82. *Hydrogen Bonding in Gaseous Mixtures. Part IV.*[1] *Infrared Intensities. The Effect of Deuterium Substitution.*

By J. E. BERTIE and D. J. MILLEN.

The infrared spectra of complexes of deuterium chloride with various alkyl ethers in the gas phase are reported and discussed. The explanation suggested for the bandwidth in the spectra of protium-bonded complexes may be extended to deuterium-bonded complexes if it is supposed that the relative intensity of the sum and difference bands is lower in this case. A model for the hydrogen bond is examined, and it is shown that this supposition of a reduction in the intensities of the combination bands is a reasonable one. The intensity in the side-bands is attributed to intensity-stealing from the hydrogen stretching vibration through mechanical anharmonicity. The anharmonic term in the potential function which is responsible is identified, and is found to be that which describes the dependence of the effective stretching force-constant of the hydrogen–chlorine bond on the hydrogen-bond length.

The integrated intensities of the bands for the protium- and deuterium-bonded complexes have been measured. The enhancement of the intensity over that for the bands of the free acids is at least fourteen-fold.

THE study of gaseous hydrogen-bonded complexes described in Parts I—III of this Series indicates that the hydrogen-stretching infrared bands are accompanied by side-bands. This Paper reports the effects of deuterium substitution on the band contours for ether–deuterium chloride systems. Band intensities have been investigated, both theoretically and experimentally, for protium- and deuterium-bonded complexes as a further step towards understanding the origin of the side-bands.

Spectra of Mixtures of Deuterium Chloride and Alkyl Ethers.—The deuterium–chlorine stretching band for the complex of deuterium chloride with dimethyl ether is shown in Fig. 1. A very similar band (Fig. 2) was obtained for mixtures of deuterium chloride with deuterated dimethyl ether. Bands for complexes formed by methyl n-propyl and methyl

---

[1] Part III, preceding Paper.

iso-propyl ether are shown in Figs. 3 and 4. A similar band with a half-width of about 250 cm.$^{-1}$ was obtained for methyl ethyl ether. For diethyl ether, the band (Fig. 5) had a somewhat different contour in which the shoulders were less evident. This parallels the observations for hydrogen chloride, where side-bands which appear quite clearly for complexes with all the methyl ethers are lost in a much smoother band contour for the diethyl ether complex.[2] Comparison of the band contours of complexes formed from deuterium chloride with each of the methyl ethers (Figs. 1—4) shows that they are all similar in half-width and frequency, although there are minor differences in the contours. The result

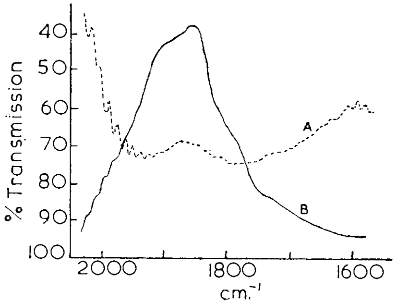

FIG. 1. Deuterium chloride and dimethyl ether. (A) Unmixed gases. (B) Difference spectrum: DCl, 150 mm.; ether, 300 mm.; 10-cm. path-length.

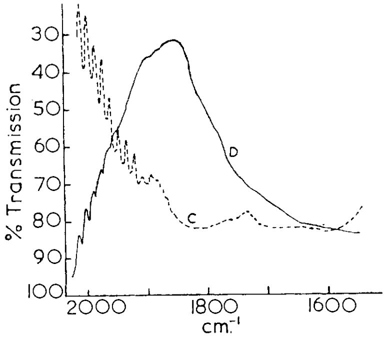

FIG. 2. Deuterium chloride and deuterated dimethyl ether. (C) Unmixed gases. (D) Difference spectrum: DCl, 300 mm.; ether, 150 mm.; 10-cm. path-length.

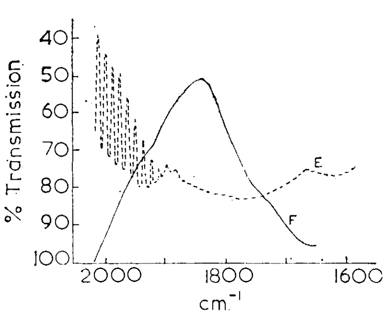

FIG. 3. Deuterium chloride and methyl n-propyl ether. (E) Unmixed gases. (F) Subtraction spectrum: DCl, 277 mm.; ether, 152 mm.; 10-cm. path-length.

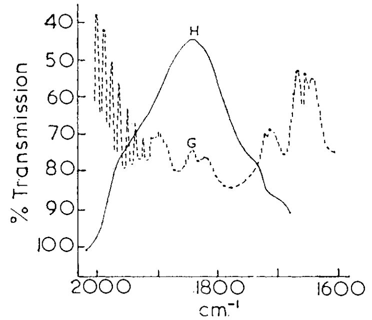

FIG. 4. Deuterium chloride and methyl isopropyl ether. (G) Unmixed gases. (H) Subtraction spectrum: DCl, 257 mm.; ether, 162 mm.; 10-cm. path-length.

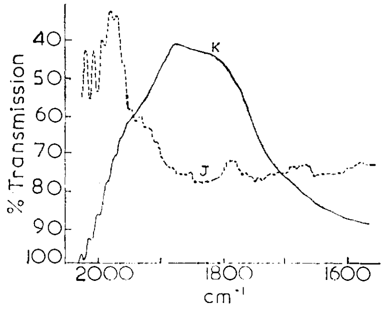

FIG. 5. Deuterium chloride and diethyl ether. (J) Unmixed gases. (K) Difference spectrum: DCl, 250 mm.; ether, 200 mm.; 10-cm. path-length.

---

[2] Part I, *J.*, 1965, 497.

for the deuterated ether confirms the view that there is no important dependence of the contour on the internal vibrational properties of the ethereal part of the complex.

It is to be expected that the interpretation of the band contours for these complexes should be essentially the same as that for complexes formed by hydrogen chloride. Inspection of the Figures shows that there are shoulders both on the low- and high-frequency sides of the main peak in each case. The high-frequency side is probably slightly less reliable than the low-frequency side, because of other absorption. The band contours were confirmed by means of observations on mixtures having several different combinations of partial pressures, using both the difference and subtraction techniques described previously. The exact positions of the inflections, particularly on the high-frequency side, are difficult to locate accurately, but for the present purpose this is not important. If the inflections are caused by weak bands overlapping the main band, as seems most probable, the frequencies of the shoulders will not, in any case, give directly the frequencies at which the weak bands occur. The sum-and-difference-band interpretation given for hydrogen-bonded complexes suggests that bands are to be expected at about 90—100 cm.$^{-1}$ from the main peak, since the low-frequency stretching vibration is unlikely to be very different for the two cases. This interpretation of the shoulders is in accord with the experimental observations if it is supposed that sum and difference bands are significantly weaker for deuterated than for non-deuterated complexes. The exact difference in the present case is difficult to estimate, since it depends on the individual contours of the component bands, but an attempt to synthesise the overall contours suggests that a decrease by a factor of about two in the intensity of the combination bands, relative to the main peak, for the deuterium-bonded complex compared with the protium-bonded complex would account for differences in the contours. It is shown, in a later section, that such a suggestion concerning relative intensities is a reasonable one.

Integrated Intensities of Absorption Bands for Protium and Deuterium Complexes.—The measured integrated absorption intensities for the hydrogen–chlorine and deuterium–chlorine stretching bands of the complexes with dimethyl ether are collected in Tables 1 and 2.

TABLE 1.

Intensities of the hydrogen–chlorine stretching band for the complex in mixtures of hydrogen chloride and dimethyl ether.

p_{DME} (mm.)	p_{HCl} (mm.)	p_{C} (mm.)	Optical density 2570 cm.$^{-1}$	2660 cm.$^{-1}$	2480 cm.$^{-1}$	$\frac{\text{O.D. (2660)}}{\text{O.D. (2570)}}$	$\frac{\text{O.D. (2480)}}{\text{O.D. (2570)}}$	I.I (cm.$^{-1}$)	S_v (cm.$^{-2}$ atm.$^{-1}$)
100	350	9·5	0·31	0·21	0·24	0·68	0·77	85·8	1580
125	250	8·5	0·34	0·22	0·25	0·65	0·74	89·5	1840
125	250	8·5	0·30	0·22	0·22	0·73	0·73	86·4	1780
250	125	8·5	0·35	0·23	0·25	0·66	0·73	92·5	1900
200	200	11	0·44	0·31	0·34	0·69	0·77	122	1940
150	300	12	0·50	0·34	0·38	0·68	0·76	140	2040
150	350	14	0·55	0·38	0·43	0·69	0·78	151	1890

p_{DME} and p_{HCl} are initial pressures; p_{C} is the equilibrium pressure of the complex; I.I. is the integrated band intensity, using $\log_{10} I_0/I$; S_v is defined in the text.

TABLE 2.

Intensities of the deuterium–chlorine stretching band for the complex in mixtures of deuterium chloride and dimethyl ether.

p_{DME} (mm.)	p_{DCl} (mm.)	p_{C} (mm.)	I.I. (cm.$^{-1}$)	S_v (cm.$^{-2}$ atm.$^{-1}$)
100	90	2·5	13·9	970
200	180	10	55·1	960
147	270	11	62·9	1000
300	135	11	65·1	1040
350	227	21	125	1040

For definitions, see footnote to Table 1.

In the Tables, p_{DME}, p_{HCl}, and p_{DCl} denote initial pressures introduced into the cell. The pressure of the complex has been calculated on the basis of a dissociation equilibrium constant of 4·3 atm.[3]

It will be noticed from columns 7 and 8 of Table 1 that, for each of the side-bands, the ratio of peak intensity relative to the central maximum is constant, within experimental error, over the whole pressure range. The assignment of all three components to the same complex, as discussed in Part I, is therefore supported by the relative intensities of the bands.

The integrated intensity (I.I.) for the complete band was obtained for each mixture by direct measurement of the area under the absorption curve, and is given in cm.$^{-1}$, the optical density being defined as $\log_{10} I_0/I$. In the last column of each Table is collected values of S_{v}, defined as

$$S_{\mathrm{v}} = \frac{\text{I.I.} \times 760 \times 2{\cdot}303}{p_{\mathrm{C}} \times \mathrm{l}},$$

where l is the length of the cell. In calculating S_{v} (column 10), which gives the integrated intensity for one atmosphere of the complex at a path length of 1 cm., optical densities were expressed as $\log_e I_0/I$, so that direct comparison could be made with values of S_{v} reported for free protium and deuterium chlorides. The accuracy of the integrated intensities is not high, though the error is probably not more than 10%. There is, however, a much greater uncertainty in S_{v}, arising from the uncertainty in the dissociation equilibrium constant. The value of 4·3 atm. employed here is estimated from the work of Shidei.[3] The determinations of Gladishev and Syrkin [4] suggest that the value may in fact be as much as 50% lower. It seems probable that the mean values of S_{v} obtained here, 1850 and 1000 cm.$^{-2}$ atm.$^{-1}$ for the complexes of protium chloride and deuterium chloride, respectively, represent lower limits. With this in mind, we may compare the intensities with those of the free acids, for which values of 130 and 66·6 cm.$^{-2}$ atm.$^{-1}$, respectively, at 300°K have been obtained.[5] The results show that, in the complex, the bands are intensified by a factor which is probably not less than fourteen. An improved value of the equilibrium constant is required before a better value of the intensification factor can be obtained.

Intensities of Sum and Difference Bands in Protium- and Deuterium-bonded Complexes.—In this section, a simple model for the hydrogen bond is examined for the effect of isotopic substitution on band intensities. In the harmonic approximation for polyatomic molecules, sum and difference bands are not allowed. The effects of introducing electrical and mechanical anharmonicity are examined in turn.

A simple model for the hydrogen bond is provided by a linear triatomic system $\mathrm{Y} \cdots \mathrm{H{-}X}$ having two stretching vibrations. The low-frequency stretching vibration is denoted by ν_1, and the high-frequency one by ν_3. Normal co-ordinates, vibrational quantum numbers, and harmonic wave functions are denoted by Q_1, n, and ϕ, and Q_3, m, and ψ, respectively. Zero-order wave functions are chosen as products of harmonic oscillator functions, $\phi_n\psi_m$.

Electrical anharmonicity. The dipole moment along the direction of the molecule may be expanded in the usual way:

$$M = M_0 + M_1Q_1 + M_3Q_3 + M_{13}Q_1Q_3 + M_{33}Q_3{}^2 + \cdots,$$

where $M_1 = \partial M/\partial Q_1$, $M_{13} = \partial^2 M/\partial Q_1 Q_3$, etc.

The transition moment for the combination band

$$\nu_1(n')\nu_3(m') \longleftarrow \nu_1(n)\nu_3(m)$$

is given by

$$\begin{aligned} R_{n'm',nm} &= \int \phi_n\psi_m M \phi_{n'}\psi_{m'} \mathrm{d}\tau \\ &= M_{13} \int\int \phi_n\psi_m Q_1 Q_3 \phi_{n'}\phi_{m'} \mathrm{d}Q_1 \mathrm{d}Q_3, \end{aligned}$$

---

[3] J. Shidei, *Mem. Coll. Sci., Kyoto Univ.*, 1925, *A*, **9**, 97.

[4] A. T. Gladishev and Ya. K. Syrkin, *Compt. rend. Acad. Sci., U.R.S.S.*, 1938, **20**, 145.

[5] W. S. Benedict, R. Herman, G. E. Moore, and S. Silverman, *J. Chem. Phys.*, 1957, **26**, 1671.

for the case under consideration. The integral, which vanishes unless $n' = n \pm 1$ and $m' = m \pm 1$, is given for the sum band $\nu_1(1)\nu_3(1) \longleftarrow \nu_1(0)\nu_3(0)$ and the difference band $\nu_1(0)\nu_3(1) \longleftarrow \nu_1(1)\nu_3(0)$ by

$$R_{11,00} = R_{01,10} = \frac{M_{13}}{2\gamma_1^{\frac{1}{2}}\gamma_3^{\frac{1}{2}}}, \text{ where } \gamma = \frac{4\pi^2\nu c}{h}.$$

The dependence of M_{13} on isotopic substitution may, to a first approximation, be allowed for by substitution of mass-weighted internal co-ordinates in the second-order terms, *viz.*,

$$Q_1 = \mu_1^{\frac{1}{2}} r_1 \quad \text{and} \quad Q_3 = \mu_3^{\frac{1}{2}} r_3,$$

where μ is the appropriate reduced mass. Hence, after writing

$$M = M_0 + M_1' r_1 + M_3' r_3 + M_{13}' r_1 r_3 + \cdots,$$

we have

$$R_{11,00} = R_{01,10} = \frac{M_{13}'}{2(\mu_1\gamma_1\mu_3\gamma_3)^{\frac{1}{2}}}.$$

The ratio of the transition moment for the sum and difference bands of the protium-bonded complex to that for the deuterium-bonded complex for is given by

$$\frac{R_{11,00}{}^{\mathrm{H}}}{R_{11,00}{}^{\mathrm{D}}} = \frac{R_{01,10}{}^{\mathrm{H}}}{R_{01,10}{}^{\mathrm{D}}} = \left[\frac{(\mu_1\gamma_1\mu_3\gamma_3)^{\mathrm{D}}}{(\mu_1\gamma_1\mu_3\gamma_3)^{\mathrm{H}}}\right]^{\frac{1}{2}},$$

where the superscripts H and D refer to the two complexes.

The major change on isotopic substitution concerns the hydrogen stretching vibration; the low-frequency stretching vibration and the corresponding reduced mass will change much less. In the approximation which regards the small changes in μ_1 and γ_1 as negligible compared with those in μ_3 and γ_3, we have

$$\frac{R_{11,00}{}^{\mathrm{H}}}{R_{11,00}{}^{\mathrm{D}}} = \frac{R_{01,10}{}^{\mathrm{H}}}{R_{01,10}{}^{\mathrm{D}}} = \left[\frac{(\mu_3\gamma_3)^{\mathrm{D}}}{(\mu_3\gamma_3)^{\mathrm{H}}}\right]^{\frac{1}{2}} = \frac{R_{01,00}{}^{\mathrm{H}}}{R_{01,00}{}^{\mathrm{D}}}$$

The effect of introducing electrical anharmonicity is to allow sum and difference bands which in each case have, to a first approximation, the same intensity relative to the protium and deuterium stretching vibrations.

Mechanical anharmonicity. The potential function for the model being considered may, for small displacements, be expressed in terms of the normal co-ordinates as

$$V = k_1Q_1^2 + k_3Q_3^2 + k_{113}Q_1^2Q_3 + k_{133}Q_1Q_3^2 + k_{111}Q_1^3 + k_{333}Q_3^2$$

The function is complete up to and including cubic terms, since it is required, by symmetry, that the coefficients of other cubic terms should be zero. The function may be written as the sum of harmonic and anharmonic contributions,

$$V = V_{\mathrm{H}} + V_{\mathrm{A}},$$

and first-order perturbation theory applied, taking V_{A} as the cubic terms and zero-order wave functions as products of harmonic oscillator functions. The first-order perturbed wave functions are given in the usual way by

$$\Psi_{nm} = \Psi_{nm}{}^{\circ} + \sum_{i,j=0}^{\infty} \frac{W_{mn,ij}}{E_{nm} - E_{ij}} \Psi_{ij}{}^{\circ},$$

where $\quad \Psi_{mn}{}^{\circ} = \phi_n\psi_m \quad$ and $\quad W_{mn,ij} = \int \phi_n\psi_m V_{\mathrm{A}} \phi_i\psi_j \mathrm{d}\tau,$

ϕ_n and ψ_m having been defined in the previous section.

Inspection of the potential function shows that the term which can lead to mixing of wave functions appropriate to sum and difference bands, through intensity-stealing from

$\nu_3(1 \longleftarrow 0)$, is $k_{133}Q_1Q_3^2$. We concentrate initially on this perturbation, choosing a model in which the dominant cubic term is $k_{133}Q_1Q_3^2$. The coefficient k_{133} will change on isotopic substitution, and, in order to take account of this effect on the cubic terms, the normal co-ordinates may, for this purpose, be approximated as mass-weighted displacement co-ordinates r_1 and r_3, the stretching of the hydrogen bond and the hydrogen stretching displacement, respectively. The isotopically independent term in the potential function, in terms of the internal co-ordinates $k_{133}'r_1r_3^2$, transforms to $(k_{133}'/\mu_1^{\frac{1}{2}}\mu_3)Q_1Q_3^2$.

The wave functions of the four states which are of interest are found to be:

$$\Psi_{00} = N_1(\phi_0\psi_0 - \alpha\phi_1\psi_0);$$

$$\Psi_{01} = N_2(\phi_0\phi_1 - 3\alpha\phi_1\psi_1);$$

$$\Psi_{10} = N_3(\phi_1\psi_0 + \alpha\phi_0\psi_0 - \sqrt{2}\alpha\phi_2\psi_0);$$

and

$$\Psi_{11} = N_4(\phi_1\psi_1 + 3\alpha\phi_0\psi_1 - 3\sqrt{2}\alpha\phi_2\psi_1),$$

where

$$\alpha = \frac{k_{133}}{2\sqrt{2}h\nu_1 c\gamma_1^{\frac{1}{2}}\gamma_3}, \gamma = \frac{4\pi^2\nu c}{h},$$

and N_i are normalisation factors.

The mixing in of states which are removed by more than about $hc\nu_3$ has been neglected. The separation will normally be about ten times $hc\nu_1$, and, in any case, such states will not contribute directly to the intensities being considered. The transition moment of the sum band $\nu_1\nu_3$, $11 \longleftarrow 00$, given by

$$R_{11,00} = N_1N_4\int\Psi_{00}M\Psi_{11}d\tau,$$

may be evaluated by taking the term in M_i which allows the harmonic oscillator transition $\nu_1\nu_3$, $01 \longleftarrow 00$, *viz.*, M_3Q_3. This leads to

$$R_{11,00} = \frac{\sqrt{2}N_1N_4M_3\alpha}{\gamma_3^{\frac{1}{2}}}.$$

Now,

$$M_3 = \frac{\partial M}{\partial Q_3} = \frac{1}{\mu_3^{\frac{1}{2}}}\frac{\partial M}{\partial r_3} = \frac{M_3'}{\mu_3^{\frac{1}{2}}} \quad \text{and} \quad k_{133} = \frac{k_{133}'}{\mu_1^{\frac{1}{2}}\mu_3},$$

where M_3' and k_{133}' are independent of isotopic substitution.

Hence,

$$R_{11,00} = \frac{N_1N_4M_3'k_{133}'}{2h\nu_1 c(\mu_1\gamma_1)^{\frac{1}{2}}(\mu_3\gamma_3)^{\frac{3}{2}}}.$$

$R_{01,10}$, the transition moment for the difference band, differs only in the normalisation factors. Alternatively, the transition moment of the sum band is given in terms of $R_{01,00}$, the moment of the harmonically allowed transition, by

$$R_{11,00} = \frac{N_4}{N_2}\alpha R_{01,00} \quad \text{or} \quad \frac{R_{11,00}}{R_{01,00}} = \frac{N_4k_{133}'}{\sqrt{2}N_2h\nu_1 c(\mu_1\gamma_1)^{\frac{1}{2}}(\mu_3\gamma_3)}.$$

The effects of isotopic substitution on the transition moment are readily investigated. The main changes produced are those in μ_3 and ν_3, and, to a first approximation, the effects on μ_1 and ν_1 may be neglected. Under these conditions, the ratio of the transition moments for the deuterium and protium complexes is given by

$$\frac{R_{11,00}^{\mathrm{D}}}{R_{11,00}^{\mathrm{H}}} = \left[\frac{N_4^{\mathrm{D}}(\mu_3\nu_3)^{\mathrm{H}}}{N_4^{\mathrm{H}}(\mu_3\nu_3)^{\mathrm{D}}}\right]^{\frac{3}{2}},$$

where the superscripts D and H refer to the two complexes. Since the absorption intensity, I, of a band is related to R by

$$I = \frac{8\pi^3N\nu R^2}{3hc},$$

the ratio of the intensities for the sum bands in the two cases is given by

$$\frac{I_{11,00}{}^{\mathrm{D}}}{I_{11,00}{}^{\mathrm{H}}} = \frac{N_4{}^{\mathrm{D}}(\mu_3{}^3\nu_3{}^2)^{\mathrm{H}}}{N_4{}^{\mathrm{H}}(\mu_3{}^3\nu_3{}^2)^{\mathrm{D}}}.$$

A similar expression is obtained for the difference bands.

In the simplest approximation, $\mu_3{}^{\mathrm{D}}/\mu_3{}^{\mathrm{H}} = 2$ and $\nu_3{}^{\mathrm{H}}/\nu_3{}^{\mathrm{D}} = \sqrt{2}$, which leads to a sum band for the deuterium-bonded complex with an intensity one quarter of that for the protium-bonded complex, when the perturbation is small and the ratio of the normalisation factors is close to unity. For larger perturbations, the intensity ratio will be somewhat less than four, on account of the normalisation factors, provided second-order effects may still be neglected. Experimentally, it is more convenient to compare the intensities of sum and difference bands with the observed intensity of the allowed X–H or X–D stretching vibration in each case. In the harmonic approximation, the former is twice as intense as the latter. It can be shown, from the equations given above and by using the same approximations, that the intensities of the sum and difference bands, relative to the intensity of ν_3, $1 \longleftarrow 0$, are twice as great for the protium-bonded as for the deuterium-bonded complex.

The model for the hydrogen bond which includes a significant perturbation $k_{133}Q_1Q_3{}^2$ is capable of explaining a lower intensity of the sum and difference bands for deuterium-bonded complexes compared with protium-bonded ones. The physical interpretation of such a perturbation can be readily seen if two terms in the potential function are written together as $(k_3 + k_{133}Q_1)Q_3{}^2$. In approximate terms, k_{133} is a measure of the variation of the X–H stretching force-constant with change in hydrogen-bond length. A particular type of anharmonicity is identified as leading, in first order, to lower relative intensities of sum and difference bands on deuterium substitution. It may be pointed out, in this connection, that the term $k_{113}Q_1{}^2Q_3$ in the potential function also leads to infrared activity in sum and difference bands. A treatment similar to that given above shows that, if the intensity is derived from this perturbation, then the combination bands for the deuterium-bonded complex are expected to be relatively more intense than for the protium-bonded one. The origin of the intensity in this case is quite different, for it is derived from the dipole-moment derivative M_1. The intensity is stolen from the protium- or deuterium-bond stretching vibration ν_1. There is very little information available about such intensities. On the other hand, it is well known that M_3 is frequently greatly enhanced for hydrogen-bonded groups. In the present case, it is shown in an earlier section that M_3 is probably about four times greater than for free hydrogen chloride. The perturbation $k_{133}Q_1Q_3{}^2$ transfers some of the intensity derived from this moment into the neighbouring combination bands, thus providing a direct explanation of their origin and of their appreciable intensity.

In general, there will be contributions to the intensity from electrical anharmonicity and from both of the cubic terms in the potential function. When one of these effects is dominant and the others are small, it is shown that one can distinguish between the three effects by means of their influence on the dependence of the intensities of combination bands on isotopic substitution. The model is too simple to be applied quantitatively to the hydrogen chloride–ether complexes, for which the intensity of the side-bands is probably sufficiently large for a first-order perturbation treatment to be inadequate. However, it shows qualitatively that it is not unreasonable to suppose that sum and difference bands for deuterium-bonded complexes will be appreciably weaker than for protium-bonded complexes.

If, in general, this is the most important mechanism for intensity-transfer into sum and difference bands, it is of interest in another connection. It provides one reason why the broadening of hydrogen stretching bands is generally greater for protium complexes than for deuterium complexes. Such observations have frequently been made for conditions under which sum and difference bands have not been resolved. If it is supposed that the combination bands are weaker for the deuterium-bonded complex, then the above general observation receives an explanation.

We are grateful to the D.S.I.R. for the award of a studentship to one of us (J. E. B.).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET, LONDON W.C.1.

[*Received, April* 14*th*, 1964.]