeated failure, however, of attempts [2, 3] to detect the rotational absorption spectrum of iodoacetylene eventually lent strength to the belief that the dipole moment of iodoacetylene must be almost identically zero, particularly since, even for the well populated excited state of the lowest bending vibration, Stark effect modulation of rotational transitions could apparently not be achieved [3]. This information, together with the known dipole moments of fluoro- and chloroacetylene [2, 4], made it probable that the dipole moment of bromoacetylene would be considerably larger than suggested by the dielectric method, and this exceptation was indeed confirmed by the observation of a strong absorption spectrum of bromoacetylene, as reported in a preliminary note [5].

We now present a full account of the subsequent work [6] on the microwave spectrum of bromoacetylene, including the determination of accurate values for the bond lengths, the quadrupole coupling constants and the dipole moment, as well as information derived from spectra due to five excited vibration states of this compound.

II. Experimental

Bromoacetylene was prepared by an established method [7] and purified by distillation. It was deuterated by direct exchange with slightly alkaline deuterium oxide.

Spectra were measured in a Stark spectrometer [8] of conventional design with a modulation frequency of 100 kHz. Absorptions, including those of the C^{13}-species in their natural abundance, were observed on the oscilloscope at a sweep rate of about 1 MHz/sec. Work was normally conducted with the cell cooled to −78 °C, but spectra of the excited vibration states near 600 cm^{-1} (Section III c) were ob-

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served at room temperature. Rotational assignments of some weak transitions were checked by microwave-microwave double resonance. The instrument used in these experiments has been described previously [9].

III. Results

A) Ground State Spectra and Molecular Structure

The ground state spectrum of bromoacetylene was investigated for twelve isotopic species. The observed transition frequencies are given in Table A I-a and A I-b of the appendix. For species containing only C^{12}-carbons, a large portion of the quadrupole pattern due to the bromine nucleus could be observed for each transition and, by inclusion of second order corrections [10a], the hyperfine splittings could be accounted for satisfactorily. For the eight C^{13}-species observed in their natural abundance (Table A I-b) only the strongest quadrupole components could be measured, hence the deduced coupling constants are not as accurate as those of the C^{12}-species. The effects of centrifugal distortion in bromoacetylene are very small so that it was not possible to derive a meaningful value for the distortion constant D_J from the low-J transitions observed. Rotational constants, moments of inertia and quadrupole coupling constants for all isotopic species are collected in Table I.

Clearly, the moments of inertia of twelve isotopic species render the structure of a linear, tetratomic molecule grossly over-determined, so that structure calculations by the usual procedure [11] could be carried out independently with different sets of data. Thus, four independent values for the C≡C distance and two independent substitution values for both the C – H and the C – Br distance were calculated (Table II). The internal consistency of independently deduced bond lengths was high, with deviations from the mean values reaching a maximum of 0.0003 Å for the C – Br distance. The averaged values of bond lengths in bromoacetylene are:

Table I. Ground state rotational constants (in MHz), moments of inertia (in a.m.u. Å²) and quadrupole coupling constants (in MHz) of isotopic species of bromoacetylene.

Species	B_0	I_0	$e\,q\,Q$
$H-C^{12}{\equiv}C^{12}-Br^{81}$	3,978.45 [a]	127.0673 [c]	541.47
$H-C^{12}{\equiv}C^{12}-Br^{79}$	4,000.08 [a]	126.3802	648.00
$H-C^{12}{\equiv}C^{13}-Br^{81}$	3,933.35 [b]	128.5243	542
$H-C^{13}{\equiv}C^{12}-Br^{81}$	3,804.88 [b]	132.8638	542
$H-C^{12}{\equiv}C^{13}-Br^{79}$	3,955.32 [b]	127.8104	648
$H-C^{13}{\equiv}C^{12}-Br^{79}$	3,826.23 [b]	132.1225	648
$D-C^{12}{\equiv}C^{12}-Br^{81}$	3,634.99 [a]	139.0736	541.08
$D-C^{12}{\equiv}C^{12}-Br^{79}$	3,655.11 [a]	138.3080	647.96
$D-C^{12}{\equiv}C^{13}-Br^{81}$	3,599.29 [b]	140.4530	541
$D-C^{13}{\equiv}C^{12}-Br^{81}$	3,493.33 [b]	144.7132	—
$D-C^{12}{\equiv}C^{13}-Br^{79}$	3,619.75 [b]	139.6591	646
$D-C^{13}{\equiv}C^{12}-Br^{79}$	3,513.29 [b]	143.8910	646

[a] ± 0.03 MHz. [b] ± 0.05 MHz.

[c] Conversion factor: 505531 MHz a.m.u. Å².

Table II. Structure calculations on bromoacetylene.

Parent Species	Bond lengths in Å		
	C – Br	C≡C	C – H
$H-C{\equiv}C-Br^{79}$	1.7916	1.2038	1.0552
$H-C{\equiv}C-Br^{81}$	1.7916	1.2039	1.0553
$D-C{\equiv}C-Br^{79}$	1.7911	1.2038	1.0552
$D-C{\equiv}C-Br^{81}$	1.7910	1.2037	1.0553

$$C-H = 1.0552\ \text{Å}, \quad C{\equiv}C = 1.2038\ \text{Å},$$
$$C-Br = 1.7913\ \text{Å}.$$

Since all isotopic shifts are appreciable, these distances are thought to be close to the equilibrium values.

B) Stark Effects and Dipole Moment

Stark effects were studied quantitatively for selected quadrupole components of the $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions. Static electric fields of up to 6000 V/cm were applied, with a small square-wave field superimposed on the D.C. for modulation. The electric field strengths were determined in the usual manner by calibration of the cell with carbonoxysulphide, for which the dipole moment was taken as $\mu_{OCS} = 0.71521$ D [12].

Since the quadrupole energy of bromoacetylene is large compared with the Stark energy, the data were fitted to the expression for the "weak field" case in the theory of Low and Townes [13]. The Stark energy $W^{(2)}$, given by these authors for $J \geqq 1$ [Eq. (10) of Ref. [13]], reduces in the limit $J = 0$ to simply

$$W^{(2)} = -\mu^2 E^2 / 6\,B \qquad (1)$$

where μ, E and B are the dipole moment, the electric field strength and the rotational constant, respectively.

The transitions investigated, and the dipole moment value deduced from each of the six Stark lobes, are listed in Table III, which indicates a dipole moment of $\mu = 0.23 \pm 0.01$ *D*.

Table III. Summary of dipole moment measurements on bromoacetylene.

Transition	Dipole Moment in D	
	$H-C\equiv C-Br^{79}$	$H-C\equiv C-Br^{81}$
$J=0\rightarrow 1$		
$F=3/2\rightarrow 5/2$,		
$M_F=1/2$	0.235	0.235
$M_F=3/2$	0.229	0.228
$J=1\rightarrow 2$		
$F=3/2\rightarrow 3/2$,		
$M_F=3/2$	0.230	0.234
	$\mu_{av.}=0.232\pm 0.004\ D$	

C) *Excited Vibration States*

The excited states giving rise to detectable rotation spectra of bromoacetylene are shown diagrammatically in Fig. 1, with vibration frequencies taken from the i.r. work of Hunt and Wilson [14]. While the spectra due to molecules in the excited states of the C – H and C – Br bending modes, ν_4 and ν_5 respectively, could in general be readily distinguished from the ground state spectra on account of their faster Stark effects, the presence of several excited states and isotopic species spectra with quadrupole hyperfine structure called for some care in the analysis.

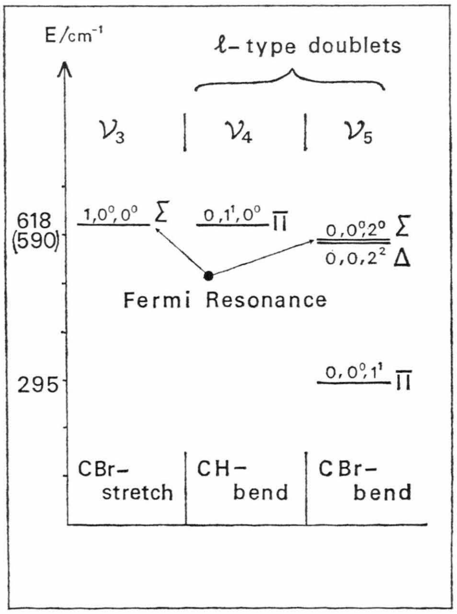

Fig. 1. Excited vibration states of bromoacetylene.

The first excited states of the degenerate bending modes ν_4 and ν_5 with internal angular momentum $|l|=1$ give rise to l-type doublets [10b] in the rotation spectrum. The second excited states of these modes consist of two substates corresponding to values of 0 and 1 of the internal angular momentum quantum number l. From Fig. 1, the second excited state of ν_5 is seen to be energetically close to the first excited state of the C – Br stretching mode ν_3, so that a Fermi resonance [10b] can occur between the $l=0$ component of the former and the first excited state of ν_3. As in Fig. 1, the excited states will be labelled in the following paragraphs by the set of quantum numbers for ν_3, $\nu_4^{\,l}$ and $\nu_5^{\,l}$.

C-1 The C – Br and C – H Bending Modes

a) *States $(0, 0^0, 1^1)$ and $(0, 0^0, 2^0)$ of the C – Br Bend ν_5*

The quadrupole pattern of the l-type doublets of the first excited state of ν_5 was easily recognizable, and the centres of the l-type pairs agreed well with the calculated frequencies of individual quadrupole components (Table A II-a). However, the separation between pairs, and hence the l-type doubling constant q_l, displayed variations analogous to those previously observed for ICN [15] and BrCN [16]. Javan [15] has ascribed this variation to the asymmetry which the bending vibration produces in the average gradient of the electric field at the quadrupolar nucleus. Accordingly, the observed doublet separations, $\Delta\nu$, are envisaged as composed of a constant l-type splitting to which an F-dependent contribution is added for each individual quadrupole component $F_i\rightarrow F_k$. Thus [Eq. (1) of Ref. [15]],

$$\Delta\nu_{F_i\rightarrow F_k}=2\,q_l(J+1)+\eta\,e\,q\,Q\{f(J+1,F_k)-f(J,F_i)\} \qquad (2)$$

where the asymmetry parameter η describes the deviation from cylindrical symmetry of the quadrupole tensor, and $f(J,F)$ is the Casimir function [10a]. From Eq. (2), a plot of $\Delta\nu/2(J+1)$ against the difference in the Casimir function of levels involved in transitions from the same J-value should be linear, with slope $\eta\,e\,q\,Q/2(J+1)$ and intercept q_l. This is confirmed in Fig. 2 which shows such a plot for the $J=2\rightarrow 3$ transition of HCCBr^{81} (Reference [17]). The average value of η from this and similar plots for the other three isotopic species for which measurements are given in Table A II-a, is $\eta=0.0098$

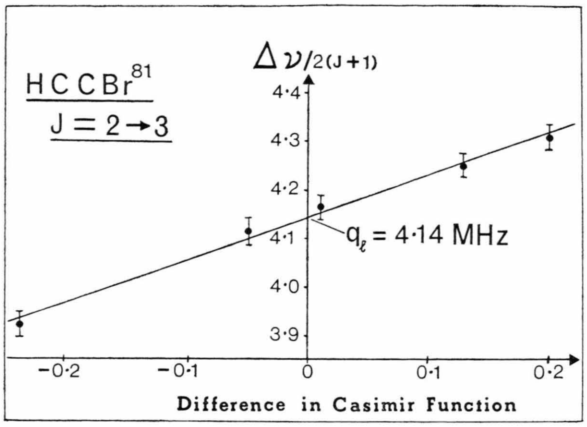

Fig. 2. Variation of the l-type splitting for different quadrupole components [Equation (2)].

±0.0002. Values of the l-type doubling constants and other molecular parameters of the $(0, 0^0, 1^1)$-state for the four isotopic species are collected in Table IV. This table also contains values for the doubling constants which were calculated with the Coriolis constants, ζ_{tk}, of Venkateswarlu and Mathew [18] and the vibrational frequencies, ν_i, of Hunt and Wilson [14] in Nielsen's [19] expression for the doubling constant:

$$q_{l_t} = (2\,B^2/\nu_t)\,[1 + 4\,\sum\{\zeta_{t,k}^2\,\nu_t^2/(\nu_k^2-\nu_t^2)\}]\,. \quad (3)$$

It is seen from Table IV that the observed and calculated values of q_{l_5} agree to better than 4% for all four isotopic species.

From the dependence of the doubling constant on the internal angular momentum, the l-type splitting for the $(0, 0^0, 2^2)$-state is about $B/\nu_5 \cong 10^{-4}$ times smaller than for the state $(0, 0^0, 1^1)$, and hence not resovable in the rotation spectrum. Absorptions due to the $(0, 0^0, 2^2)$-state could thus be predicted from the rotation-vibration constant α_5, as determined from the first excited state, and with the quadrupole pattern calculated like that of a symmetric rotor with $K = 2 = |l|$. The transitions (Table A II-b) were observed at almost exactly the predicted frequencies, but the deduced value of α_5 turned out slightly smaller than the one calculated from the $(0, 0^0, 1^1)$-spectrum. This result parallels the findings in BrCN [16] and arises from approximations in the expression

$$B_{v_i} = B_e - \sum \alpha_i (v_i + d_i/2) \quad (4)$$

which was used in the evaluation of the rotation-vibration constant α_5.

b) State $(0, 1^1, 0^0)$ of the C – H Bend ν_4

The l-type doublets of the first excited state of the C – H bending mode ν_4 (Table A II-c) were very much weaker than those of the state $(0, 0^0, 1^1)$ and some difficulty was encountered in identifying these transitions. Only slight variations in the l-type splittings were observed and the values quoted for q_{l_4} (Table IV) are averages over the few doublets observed.

While the doubling constants q_{l_4} and q_{l_5} in both fluoroacetylene [3] and chloroacetylene [4], as well as q_{l_5} in bromoacetylene, conform quite closely to the approximate expression [19]

$$q_{l_t} = 2.3\,B^2/\nu_t\,, \quad (5)$$

the constant q_{l_4} of bromoacetylene is found to be about 30% greater than expected from this equation. This discrepancy is readily understood by consideration of the extact expression (3), above, and the proximity of the first excited states of ν_3 and ν_4 (Fig. 1), which entails an abnormally large contribution to q_{l_4} by the term $\zeta_{4,3}^2\,\nu_4^2/(\nu_3^2-\nu_4^2)$. Since the Coriolis constants of Venkateswarlu and Mathew [18] had given good agreement between the observed value of q_{l_5} and that calculated from Eq. (3), it seemed reason-

Table IV. Rotational and vibrational parameters of excited states of bromoacetylene (all in MHz).

State	$e\,q\,Q$	B	α	Doubling constant	
$(\nu_3, \nu_4^l, \nu_5^l)$				$q_l^{\text{obs.}}$	$q_l^{\text{calc.}}$
H – C – C – Br^{81}					
$(0, 0^0, 0^0)$	541.47	3978.45	—	—	—
$(0, 0^0, 1^1)$	538.54	3989.43	−10.98	4.14	4.00
$(0, 0^0, 2^2)$	540	3989.14	−10.93	—	—
$(0, 0^0, 2^0)$	540	3989.14	− 5.34	—	—
$(0, 1^1, 0^0)$	538.5	3980.02	− 1.57	2.6	[a]
$(1, 0^0, 0^0)$	540	3976.80	+ 1.65	—	—
$(1, 0^0, 0^0)$ corr.	—	3965.57	+12.88	—	—
H – C – C – Br^{79}					
$(0, 0^0, 0^0)$	648.00	4000.08	—	—	—
$(0, 0^0, 1^1)$	644.90	4011.10	−11.02	4.17	4.04
$(0, 0^0, 2^2)$	644.9	4022.06	−10.99	—	—
$(0, 0^0, 2^0)$	646	4011.28	− 5.60	—	—
$(0, 1^1, 0^0)$	644.9	4001.69	− 1.61	2.6	[a]
$(1, 0^0, 0^0)$	646	3997.50	+ 2.58	—	—
$(1, 0^0, 0^0)$ corr.	—	3989.68	+13.40	—	—
D – C – C – Br^{81}					
$(0, 0^0, 0^0)$	541.08	3634.99	—	—	—
$(0, 0^0, 1^1)$	538.80	3644.62	− 9.63	3.62	3.48
D – C – C – Br^{79}					
$(0, 0^0, 0^0)$	647.96	3655.11	—	—	—
$(0, 0^0, 1^1)$	644.88	3664.80	− 9.69	3.64	3.52

[a] See section C-1-b.

able in the present situation to reverse this calculation, and to use the experimental value of q_{l4} in order to obtain an estimate of the difference between the bands ν_3 and ν_4 which had not been resolved in the i.r. study[14]. The result of this procedure indicates $\nu_3 - \nu_4 \cong 37\ \text{cm}^{-1}$. Hence, if it is assumed that the i.r. peak at $618\ \text{cm}^{-1}$ corresponds to the centre of these two bands, values of $\nu_4 \cong 600\ \text{cm}^{-1}$ and $\nu_3 \cong 637\ \text{cm}^{-1}$ are obtained, a result which is in good agreement with the breadth of the i.r. band.

C-2 Fermi Resonance Between the States $(1.0^0, 0^0)$ and $(0, 0^0, 2^0)$ of the C – Br Stretch ν_3 and the C – Br Bend ν_5

By analogy with cyanogen bromide, in which the rotation-vibration constant α_3 for the C – Br stretch ν_3 has been determined[16] as $\alpha_{3,\text{BrCN}} \cong +15$ MHz, it seemed reasonable to except that the satellites arising from the state $(1, 0^0, 0^0)$ of bromoacetylene would occur on the low-frequency side of the ground state transitions, displaced by about $2\,\alpha_{3,\text{BrCN}}(J+1)$. However, a careful search of such frequency ranges did not meet with success, and low-frequency satellites of the appropriate intensity were found only very close to the ground state lines. As these transitions (Table A II-d), moreover, yielded consistent and comparable values of α for the Br^{81}- and Br^{79}-species (1.65 MHz and 2.58 MHz, respectively), it was suspected that they might indeed represent the desired $(1, 0^0, 0^0)$ spectrum, and that the discrepancy of ~ 13 MHz between the observed α-values for the C – Br stretch in BrCN and BrCCH might arise from a Fermi resonance. This phenomenon (which implies the mutual repulsion of two states interacting through the anharmonic part, $V^{\text{anh.}}$, of the potential energy) becomes noticeable only when the energy difference between two states of the same symmetry is small, and it followed therefore (Fig. 1) that the coupling state had to be the state $(0, 0^0, 2^0)$, and that the rotational transitions of the latter should then be displaced to the low-frequency side of the $(0, 0^0, 2^2)$-spectrum by approximately the same amounts as those of the $(1, 0^0, 0^0)$-spectrum appeared to be shifted to higher frequencies. Thus, an approximate prediction of transitions due to the (assumedly) perturbed state $(0, 0^0, 2^0)$ could be made, and the occurrence of a Fermi resonance could be proved through the subsequent observation of the predicted $(0, 0^0, 2^0)$ transitions (Table A II-e).

The theory of Fermi resonance is well established, and the aspects relevant for the states $(1, 0^0, 0^0)$ and $(0, 0^0, 2^0)$ of bromoacetylene, which for brevity will be referred to by the indices 3 and 5, respectively, may be summarised as follows: The effective rotational constants, B^c, of the coupled states $\psi_3{}^c$ and $\psi_5{}^c$

$$\psi_3{}^c = a\,\psi_3{}^0 - b\,\psi_5{}^0\,,\qquad \psi_5{}^c = b\,\psi_3{}^0 + a\,\psi_5{}^0\,, \tag{6}$$

become mixtures of the constants B^0 of the unperturbed states $\psi_3{}^0$ and $\psi_5{}^0$, i. e.

$$B_3{}^c = a^2\,B_3{}^0 + b^2\,B_5{}^0\,,\qquad B_5{}^c = b^2\,B_3{}^0 + a^2\,B_5{}^0\,. \tag{7}$$

But, from the normalisation of the state functions (6),

$$B_3{}^c + B_5{}^c = B_3{}^0 + B_5{}^0\,. \tag{8}$$

Hence, from Eq. (8), knowledge of one of the unperturbed constants B^0 (below: $B_5{}^0$) together with the experimental values of B^c allows the evaluation of the other perturbed constant (below: $B_3{}^0$) and, therefore, the determination of the mixing coefficients **a** and **b** from Eq. (7) and the normalisation. These coefficients, in turn, depend on the unperturbed energy difference $\delta_{3.5}$ and the interaction energy $W_{3.5}$, e. g.

$$a^2 = (1/2) + (\delta_{3.5}/2)\,\{\delta_{3.5}^2 - 4\,|\,W_{3.5}\,|^2\}^{-1/2}\,, \tag{9}$$

so that $W_{3.5}$ can be obtained as a function of $\delta_{3.5}$ once the mixing coefficients are known. If it is finally assumed that contributions to

$$W_{3.5} = \langle 3\,|\,V^{\text{anh.}}\,|\,5\rangle$$

from terms beyond the cubic part of the potential energy are negligible, the cubic force constant $k_{3.55}$ may be determined as, in the present case,

$$k_{3.55} = \sqrt{2}\,W_{3.5}\,(\delta_{3.5}) \tag{10}$$

Accordingly, by inserting into Eq. (8) the rotational constants of the assumedly unperturbed state $(0, 0^0, 2^2)$ for $B_5{}^0$ together with the observed constants of the coupled states $(1, 0^0, 0^0)$ and $(0, 0^0, 2^0)$ to yield $B_3{}^0$ of the state $(1, 0^0, 0^0)$, one obtains from Eq. (7) for the $\text{Br}^{81}(\text{Br}^{79})$ species of bromoacetylene $a^2 = 0.678\ (0.695)$, and hence from Eq. (9) $W_{3.5} = 1.313\ (1.181)\ \delta_{3.5}$.

Unfortunately, the further evaluation of $W_{3.5}$ and $k_{3.55}$ is subject to considerable uncertainty. This stems from the absence of i.r. data from which the absolute positions, and hence the energy difference

$\Delta_{3.5}$ of the two perturbed states could be deduced, so that the unperturbed energy separation

$$\delta_{3.5} = \Delta_{3.5}\,(2\,a^2 - 1) \qquad (11)$$

could be determined. To overcome this difficulty, we have tentatively placed the unperturbed level of the state $(0, 0^0, 2^0)$ at $2\,\nu_5 = 2 * 295 = 590\ \text{cm}^{-1}$ (thereby ignoring small effects of l-type resonance [20] and anharmonicity) and constrained the value of $\delta_{3.5}$ by the requirement that the energy of the perturbed state $(1, 0^0, 0^0)$ should be close to $637\ \text{cm}^{-1}$, as estimated from the value of q_{l_4} in Sect. C-1-b, above. With these approximate assumptions one obtains for both isotopic species $\delta_{3.5} \cong 25\ \text{cm}^{-1}$, which implies a value of $\nu_3{}^0 \cong 615\ \text{cm}^{-1}$ for the unperturbed energy of the state $(1, 0^0, 0^0)$ and also, from Eqs. (9) and (10), $W_{3.5} \cong 32\ \text{cm}^{-1}$ and $k_{3.55} \cong 44\ \text{cm}^{-1}$.

IV. Discussion

An appraisal of the molecular data on bromoacetylene inevitably involves comparisons with the other two monohalogen acetylenes, FCCH and ClCCH, and with the four closely related halogen cyanides which have all been studied by rotational spectroscopy. We thought it appropriate, therefore, to collect corresponding data on these molecules as background information in Table V. Also included in this table are data on iodoacetylene which have been derived by infrared and Raman spectroscopy [21, 22], and parameters for this substance predicted by speculative extrapolation from the data on the other seven molecules.

The C – C and C – H distances of bromoacetylene coincide with the values for ClCCH, but are both longer than their counterparts in FCCH. In comparing the C – Br distance in the acetylene with that of the cyanide, the acetylene value is found to be 0.002 Å larger, which is in qualitative agreement with the finding on the other two acetylene/cyanide pairs. A more careful comparison of the halogen distances in acetylenes and cyanides reveals that the three differences δ_X (X = F, Cl, Br) between the halogen bond lengths in corresponding acetylenes and cyanides vary linearly with the C – X length in X – CN according to the expression

$$\delta_X = d^{X-CCH} - d^{X-CN} = -0.025\,d^{X-CN} + 0.046\,.$$

Hence, unless this correlation should be entirely accidental, it would seem possible to predict the halogen distance in iodoacetylene as 1.992 Å from the known C – I bond length in ICN (1.9952 Å). With the reasonable assumption that the C – C and C – H bond lengths remain as in BrCCH and ClCCH,

Table V. Comparison of molecular data of mono-halogen acetylenes and halogen cyanides.

Molecule References		F – CN 2, a	F – CCH 2, 14	Cl^{35} – CN 2, b	Cl^{35} – CCH 14, 2, 6	Br^{79} – CN 16, c	Br^{79} – CCH 16, 6	I – CN d	I – CCH 21, 22, e
B_0	in MHz	10554.20	9706.19	5970.84	5684.24	4120.20	4000.08	3225.54	(3174)
Structure, Quadrupole coupling constants and Dipole moment									
X – C	in Å	1.262	1.279	1.631	1.6366	1.789	1.7913	1.9952	(1.992)
C≡N / C≡C		1.159	1.198	1.159	1.2036	1.158	1.2036	1.1581	(1.204)
C – H		—	1.053	—	1.0551	—	1.0552	—	(1.055)
$\lvert e\,q\,Q \rvert$	in MHz	—	—	83.39	79.76	686.06	648.00	2420.5	(2280)
μ	in D	2.17	0.73	2.80	0.44	2.94	0.23	3.71	(0.1 ?)
Vibration frequencies, rotation-vibration-, l-type doubling- and cubic force constants									
$\nu_{X-C\text{-stretch}}$	in cm^{-1}	1070	1045	740	756	588	635	486	490
$\nu_{CCH\text{-bend}}$		—	578	—	604	—	618	—	635
$\nu_{XCN/XCC\text{-bend}}$		451	367	378	326	342	295	305	267
$\alpha_{X-C\text{-stretch}}$	in MHz	~47	—	24.7	21.2	15.5	13.4	11.9	(10.5)
$\alpha_{CCH\text{-bend}}$		—	−8.8	—	−3.7	—	−1.6	—	(−0.5)
$\alpha_{XCN/XCC\text{-bend}}$		−30.8	−27.6	−16.3	−15.1	−11.5	−11.0	−9.5	(−8.5)
$q_{l,\,CCH\text{-bend}}$		—	12.6	—	4.3	—	2.6	—	(2.0)
$q_{l,\,X-C\text{-bend}}$		19.7	19.1	7.5	7.6	3.9	4.2	2.6	(2.8)
$k_{X-C\text{-stretch/bend}}$	in cm^{-1}	49.8	—	49.1	31.7	50.1	~44	49.5	—

[a] W. J. Lafferty and D. R. Lide, J. Mol. Spectry **23,** 94 (1967). [b] W. J. Lafferty, D. R. Lide, and R. A. Toth, J. Chem. Phys. **43,** 2063 (1965). [c] A. Maki, J. Chem. Phys. **38,** 1261 (1963). [d] J. B. Simpson, J. C. Smith, and D. H. Whiffen, J. Mol. Spectry **44,** 558 (1972). [e] Values in brackets are estimated from the trends in the data of the previous columns.

this yields a prediction of $B_0 = 3174$ MHz (0.10588 cm^{-1}) for the rotational constant of ICCH which is only slightly lower than the B_0-value previously deduced from rotational Raman spectroscopy ($B_0 = 0.10622 \pm 0.0001\ \text{cm}^{-1}$, or 3184 MHz).

The nuclear coupling constants in bromoacetylene are less than for the corresponding nuclei in BrCN, in qualitative analogy with the behaviour of the chlorine couplings in ClCCH and ClCN. A more detailed interpretation of such coupling constants in terms of the ionicity of the C – X σ-bond and the contribution of π-bonded resonance structures such as $H - \overset{-}{C} = C = \overset{+}{X}$ has frequently been discussed[23], and will therefore not be repeated here. It is interesting to note that the coupling constants in BrCCH are very close to those found, less accurately, for methyl bromoacetylene[24]. This suggests that the coupling constant of iodoacetylene would be close to the value found in methyl iodoacetylene[24] (2230 MHz), whereas the extrapolation of the data in Table V would suggest a slightly greater value (2280 MHz).

According to Javan[15], a portion of the variation of the effective quadrupole coupling constant with excitation of the bending mode ν_5, and the observed asymmetry in the effective field gradients perpendicular to the molecular axis in the state $(0, 0^0, 1^1)$, arises from vibrational averaging over the bent molecular configuration, while another portion may be ascribed either to the occurrence of a bent bond (which would entail a deviation of the axis of cylindrical charge distribution from the C – Br bond direction) or it may be interpreted as due to the nonequivalence of the π_x and π_y orbitals associated with the ionic resonance structures. Unfortunately, as in the previous studies on ICN and BrCN, the experimental data on bromoacetylene do not allow either of these latter effects to be identified, since the purely kinematical effect cannot be isolated quantitatively, and since a change of the field gradient at the bromine nucleus with excitation of ν_5 cannot be detected.

From the present study, the dipole moment of BrCCH is considerably larger than indicated by the dielectric work[1] and, although the errors in the latter method obviously increase for small dipole moments, it seems unlikely that an error in excess of 0.2 D could be ascribed entirely to experimental inaccuracies. The present value (0.23 D) is in qualitative agreement with the trend in the electronegativities and quadrupole data, and the electronic effects responsible for the decreasing polarity of the mono-halogen acetylenes from FCCH to BrCCH are obviously the same as those invoked in the discussion of distances and coupling constants. A numerical correlation with any of those parameters is not easily recognizable, however. Although Zeeman effect experiments on bromoacetylene[25] did not yield the direction of the dipole moment, the trends in the halogen acetylene series make it highly probable that this is the same as deduced from Zeeman work in the case of ClCCH[26], i. e. that the moment points towards a negative bromine atom corresponding to $\overset{+}{H} - C \equiv C - \overset{-}{Br}$. Unbiased speculation about the dipole moment of iodoacetylene is, clearly, prevented by the negative outcome of previous attemps to detect the rotation spectrum of this last member of the mono-halogen acetylene series. While, from the general trends within the known data, one would not expect the moment of iodoacetylene to exceed 0.1 D, the direction of this moment would be a feature of particular chemical interest.

The vibrational and rotation-vibration data collected in the lower half of Table V reveal parallel trends in the halogen cyanide and acetylene series, with the bromoacetylene data in qualitative agreement with values expected from FCCH and ClCCH. As the major portion of the vibrational changes along the halogen series can be ascribed to the increase in the reduced mass in going from fluorine to iodine, it seems reasonable to conclude that the changes in the force field, and hence the variation of the chemical bonding, are not large within these series of compounds. Further evidence in support of this conclusion may be seen in the small variation within the cyanides of the cubic force constant interlinking the halogen stretching and bending modes. In comparing the acetylenes with corresponding cyanides, the former are seen to bend more easily than the cyanides with rotation-vibration and l-type doubling constants $\sim 10\%$ and $\sim 5\%$, respectively, smaller than in the halogen cyanides. Compared with the 50 cm^{-1} in BrCN, the cubic force constant for BrCCH ($\sim 44\ \text{cm}^{-1}$) seems also to be in good agreement with this trend.

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Appendix

The following tables give the observed transition frequencies of bromoacetylene. Uncertainties in the measurements and differences between calculated and observed frequencies are, typically, ± 0.05 MHz.

Table A I. Observed transitions of the ground state spectra of bromoacetylene.

Table A I-a: C^{12}-species.

		$H-C=C-Br^{81}$	$H-C=C-Br^{79}$	$D-C\equiv C-Br^{81}$	$D-C\equiv C-Br^{79}$
$J = 0 \rightarrow 1$	3/2−5/2	7930.18	7968.26		
	3/2−3/2	8065.85	8130.64		
	3/2−1/2	7822.36	7839.28		
$J = 1 \rightarrow 2$	5/2−7/2 3/2−5/2	15902.33	15986.50	14528.48	14606.76
	1/2−3/2	16049.76	16163.54	14676.08	14783.64
	5/2−5/2	16037.98	16148.82	14664.06	14769.06
	3/2−3/2	15806.38	15871.95	14632.77	14492.32
	1/2−1/2	15913.65	16000.16	14539.93	14620.41
	5/2−3/2	15942.00	16034.35	14568.31	14654.70
	3/2−1/2	15670.37	15708.88	14296.49	14329.07
$J = 2 \rightarrow 3$	7/2−9/2 5/2−7/2	23864.28	23992.73	21803.52	21923.07
	3/2−5/2	23897.27	24032.11	21836.60	21962.50
	1/2−3/2	23897.83	24032.98	21837.18	21963.28
	7/2−7/2	23999.69	24154.78		
	5/2−5/2	23801.54	23917.78		
	3/2−3/2	23761.74	23869.88		
$J = 3 \rightarrow 4$	9/2−1/2 7/2−9/2	31823.48	31995.59		
	5/2−7/2 3/2−5/2	31838.96	32014.15		
	9/2−9/2	31958.70	32157.56		
	7/2−7/2	31776.16			
	5/2−5/2	31703.15			

Table A I-b: C^{13}-Species.

		$HCC^{13}Br^{81}$	$DCC^{13}Br^{81}$	$HC^{13}CBr^{81}$	$DC^{13}CBr^{81}$	$HCC^{13}Br^{79}$	$DCC^{13}Br^{79}$	$HC^{13}CBr^{79}$	$DC^{13}CBr^{79}$
$J = 1 \rightarrow 2$	5/2−7/2 3/2−5/2	15721.93	14385.66	15208.05	13961.82	—	14465.25	15291.22	14039.43
$J = 2 \rightarrow 3$	7/2−9/2 5/2−7/2	23593.73	21589.39	22822.86	20953.55	23724.32	21710.82	22949.77	21072.08
	3/2−5/2		21622.39		—		21750.25		21111.48
	1/2−3/2		21613.00		—		21751.03		21112.30
$J = 3 \rightarrow 4$	9/2−11/2 7/2−9/2	31462.79		30435.01		31637.68		30604.86	
	5/2−7/2 3/2−5/2	31478.30		30450.50		31654.22		30623.46	

Table A II. Observed transitions of excited vibrational states.

Table A II-a: State $(0, 0^0, 1^1)$.

Transition		$HCCBr^{81}$		$HCCBr^{79}$		$DCCBr^{81}$		$DCCBr^{79}$	
		l-doublets	q_l	*l*-doublets	q_l	*l*-doublets	q_l	*l*-doublets	q_l
$J = 1 \to 2$	5/2–7/2	15916.87 15933.69	4.20	15997.30 16014.06	4.19	14538.79 14553.35	3.64	14613.14 14627.86	3.68
	3/2–5/2	16052.35 16069.04	4.17	16159.51 16176.36	4.21	14674.26 14688.80	3.64	14775.42 14790.17	3.69
	1/2–3/2	15899.32 15884.11	3.80	— —	—	14505.99 14519.10	3.28	14574.09 14587.06	3.24
	5/2–5/2	15985.45 16000.81	3.84	16079.47 16094.66	3.80	14607.46 14620.60	3.29	— —	—
	3/2–3/2	16004.00 16021.31	4.33	16101.58 16119.53	4.49	14625.79 14641.47	3.92	14717.53 14733.44	3.98
	1/2–1/2	15816.49 15833.08	4.14	15877.40 15894.05	4.16	14638.52 14452.97	3.61	14493.45 14508.07	3.63
$J = 2 \to 3$	7/2–9/2	23934.68 23909.74	4.16	24036.90 24062.10	4.20				
	5/2–7/2	23968.00 23943.07	4.16	24076.76 24101.91	4.19				
	3/2–5/2	23968.92 23944.25	4.11	24078.06 24102.99	4.16				
	1/2–3/2	23934.68 —	—	— 24062.10	—				
	7/2–7/2	24011.66 24035.18	3.92	24159.00 24182.60	3.93				
	5/2–5/2	23921.38 23895.86	4.25	24020.43 24046.10	4.28				
	3/2–3/2	23868.62 23842.78	4.31	23983.22 23956.79	4.41				
$J = 3 \to 4$	9/2–11/2	31923.94 31890.88	4.13	32096.04 32062.52	4.19				
	7/2–9/2	31937.22 31904.15	4.13	32111.92 32078.45	4.13				
	5/2–7/2	31944.14 31911.18	4.12	32120.26 32086.92	4.17				
	3/2–5/2	31930.68 31897.59	4.14	32103.88 32070.66	4.15				
	9/2–9/2	32037.43 32005.96	3.93	32232.44 —	—				
	7/2–7/2	31897.59 31863.82	4.22	— 32030.50	—				
	5/2–5/2	31830.39 31796.14	4.28	31983.07 31949.20	4.23				

Table A II-b: State $(0, 0^0, 2^2)$.

	$HCCBr^{81}$	$HCCBr^{79}$
$J = 2 \to 3$		
7/2–9/2 7/2–7/2	23963.65	24086.70
5/2–7/2 5/2–5/2	24098.04 *	—
3/2–5/2 3/2–3/2	24002.0	24133.02
$J = 3 \to 4$		
9/2–11/2	31983.07	32153.13
7/2–9/2	32036.35 *	32216.95
9/2–9/2	32037.43	
5/2–7/2 7/2–7/2	32017.96	32194.90
3/2–5/2 5/2–5/2	31964.10	32130.06

Table A II-c: State $(0, 1^1, 0^0)$.

		$HCCBr^{81}$		$HCCBr^{79}$	
		l-doublet	q_l	*l*-doublet	q_l
$J = 2 \to 3$	7/2–9/2	23857.88 23873.85 *	2.66	23985.17 24000.70	2.59
$J = 3 \to 4$	9/2–11/2	— 31843.12	—	— 31993.40	—
	7/2–9/2	— 31856.47	—	32009.57 32030.50	2.62
	5/2–7/2	— 31863.82	—	32017.96 32038.96	2.62
	3/2–5/2	— 31849.55	—	32001.62 32022.67	2.63

Table A II-d: State $(0, 0, 2^0)$.

	$HCCBr^{81}$	$HCCBr^{79}$
$J = 1 \to 2$		
5/2–7/2	15945.26	16031.44
$J = 2 \to 3$		
7/2–9/2	23928.15 *	24060.05
$J = 3 \to 4$		
9/2–11/2	31909.27 *	32085.27

Table A II-e: State $(1^0, 0, 0)$.

	$HCCBr^{81}$	$HCCBr^{79}$
$J = 1 \to 2$		
5/2–7/2	15895.83	15976.38
$J = 2 \to 3$		
7/2–9/2	23854.08 *	23976.98 *
$J = 3 \to 4$		
9/2–11/2	31810.54 *	31975.37 *

* confirmed by DRM.

[1] L. O. Brockway and I. E. Coop, Trans. Farad. Soc. **34,** 1429 [1938].

[2] J. K. Tyler and J. Sheridan, Trans. Farad. Soc. **59,** 2661 [1963].

[3] J. K. Tyler, private communication.

[4] A. A. Westenberg, J. H. Goldstein, and E. B. Wilson, J. Chem. Phys. **17,** 1319 [1949].

[5] H. Jones, N. L. Owen, and J. Sheridan, Nature **213,** 175 [1967].

[6] H. Jones, Ph.D. Thesis, U.C.N.W., Bangor [1969]. Also: Paper D2−5 of the '1st European Microwave Spectroscopy Conference', Bangor 1970.

[7] L. A. Bashford, H. J. Emeleus, and H. V. A. Briscoe, J. Chem. Soc. 1358 [1938].

[8] R. H. Hughes and E. B. Wilson, Phys. Rev. **71,** 562 [1947].

[9] O. L. Stiefvater, H. Jones, and J. Sheridan, Spectrochim. Acta **26 A,** 825 [1970].

[10] See, for example: C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy" [McGraw-Hill, 1955], a) Chapter 6, b) Chapter 2.

[11] a) J. Kraitchman, Amer. J. Phys. **21,** 17 [1953]; b) C. C. Costain, J. Chem. Phys. **29,** 864 [1964].

[12] J. S. Muenter, J. Chem. Phys. **48,** 4544 [1968].

[13] W. Low and C. H. Townes, Phys. Rev. **76,** 1295 [1949].

[14] G. R. Hunt and M. K. Wilson, J. Chem. Phys. **34,** 1301 [1961].

[15] A. Javan, Phys. Rev. **99,** 1302 [1955].

[16] S. J. Tetenbaum, Phys. Rev. **86,** 440 [1952].

[17] The authors are grateful to Professor R. F. Curl for pointing out an error in earlier plots of this type.

[18] K. Venkateswarlu and M. P. Mathew, Z. Naturforsch. **23 b,** 1296 [1968].

[19] H. H. Nielsen, Phys. Rev. **75,** 1961 [1949].

[20] G. Amat and H. H. Nielsen, J. Mol. Spectry **2,** 163 [1958].

[21] J. H. Carpenter, D. F. Rimmer, and D. H. Whiffen, J.C.S. Faraday II, **66,** 1914 [1972].

[22] W. J. Jones, B. P. Stoicheff, and J. K. Tyler, Canad. J. Phys. **41,** 2098 [1963].

[23] See, for example: W. Gordy and R. L. Cook, "Microwave Molecular Spectra" (Interscience Publishers, 1970) Chapter 14.

[24] J. Sheridan and W. Gordy, J. Chem. Phys. **20,** 735 [1952].

[25] S. L. Hartford, Wm. C. Allen, C. L. Norris, E. F. Pearson, and W. H. Flygare, Chem. Phys. Lett. **18,** 153 [1973].

[26] W. C. Allen and W. H. Flygare, Chem. Phys. Lett. **15,** 461 [1972].