$$\delta\rho(Lr)=-\frac{\alpha e}{16\pi^5}\frac{(2a)^{3/2}\lambda_0^{3/2}}{[1+a^2|\mathbf{K}+\mathbf{k}|^2]^2}\{\exp i\mathbf{K}\cdot\mathbf{r}/\lambda_0\}\int_0^{\pi/2}\cos^3\psi d\psi\log[1+\tfrac{1}{4}\{k^2-(k_0-E_1/\hbar c)^2\}\cos^3\psi]. \quad (38)$$

Integrating over all values of $\mathbf{L}$ and introducing $\delta\rho(r)$ into Eq. (35) one obtains for the dominant term of V_{1k}

$$V_{1k}\sim-\frac{4Z\alpha e^2}{15\pi^2}\frac{(2a)^{1/2}\lambda_0^{1/2}}{1+a^2k^2}\log\{1+\tfrac{1}{2}[(1+k^2)^{1/2}-1]\}. \quad (39)$$

For large values of k this expression behaves like $(\log k)/k^2$ instead of like $1/k$ as obtained using the d'Alembertian. The integral for δE_{1s} will, therefore, converge, and the result for the non-secular terms is that δE_{1s} is of the order $Z^3\alpha^5$.

As a consequence of these calculations one finds that the energy levels are depressed, the displacement corresponding to a quantum defect $\Delta=n-n^*$ which is positive. It is not possible, therefore to ascribe any part of the observed discrepancy in the doublet separations of hydrogen to the new potential, since the experimentally observed values of the doublet separations in the Balmer series are always less than those predicted by the relativistic fine-structure theory, whereas, the displacement in the energy levels corresponding to the new potential correspond to an increased separation of the doublet components. Furthermore, the percentage change in the doublet separations would be smaller than the experimentally observed discrepancy of about 3 percent by a factor of at least 10. The nature of the potential necessary to explain the observed results has been considered by Kemble and Present.[13] It needs to be emphasized here, only that the potential to which the electron-positron theory gives rise is not of the requisite character.

The author wishes to express his gratitude for frequent suggestions and help given by Professor J. R. Oppenheimer throughout the course of this investigation and to Dr. R. Serber and Mr. A. Nordsieck for many helpful discussions of the problem.

[13] Kemble and Present, Phys. Rev. **44**, 1031 (1933).

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The Raman Spectrum of Heavy Chloroform

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The Raman spectrum of chloroform made from deuterium has been photographed and the line shifts measured. The three types of isotope effects observed in the spectrum of heavy chloroform have been discussed. By treating different groups of atoms in the molecule as entities satisfactory agreement between calculated and observed values for the isotope displacements can be secured. Some idea of the nature of the role played by the chlorines in the C–H "bending" and "stretching" vibrations is obtained.

THE heavy chloroform, made from deuterium by Dr. F. W. Breuer of the Chemistry Department of Pennsylvania State College, was placed at our disposal for the study of its Raman spectrum. It was contained in a sealed glass tube 6 mm in diameter and 30 cm long, wrapped in black insulation tape with the exception of the lower 5 cm adjacent to the flat Pyrex glass window, the portion occupied by the fluid.

The arrangement of apparatus for irradiating the tube was essentially the same as that described by one of us[1] except that the high potential quartz mercury tube was replaced with the 220-volt Hanovia quartz mercury arc in its metal housing turned to the vertical position. As was shown in the previous paper this disposition prevents a temperature gradient across the diameter of the irradiation tube, with its attendant troublesome refraction, obviating as well the necessity of an air blast. The light from the arc

[1] R. W. Wood, *Raman Spectra of Heavy Water*, Phys. Rev. **45**, 392 (1934).

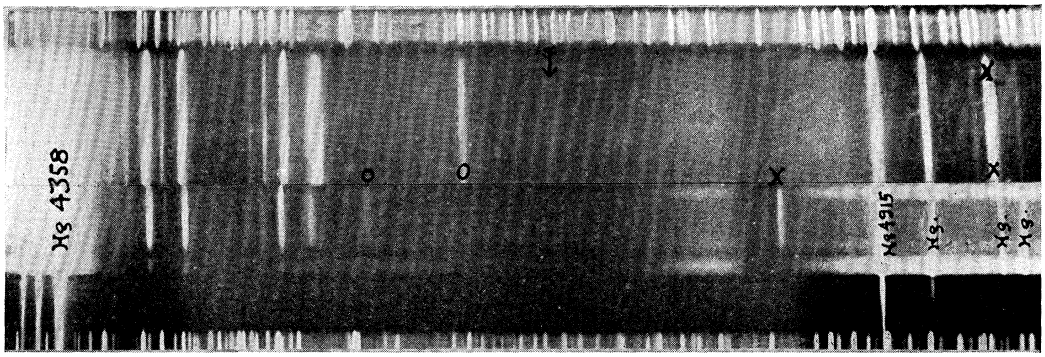

FIG. 1. Raman spectra of light chloroform (above) and heavy chloroform (below).

was focused on the tube by a cylindrical lens consisting of a long tube 4 cm in diameter filled with a solution of sodium nitrite. An absorption cell made from one of the flat glass tubes (in which a certain brand of tooth brush is sold) filled with a strong solution of praseodymium was interposed between the cylindrical lens and the irradiation tube which was backed by a concave cylindrical reflector of this sheet aluminum. A total reflecting prism, immediately below the window of the vertical irradiation tube reflected the emitted light to the achromatic lens which focused the image of the end of the tube on the spectrograph slit. Very full directions for the alignment of tube, prism and lens will be found in the paper referred to above. An exposure of twenty-four hours was given with the large single prism spectrograph of 1-meter focus employed by one of us in work on the Raman effect during the past six years. Excitation by lines of shorter wavelength than 4358 was not employed as chloroform suffers photochemical changes in ultraviolet light.

Spectrograms of ordinary and heavy chloroform are reproduced in Fig. 1. The line marked x, due to the vibration of the hydrogen is shifted towards the exciting line (4358) falling at the center of the praseodymium absorption band, the line marked O, to a lesser degree, and the other lines by still smaller amounts. A faint trace of the line at 1505 was found on the plate made with ordinary chloroform. It was very broad and hazy and its position is marked with an arrow in Fig. 1 as it may be too faint to reproduce. The $\Delta\nu$ values are given in Table I.

The weighted means of the frequency shifts from the exciting lines which are given in Table I should be accurate within one or two wave numbers.

TABLE I. *Raman spectrum of ordinary and heavy chloroform.* Exciting lines $a=\lambda4358$, $b=\lambda4347$, $c=\lambda4339$.

		$CHCl_3$ $\Delta\tilde{\nu}$	$CDCl_3$ $\Delta\tilde{\nu}$			$CHCl_3$ $\Delta\tilde{\nu}$	$CDCl_3$ $\Delta\tilde{\nu}$
	C	261.4		V_3	b	668.2	651.2
V_1	b	261.5	264.1		a	668.4	650.5
	a	262.3	261.7	V_4	a	761.2	737.6
V_2	b	365.9	368.0	V_5	a	1215.6	908.3
	a	365.9	366.2	$2V_4$*	a	1505	
	c	670.2		V_6	a	3018.9	2256.0

Weighted means of frequency shifts

$CHCl_3$	$\Delta\tilde{\nu}=$ 262.0 (15)	365.9 (10)	668.3 (10)	761.2 (10B)	
	1215.6 (5)	1505 (0)	3018.9 (10)		
$CDCl_3$	$\Delta\tilde{\nu}=$ 262.0 (15)	366.5 (10)	650.8 (10)	737.6 (10B)	
	908.3 (5)	2256.0 (10)			

* Could not be measured on comparator. Position could be quite accurately estimated with respect to neighboring iron comparison lines.

DISCUSSION OF RESULTS

The modes of vibration of a symmetrical pentatomic tetrahedral molecule are worked out in Born's *Electromagnetischen Lichttheorie*.[2] This type of molecule gives rise to four distinct vibrational frequencies. Two of these vibrations are triple, one double and the remaining one singly degenerate. It is well known[3] that in the unsymmetrical molecule six distinct frequencies should appear. (The triple vibrations split up into a single and a double vibration.) Chloroform is obviously a molecule of the latter type.

From an inspection of the results given in Table I it is apparent that three distinct types of isotope effects are present in the spectrum of

[2] Max Born, *Electromagnetischen Lichttheorie*, p. 554.
[3] Jenny E. Rosenthal, Phys. Rev. **45**, 538 (1934).

$CDCl_3$. From the magnitude of the isotope shifts we are able immediately to tell the manner in which the hydrogen moves with respect to the other atoms in the molecule in the execution of particular modes of vibration.

We shall show that the isotope effects can be calculated with considerable exactness by treating the chloroform molecule as a simple diatomic oscillator in which composite groups of atoms vibrate as entities.

Case I

The lines in the $CDCl_3$ spectrum unshifted with respect to those of $CHCl_3$ (V_1 and V_2). In this case, effectively, HCl_3 is vibrating against the central carbon atom. It is obvious, however, that the substitution of a deuterium atom for hydrogen in such an oscillator will produce so small a change in the reduced mass as to make the isotope effect too small to be observed. Inspection of the normal modes of vibration of chloroform shows that V_1 and V_2 involve hydrogen bending and stretching. It is apparent, however, that these should be the lowest frequencies of the molecule.

Case II

The lines in the $CDCl_3$ spectrum slightly shifted with respect to those of $CHCl_3$ (V_3 and V_4). To account for this small isotope effect in a simple manner it is only necessary to assume that C–H vibrates as an entity against the chlorine atoms in these particular vibrations. Assuming the frequency of the oscillator can be expressed by the equation

$$\tilde{\nu}_H=(1/2\pi)(f/\mu_1)^{\frac{1}{2}},\quad \mu_1=M_{CH}\cdot M_{Cl_3}/M_{CHCl_3}. \quad (1)$$

A similar expression can be written for $\tilde{\nu}_D$. Since the force constants for the two isotopic molecules are identical, the ratio of the frequencies becomes

$$\tilde{\nu}_H/\tilde{\nu}_D=(M_{CD}\cdot M_{CHCl_3}/M_{CH}\cdot M_{CDCl_3})^{\frac{1}{2}}. \quad (2)$$

A substitution of the numerical data in Eq. (2) yields the calculated values given in Table II. The agreement between the observed and calculated values is all that could be desired from such simple considerations. This agreement seems to show quite definitely that the assumption of CH vibrating as an entity in V_3 and V_4 is not very far from the actual state of affairs.

TABLE II. *Calculated and observed values of doublet separations.*

	$\Delta\tilde{\nu}_H-\Delta\tilde{\nu}_D$ (Obs.)	$\Delta\tilde{\nu}_H-\Delta\tilde{\nu}_D$ (Calc.)
V_3	17.5 cm^{-1}	21.4 cm^{-1}
V_4	23.6	24.9
V_5†	307.3	307.3
V_6	762.9	763.2

† V_5 Calc. and V_5 observed were made to agree purposely by the choice of α.

Case III

The lines in the $CDCl_3$ spectrum greatly shifted with respect to those of $CHCl_3$ (V_5 and V_6). To account for these large isotope displacements in a rough manner it is only necessary to consider the hydrogen atom as vibrating against the rest of the molecule. Such a calculation will give displacements of the correct order of magnitude. V_5 is a double vibration and consists mainly of CH "bending." V_6 is single and is of the type commonly called a CH "stretching" vibration. We can consider V_5 and V_6 to be C–H vibrations to a first approximation. However, we certainly cannot neglect the influence of the other atoms in the molecule on these vibrations. The effect of the chlorines on this simple C–H oscillator leaves two alternatives. The chlorine atoms can vibrate in such a manner as effectively to increase the mass of the carbon atom or effectively increase the mass of the hydrogen atom. A trial calculation showed the latter alternative to be in agreement with experiment. In this case our oscillator is assumed to be $(M_H+\alpha)\longleftrightarrow M_c$. The expression for the ratio of the frequencies becomes.

$$\tilde{\nu}_H/\tilde{\nu}_D=((M_D+\alpha)M_{CH}/(M_H+\alpha)M_{CD})^{\frac{1}{2}}. \quad (3)$$

Using the experimental values of V_{5H} and V_{5D} we are able to determine the value of α from Eq. (3). The value found for α was 0.074 atomic weight units. Once α has been determined it is now possible to calculate V_{6H} or V_{6D} if one or the other is known. The calculated value of the doublet separation is given in Table II.

We are deeply indebted to Dr. F. W. Breuer for the loan of the heavy chloroform we have used. His paper on its preparation will appear elsewhere. One of us (R) has had the benefit of helpful discussions with Dr. W. Altar of the Physics Department, Pennsylvania State College, concerning the modes of vibration of the chloroform molecule.

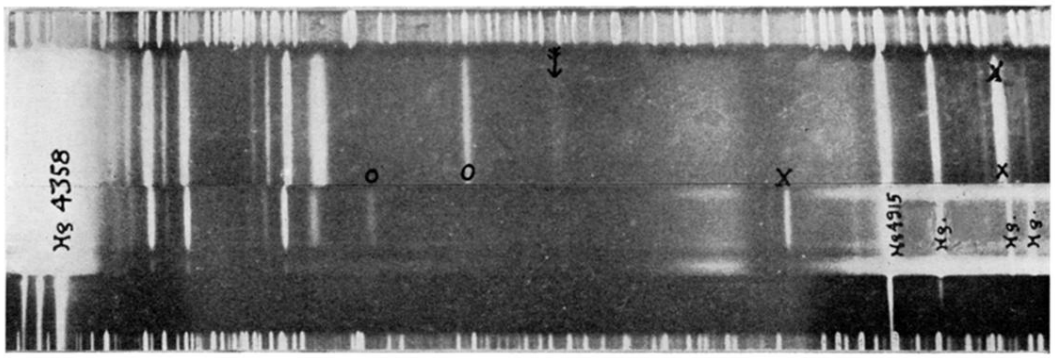

FIG. 1. Raman spectra of light chloroform (above) and heavy chloroform (below).