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Nuclear Isotope Shift in the Spectra of HgH^+ and HgD^+

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The structure of the lines in the band spectra of HgH^+ and HgD^+, excited in a hollow cathode tube, is studied with Fabry-Perot etalons. The lines are found to be broadened, with traces of structure, an effect caused by the isotopic constitution of mercury. The structure shows that there is no anomalous behavior of components belonging to the odd Hg isotopes due to hyperfine splitting, but the half-widths of the lines differ widely from the expected ones. From the measured half-widths the shifts between the consecutive even isotopes of Hg are evaluated and then the differences between these and the values obtained from the formulas for the normal vibrational and rotational isotope effect calculated. These additional shifts show the same behavior as the shifts found some years ago in HgH and HgD and therefore must be explained as nuclear isotope shifts, that is, shifts connected with differences in nuclear volume of the different isotopes of Hg. For the lowest vibrational bands the shifts are of the same sign as in HgH, but decrease with the vibrational energy of both upper and lower states, changing sign for sufficiently high vibrational energies and probably tending in the limit of dissociation to the shifts found in the corresponding quadrupole line 2815A of Hg II. Consideration of the data on the nuclear isotope shifts in HgH, HgH^+, Hg I and Hg II permits some conclusions about the deformation of the electron clouds in Hg and Hg^+ caused by the attachment of a hydrogen atom, and a rough calculation of the nuclear shifts in the molecular levels of HgH and HgH^+.

THAT different isotopes of the same element emit spectra in which the lines are relatively shifted is well known in atomic spectra. The shifts found in the light elements are caused by differences in the masses of the nuclei; in proceeding from the lighter to heavier elements these mass isotope shifts are found to become rapidly smaller, and for Mg are difficult to observe. For elements heavier than argon the shifts are so small that they can be of no importance experimentally and therefore the shifts found in the spectra of heavier elements must be explained in a different way. Probably these latter shifts are caused by differences in the distribution of the electric field in the immediate neighborhood of the nuclei, i.e., in the region where the field differs considerably from the Coulomb field. Following a suggestion of Professor Oppenheimer, I shall hereafter call these *nuclear* isotope shifts. For several years I have been interested in the question as to whether the influence of other nuclear properties besides mass could be detected in band spectra. For example, one would expect differences in the electric fields to influence the positions of lines, and the presence of magnetic moments to produce hyperfine structure. Both problems are more complicated than in atomic spectra. In the former case, with which we shall be mainly concerned in this paper, the chief difficulty is that the mass shifts of the corresponding lines of isotopic molecules are considerable, and even in the most favorable cases cannot be neglected. But a similarity with the case of atomic spectra is revealed if we consider the *differences* between the observed shifts and the ones calculated by the well-known formulas for the rotational and vibrational isotope effects. For isotopic molecules differing very much in reduced mass (i.e., when a light atom in the molecule is exchanged for its isotope) the true mass shift differs from the shift given by the above-mentioned formulas. Differences in the rotational and vibrational effects, as well as shifts of whole band systems, have been found in many spectra, especially in the hydrides and deuterides, during the last eight years. As was shown by Van Vleck[1] and others, their magnitudes are in agreement with calculations based on general quantum-mechanical theory. These departures from the usual formulas diminish with the differences of reduced mass so rapidly that even for the isotopic pair $C^{13}N^{14}$ and $C^{12}N^{14}$ excellent agreement with the usual formulas has been obtained.[2] But some years ago additional

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[1] J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

[2] F. A. Jenkins and D. E. Wooldridge, Phys. Rev. **53**, 137 (1938).

shifts were discovered by the author[3] in the case of isotopic molecules $Hg^{198}H$, $Hg^{200}H$, $Hg^{202}H$, and $Hg^{204}H$, for which the mass differences cannot be responsible, the shifts found being more than a hundred times larger than the expected mass correction shifts. These shifts have been explained as nuclear isotope shifts. Bohr[3] has shown how the correlation with the shifts in the atomic spectrum of Hg as well as the observed dependence of this effect on the vibrational and possibly also rotational energy of the molecule is to be understood. A confirmation of this effect has been found in the case of the HgD spectrum,[4] but up to the present it has been detected in no other spectrum. It was pointed out[4] that if the explanation is correct, the investigation of the spectra of the molecules HgH^+ and HgD^+ would be very promising for this purpose. Consequently experiments were performed with a Lummer-Gehrcke plate for high resolving power, but in view of the low intensity of this spectrum in the mercury arc I have not been able to photograph it in a reasonable exposure time. Recently, while performing some experiments with the spectrum of boron[5] I succeeded in examining the pattern of some exceedingly weak lines in the region of 2400A arising from Fe contamination. This was made possible by the relatively great transparency of Hochheim amalgam used on the Fabry-Perot plates. The etalon also proved to have sufficient resolving power in the farther ultraviolet, as the study of the fivefold structure of the line 2262A of HgII has shown. On the other hand, it was shown by Almy and Horsfall[6] that the spectrum of HgH can be excited in a hollow cathode discharge with great intensity, and therefore a new attempt to analyze the structure of the lines of the spectra HgH^+ and HgD^+ was made. This time the experiments were successful and the results are reported here.

The band spectra of HgH^+ and HgD^+ were excited in a hollow cathode discharge tube, with a d.c. power supply described in detail in an earlier paper.[5] The tube has proved to be very efficient for producing intense spectra, as experiments with B,[5] Be,[7] HgII,[8] HgH^+ and HgD^+, and ZnH[9] have shown, and therefore it seems worth while to give a more detailed description of this tube, in spite of the fact that during recent years many hollow cathode discharge tubes of different shapes have been reported. The tube is especially suitable for experiments in which high electric currents must be used. It has been tried with 2.5 amp. for short intervals of time and with continuous running at 1.5 amp. A schematic diagram of the tube is given in Fig. 1. The water-cooled anode *A* and the removable water jacket *W* are of brass and the cathode *K* (about 7 cm long and 8 mm in diameter) of pure copper. As has been previously pointed out,[5] copper cathodes are especially advantageous in view of the purifying action of the clean-up. The anode is separated from the cathode by a gap of about 1 mm and they are held in position by a glass cylinder *G*. The smallness of the gap is very important when high currents are used, because in case of larger separations the discharge changes suddenly into an arc burning along the walls of the glass cylinder, which after a short while causes the glass to crack.[10] The glass cylinder is sealed to the anode and cathode with Apiezon Q wax. With

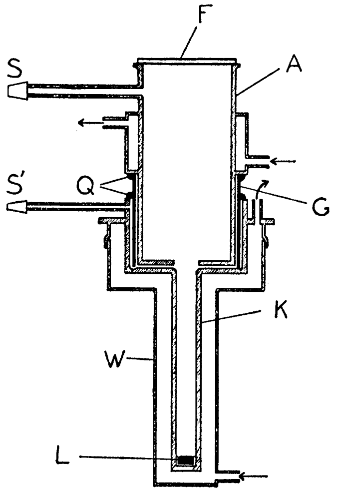

FIG. 1. Diagram of discharge tube.

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[3] S. Mrozowski, Zeits. f. Physik **95**, 524 (1935).

[4] S. Mrozowski, Zeits. f. Physik **99**, 236 (1936).

[5] S. Mrozowski, Zeits. f. Physik **112**, 223 (1939).

[6] G. M. Almy and R. B. Horsfall, Phys. Rev. **51**, 491 (1937).

[7] S. Mrozowski, Phys. Rev. **55**, 798 (1939).

[8] S. Mrozowski, Phys. Rev. **57**, 207 (1940).

[9] The results of these experiments will be reported in the near future.

[10] Cf. R. M. Elliott and J. Wulff, Phys. Rev. **55**, 170 (1939). These investigators solved the difficulty in the opposite way—that is, by enlarging the gap. Their solution does not give the high electric field desired in the neighborhood of the hollow part of the cathode.

very high currents (more than 1.5 amp.) this wax softens after a short while and in case of steady running, to prevent the heating of the glass cylinder, the anode should probably be cooled from the inside with water down to the bottom. For liquid-air cooling the lower wax joint must be heated with running water. A special water circuit for this purpose was arranged in one of the cathodes used. The discharge tube was connected with the pumping system at *S* and with the gas supply at *S′*. From *S′* the gas was let into the tube through a groove made in the cathode wall and extending beyond the bottom of the glass cylinder. If gas circulation is needed this groove can be extended along the walls to the bottom of the hollow part of the cathode and covered with long plates tightly fitting so as to allow the gas to flow out only at the bottom of the cathode. This device was used only at the start of these experiments, when an iron cathode was used because the purifying effect of the clean-up on copper was not then appreciated.

A large drop of mercury was placed in an iron cup at the bottom of the cathode and during the experiments the mercury slowly vaporizes, producing a layer of amalgam on the walls of the hollow cathode, but most of it condenses at the bottom of the anode. The latter gives some trouble, because when the drops of mercury grow too large they short-circuit the discharge. The tube must then be opened and the anode cleaned by wiping off the liquid mercury. After setting the tube back into position the discharge runs unsteadily for some time, changing frequently into an arc in the small gap, until all impurities are removed by the discharge from the surface of the cathode.

The discharge occurred in a mixture of helium and hydrogen (or deuterium). Spectroscopically pure helium was admitted in small quantities by a suitable arrangement of stopcocks and as a source of hydrogen a platinum-palladium tube heated by a gas flame was used. Deuterium was obtained from 99.2 percent heavy water by electrolysis and then purified by diffusing it through palladium. A very useful arrangement for this purpose, which is a modification of one used by Professor W. Dziewulski in Wilno, is shown in Fig. 2. It makes possible the admission of any desired small quantity of the purest deuterium while by removing the fused silica cap *Q* it can also be used for the introduction of hydrogen. In most of the experiments helium at about 1 mm pressure mixed with H_2 (or D_2) at a pressure of some tenths of a mm was used. This was found to be the best condition for obtaining an intense HgH^+ spectrum. During operation the hydrogen disappeared by absorption (chiefly in the mercury deposited on the anode), and the proper pressure in the discharge tube was maintained by diffusion from a large container connected with the tube and filled with the $He+H_2$ mixture. But the absorption was so rapid that a new portion of hydrogen had to be added every 10–15 minutes. In view of the slowness of the diffusion along the thin tubes connecting the container with the discharge tube, the hydrogen pressure in the hollow cathode was certainly much lower than in the container.

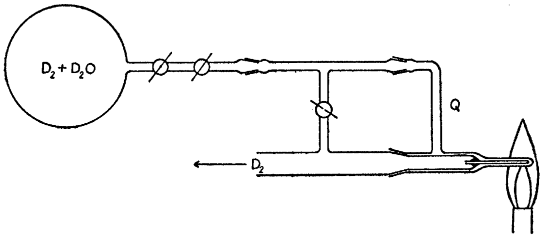

FIG. 2. Arrangement for admitting gas. *Q* is a fused silica cap.

The discharge showed some interesting features. Three types of discharge were observed. When a potential difference is applied which is insufficient for starting the usual glow discharge, only a very weak luminosity in the center of the cathode can be seen. The current is undetectable on an instrument reading to 1/100 amp. This type of discharge is of no use for spectroscopic purposes. If we increase the voltage the usual glow discharge starts suddenly, and if we immediately lower the voltage to such an extent that the current is not more than about 0.3 amp. the glow discharge runs steadily. With higher currents (the limit varies according to circumstances from 0.25 to 0.35 amp. and more) the discharge is unsteady, and after a short while suddenly changes into a new type, apparently not previously described. A sudden increase of current (by about 2 to $2\frac{1}{2}$ times) is accompanied by a corresponding increase of intensity of the cathode glow. This new type has some of the features of an arc discharge, because the mercury drop evaporates very quickly from the iron cup (in about 15 minutes) and the discharge emits a quite different spectrum. No helium lines occur at all, while the Hg, H_2 and HgH lines have very high intensity. But that it is not an ordinary arc is shown by the relatively low temperature. This is not appreciably higher than in the usual glow discharge as can be seen from the distribution of intensities in bands of HgH and HgH^+. In an ordinary mercury arc running on low current the temperature is much higher, since many more lines are observed in branches and higher vibration bands are emitted. Very often this new type of discharge changes suddenly into an arc discharge burning between the upper amalgamated end of the cathode and the anode. In this case a cathode spot is formed, moving rapidly around the cathode, and sometimes going into the hollow part, but never deeper than about 1 cm. This occurs with higher currents while for lower currents the discharge runs with frequent changes back into the ordinary glow discharge.

The condition of the inner surface of the cathode has a very strong influence on the above phenomena. The effects described were observed for cathodes which had been in long use and which had a heavily amalgamated inner surface. The discharge ran in helium with an admixture of hydrogen or in pure helium. If the surface does not contain mercury, as in case of a Fe cathode or a fresh Cu cathode, the limits of instability are much higher, say above 1 amp. The spectrum of the high current type does not differ from that described above, but in the glow discharge the intensity of the HgH bands is very low. The behavior of the bands HgH^+ was not studied, but probably is similar. The intensity distribution is normal in the case of a fresh Cu cathode, but in the case of a Fe cathode shows an abnormally low temperature distribution, only a few lines in each branch being observed. Such abnormal distributions were found by Schüler and his co-workers[11] in other hydride spectra from the hollow cathode. They gave an explanation based on a mechanism of the formation of molecules at the surface of the cathode. The results reported here undoubtedly show the importance of the state of the surface, but seem to indicate that the relations are more complicated than assumed in their explanation.

The spectrograms of the HgH^+ and HgD^+ bands were mostly obtained with the ordinary glow discharge. The new type of discharge was not used for several reasons: The greater steadiness of the glow discharge; the necessity of frequent refilling with fresh mercury; the slightly higher temperature and consequent lack of sharpness of the lines (in the hollow cathode about 20 lines and in the new discharge type one or two more in both branches of the (0,0) band of HgH^+ were observed, in contrast to the usual low current mercury arc, where more than 30 lines have been reported[12]); and finally perhaps the most important reason was the very high intensity of the continuous spectrum of hydrogen in the new type of discharge. This continuum is much more intense in the case of deuterium,[4] and the investigations are still more difficult. The continuous spectrum is especially unfavorable with the Fabry-Perot etalon used which gives, in contrast to the Lummer-Gehrcke plates, a strong continuous background for every line of about 8 percent of the maximum intensity of the line.[5] The Fabry-Perot etalon was used with fused silica spacers of from 7 mm to 30.2 mm. The patterns were photographed in a large interchangeable Hilger spectrograph having a high luminosity quartz optical system. Ilford Monarch and Wellington XPress photographic plates were used. The time of exposure of $\frac{1}{2}$ to $1\frac{1}{2}$ hours was within reasonable limits, so that no special arrangement for constancy of temperature was needed.

On the first exposures no structure could be found in the lines, all lines showing excessive broadening, especially those lying in the longer wave-length region of the spectrum. The lines of Hg II observed under the same conditions and in the same spectral region showed smaller widths which were in agreement with the calculated

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[11] H. Schüler and H. Haber, Zeits. f. Physik **112**, 614 (1939) and other references there given.

[12] The band spectrum of HgH^+ was first found by H. Jeżewski, J. de phys. et rad. **9**, 278 (1928) and later analyzed more correctly by T. Hori, Zeits. f. Physik **61**, 481 (1930). The spectrum of HgD^+ was found and analyzed by the author, Acta. Phys. Polonica **4**, 405 (1936). The analysis of Hori has been corrected and improved constants for both HgH^+ and HgD^+ have been given in a paper by S. Mrozowski and M. Szulc, Acta Phys. Pol. **6**, 44 (1937).

Doppler widths. The latter were obtained by using the temperature of the discharge estimated earlier from the broadening of the boron lines.[5] Therefore the excessive broadening of the HgH^+ and HgD^+ lines was clearly due to some other cause, probably to the isotope effect. A more careful examination of the lines in the (0,0) band revealed that the width of the lines was greatest in the neighborhood of the band head and decreased in the direction of longer wave-lengths, a behavior directly opposite to the expected influence of the normal isotope effect (combined vibrational and rotational effect). This observation led me to measure as carefully as possible the half-widths of the lines. This was done by making series of photographs with a stepwise increase of the plate separation and measuring the breadths of the fringes with a comparator. No photographic photometry was applied because of the time required. But my experience with photometric measurements of the intensity distribution in the boron lines[5] showed the reliability of such direct estimates. The values found for different plate separations differed by no more than 10 percent and the mean values probably differ from the true half-widths by still less. The relative widths are naturally more exact. In the (1,2) band the results have been checked by finding the smallest plate separation for which the interference pattern is continuous, in which case the separation of consecutive orders is equal to the half-width of the line. This estimate is not as reliable as the former ones because the traces of structure found in the wider lines (see below) make the exact point of merging difficult to determine. Some results of these measurements are shown in Table I. In order to get some information from these values about the isotope effect, curves of the intensity distribution were drawn as in Fig. 3. A Doppler shape and a half-width 0.05 cm^{-1} were assumed. The lines due to different isotopes of mercury were taken to have isotope shifts of equal magnitude between the consecutive isotopes. This last assumption holds strictly for the normal isotope effect (vibrational and rotational), but for nuclear isotope shifts the components due to the odd isotopes lie closer to the components due to the even isotopes one unit lighter. This dissymmetry influences the shape of a line considerably when the nuclear isotope shift is greater than the normal one, as happens in a great part of HgH and HgD bands formerly studied. From the calculations given below it follows that in the present case the broadening of the lines is principally due to the normal effect (excluding the case of (0,0) bands, there the dissymmetry again plays no role, but this time because of the relatively larger Doppler broadening) and the components of the odd isotopes lie nearly midway between those of the even isotopes, as was assumed in Fig. 3.

As was previously pointed out[3] the dissymmetry of the nuclear isotope shift is not sufficient to explain the surprising absence of the odd components in the bands of HgH and HgD. A provisional explanation was given in assuming hyperfine structure splitting of these components. That their apparent absence is not at all connected with the nuclear isotope shift follows from the investigations of Svensson[13] in the spectrum of CdH, where the components of the odd Cd isotopes are again missing and where the nuclear isotope shift is negligible in comparison to the normal shifts. The supposition of a hyperfine structure splitting found a strong support in the presence of additional components observed in $^2\Sigma^* \rightarrow {}^2\Sigma$ bands of HgH^3. Possibly the additional

TABLE I. *Width of lines in* HgH^+ *and* HgD^+.

	HgH^+				HgD^+		
BAND	LINE	MEASURED WIDTH	CALC. NORMAL EFFECT WIDTH	BAND	LINE	MEASURED WIDTH	CALC. NORMAL EFFECT WIDTH
(0,0)	44,058 cm^{-1}	0.077 cm^{-1}	0.058 cm^{-1}	(0,0)	44,060 cm^{-1}	0.079 cm^{-1}	0.065 cm^{-1}
(0,0)	43,712	0.059	0.075				
(0,1)	42,110	0.085	0.135	(0,1)	42,670	0.125	0.19
(0,1)	41,916	0.115	0.153				
(1,2)	41,723	0.17	0.155	(1,2)	42,400	0.175	0.22
(1,2)	41,619	0.18	0.168				

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[13] E. Svensson, *Die Bandenspektren des Cadmiumhydrides und -deuterides* (Ivar Hæggström Boktrykeri A. B., Stockholm, 1935), p. 91.

components found in CdH could be explained in the same way although the whole question seems to be more uncertain in this case in view of the possibility pointed out by Svensson of the existence of Cd isotopes not yet detected by the mass spectrograph. The point has been made,[4] that if the apparent absence is connected with hyperfine structure, it should not appear in bands of the type $^1\Sigma \rightarrow {}^1\Sigma$. This agrees with the results on HgH^+ and HgD^+. If the components of the isotopes 199 and 201 should be missing or at least if their intensity were distributed over a larger region, the minimum in the last curve in Fig. 3 would be more pronounced and a splitting of the lines of the (1,2) band into two groups easily observed. The experiments gave only slight traces of structure, corresponding quite exactly to the curves of Fig. 3, and giving support to the correctness of this explanation. Quite recently conclusive evidence for the existence of hyperfine structure in band spectra has been obtained in a reinvestigation of the HgH bands under much improved conditions. New components and differences in structure of the *R* and *Q* lines have been found. These results will be published as soon as microphotometer records of the plates have been evaluated.

On the basis of the curves of Fig. 3 the total isotope shift between the even isotopes of Hg (for instance, 202 relative to 200) can be found by interpolation in the case of the lines whose total half-widths are given in Table I. The values found are presented in Fig. 4. Their accuracy is probably greater than 10 percent and, as can easily be seen from the curves of Fig. 3, is practically independent of the assumption made about the symmetrical position of the odd isotopes. The continuous lines in Fig. 4 give the normal isotope shift (vibrational and rotational effect) calculated from the constants previously found by the author in collaboration with M. Szulc.[12] That the difference of the measured and calculated shifts given in Fig. 4 by thick arrows constitutes a real effect can be seen from Table I, where the widths of the lines calculated for the normal isotope effect are included for comparison. The differences are in some cases so far outside the limits of experimental error that there can be no question about the presence of a nuclear isotope shift. The accuracy of the measured half-widths is shown by the equality of the inclination of the straight lines in Fig. 4, which shows the observed and calculated dependence of the isotope shift on the frequency of the lines in each band of HgH^+.

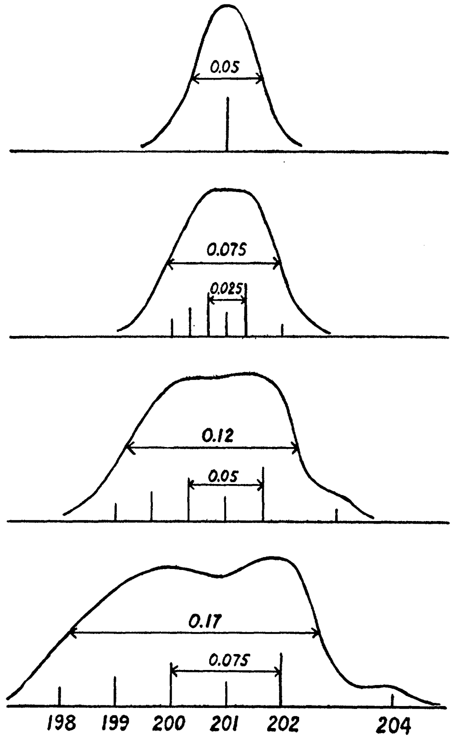

FIG. 3. Intensity distribution in spectral lines.

The differences between the observed and calculated values (Fig. 4) represent the additional isotope shift of the band origins, which are of the same order of magnitude as in HgH and HgD, though considerably smaller. As in the case of HgH they are some orders of magnitude greater than the mass correction shifts of the system origins, especially in the case of a $^1\Sigma \rightarrow {}^1\Sigma$ transition. It was shown[4] that in HgH and HgD these shifts are linear functions of the vibrational energy in both lower and upper states. Their constancy in the $^2\Pi$ state does not contradict this. Furthermore, it was found that this dependence is approximately the same for the hydride and deuteride, although differences were found lying somewhat outside the experimental error. Unfortunately in the HgH^+ and HgD^+ spectra only three bands of each molecule were observed, and the applicability of these rules cannot be proved

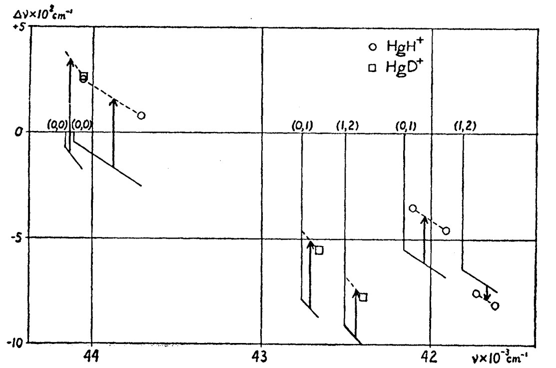

FIG. 4. Shifts of spectral lines. Differences between measured and calculated shifts are shown by the arrows.

directly. Nevertheless the three values allow one to calculate the three coefficients in the linear equation $\Delta\nu = a - b_1E_1 + b_2E_2$, and the approximate equality of the coefficients for the two spectra can be considered as an indirect proof of the correctness of the formula. The equations found are

$$\Delta\nu = 0.0450 \text{ cm}^{-1} - 12\times10^{-6}E_1 - 5.6\times10^{-6}E_2 \quad (\text{HgH}^+)$$

$$\Delta\nu = 0.0503 \text{ cm}^{-1} - 7.6\times10^{-6}E_1 - 5.7\times10^{-6}E_2 \quad (\text{HgD}^+)$$

where $\Delta\nu$ gives the shift of the component of the isotope 200 relative to 202 and the vibrational energy E is expressed in cm^{-1}. The difference in the coefficients b_1 is probably due to the fact that the shift for the (1,2) band of HgD^+ is in error. In general the measurements for HgD^+ are less reliable than for HgH^+ and in the case of the (1,2) band of HgD^+ there are so many lines close together that the value of the nuclear shift is very uncertain.

The shifts decrease for both upper and lower states. If they are true nuclear isotope shifts the value of $\Delta\nu$ must tend in the limit of dissociation of both upper and lower states to the value corresponding to the nuclear isotope shift in the corresponding atomic line. As was shown by Hori[12] and subsequently confirmed by the author[12] the atomic line in question is the forbidden quadrupole line 2815A of HgII[14] recently studied by the author.[8] The nuclear isotope shift amounts to about -0.28 cm^{-1} for 200 relative to 202. Instead of this we obtain by extrapolation of the linear formulas for HgH^+ and HgD^+ about -0.153 and -0.120 cm^{-1}, respectively, if we assume as dissociation energies 1.0 volt for the upper state, $^1\Sigma^*$, and 2.15 volts for the lower state, $^1\Sigma$. The latter values were obtained from the constants of the band spectra[12] and were corrected to agree with the frequency of the corresponding atomic line, the correction being equally distributed between the two values. The difference between the shift found for the atomic line and the extrapolated band spectrum value is not surprising in view of the very small accuracy of such long extrapolations. It shows without question that in the neighborhood of the dissociation limit the linear rule breaks down. In the lower $^1\Sigma$ state this is probably connected with the detachment of one of the $6s\sigma$ electrons, which goes over to the hydrogen atom removed, just as occurs in the upper state $^2\Pi$ of HgH. In HgH the extrapolated value[4] was about one-half of the shift observed in the corresponding atomic line 2537A of HgI, very much as in the case here reported. We can therefore assume that here also the whole difference is caused by the detachment of the $6s\sigma$ electrons, an assumption which seems to be in agreement with the well-known strong dependence of the nuclear isotope shift on the presence of s electrons. The resulting nuclear shifts $\delta\nu$ of the minima of the potential curves are collected, together with other data for the molecules HgH^+ and HgH, in Table II. In this table the values given for the shifts of the atomic levels of HgII and HgI are based on the assumption of zero shift for the configuration $(5d)^{10}$. As is well known, the nuclear shifts are proportional to the densities of the electron cloud in the neighborhood of the nucleus. The data recently obtained from the spectrum of HgII[8] show the great influence of holes in the $(5d)^{10}$ shell on the electron density in the vicinity of the nucleus (see Table III, where the value ~ 0.285 cm^{-1} was obtained from some as yet unpublished and very rough measurements of the lines 2916A and 5162A in HgII), the presence of electrons in levels higher than $6s$ playing a comparatively small role. From the

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[14] Some predictions made in the paper (reference 4) were incorrect, being based on the correlation given in Mulliken's article in Rev. Mod. Phys. **4**, 80 (1932). The true correlation of the states is similar to that given by Mulliken for AgH and AuH in another paper, Phys. Rev. **33**, 735 (1929).

values of Table III it follows that the contribution of the first electron in an *s* shell is considerably greater than of the second one. In discussing the level shift in HgH and HgD in a former paper[4] equal contributions of 0.178 cm^{-1} for both *s* electrons were assumed because of insufficient data, and on this basis the lowering of the density of all electrons in the neighborhood of the Hg nucleus caused by the presence of a proton at a distance of 1.59A was calculated to be 26 percent of the density of both 6*s* electrons. With the exact values now available this now becomes 23 percent. Another assumption was made in this discussion concerning the nondeformation of the shell of 5*d* electrons. This is a very poor approximation because the proton has an equilibrium position deep inside of the electron cloud surrounding the Hg atom. That this assumption is not in agreement with experiment can be seen from Table II. The configurations outside the 5*d* shell show some similarity in the two pairs of states $^1\Sigma^*$ and $^2\Sigma$, $^1\Sigma$ and $^2\Pi$; hence in case of nondeformability of the 5*d* shell a negative nuclear isotope shift in the spectra of HgH^+ and HgD^+ would be expected. The observed positive effect arises from several causes: In the $^1\Sigma^*$ state relative to the $^2\Sigma$ state the lack of a 5*d* electron strengthens the binding of the $6s\sigma$ electrons thus increasing the level shift, but at the same time the smaller distance of the proton and the absence of the density of one $5d\sigma$ electron work in the opposite direction. There probably results a diminution of the level shift, because the value 0.410 found by extrapolation for $^1\Sigma^*$ appears to be too high from comparison of the other two states. That is, it seems quite improbable that the absence of a $6p\pi$ electron could strengthen the binding of the $6s\sigma$ electron enough to give an increase of the shift by 0.144 cm^{-1}—an increase by not more than 0.050 cm^{-1} seems reasonable. Therefore both values for the HgH^+ states are to be lowered by at least 0.100 cm^{-1}. The resulting approximate values are given in the last column of Table II. That they are quite reasonable can be seen by comparison of two different pairs of states. In $^1\Sigma$ the internuclear distance is smaller than in $^2\Sigma$. The distortion of the electronic cloud is larger but the absence of one electron increases the density to nearly compensate for this. In the $^1\Sigma^*$ state the r_e is larger, and the stronger binding of the $6s\sigma$ electron (than in $^2\Pi$) is nearly compensated by the absence of the density due to a $5d\sigma$ electron. From these considerations the somewhat unexpected fact follows that the density of the $5d\sigma$ electron must be relatively quite large.

The accuracy of the linear extrapolation is very low, except for the $^2\Sigma$ state of HgH where the measurements extend nearly to the limit of dissociation. The values of the coefficients *b* must be considered only as rough approximations. Nevertheless a comparison of the values given in Table II shows the dependence on the dissociation energy of the state previously pointed out,[4] namely for larger dissociation energies the absolute value of *b* is smaller. For an ionized molecule the *b* values are larger than for a neutral one, as was expected. All in all the relations in the nuclear isotope shift in the spectrum of HgH^+

TABLE III. *Contributions to shifts.*

CONFIGURATION	$5d^{10}6s^2$	$5d^96s^2$	$5d^86s^2$
Total shift	0.404 cm^{-1}	0.508 cm^{-1}	$\sim$0.750 cm^{-1}
Contribution of the 1th electron	0.226	$\sim$0.285	——
Contribution of the 2nd electron	0.178	$\sim$0.223	——

TABLE II. *Comparison of shifts of lines.*

MOLECULAR STATE	r_e A	D_{DISS} VOLT	$b\cdot 10^6$	CORRESPONDING ATOMIC STATE	$\delta\nu_{\text{ATOMIC}}$ CM^{-1}	$\delta\nu_{\text{MOL}}$ CM^{-1}	(LIMIT) CM^{-1}	$\delta\nu_{\text{M. CORR.}}$ CM^{-1}
HgH^+								
$5d\sigma 5d\pi^4 5d\delta^4 4s\sigma^2 6p\sigma\, ^1\Sigma^*$	1.69	1	+12	$5d^96s^2\, ^2D_{5/2}$	0.508	0.410	(0.508)	$\leq$0.310
$(5d)^{10}6s\sigma^2\, ^1\Sigma$	1.59	2.15	−5.6	$5d^{10}6s^2S_{1/2}$	0.226	0.455	(0.355)	$\leq$0.355
HgH								
$(5d)^{10}6s\sigma^2 6p\pi\, ^2\Pi$	1.59	1.94	$\sim$0	$5d^{10}6s6p\, ^3P$	0.226	0.311	(0.311)	0.311
$(5d)^{10}6s\sigma^2 6p\sigma\, ^2\Sigma$	1.73	0.37	+8	$5d^{10}6s^2\, ^1S_0$	0.404	0.372	(0.404)	0.372

can be interpreted, although they are not as clear as in the case of HgH.

My best thanks are due to Professor C. Bialobrzeski for his continued interest in the progress of this work. This paper was submitted in August of last year for publication in the *Acta Physica Polonica*. Subsequent events have made it impossible to proceed with the printing of this journal, and the paper has therefore been rewritten and is presented here. I am very much indebted to Professor F. A. Jenkins for the kind help he has given me in the writing of this paper.

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The Ionization and Dissociation of Water Vapor and Ammonia by Electron Impact

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The results of a mass-spectrometric study of the products of ionization and dissociation of water vapor and ammonia by electron impact are given. The ionizing potential of the H_2O molecule is found to be 13.0 ± 0.2 volts, and of the NH_3 molecule 10.5 ± 0.1 volts. The possible processes responsible for the formation of the various ions observed, both positive and negative, are discussed. Ions observed in H_2O vapor are H_2O^+, OH^+, O^+, H^+, H_2^+, H_3O^+, O^-, and H^-. Ions observed in NH_3 are NH_3^+, NH_2^+, NH^+, N^+, H^+, NH_3^{++}, NH_2^-, and H^-.

INTRODUCTION

THE use of the mass spectrometer for the study of products of ionization and dissociation has come to be recognized as a valuable method of attack on the problem of molecular structure.[1–4] In view of the excellent and thorough exposition of the method in previous papers, particularly that of Smith,[3] it will be sufficient to state here that the procedure is, briefly, as follows: (1) ions formed by collision between the bombarding electrons and the vapor or gas are observed and identified; (2) their intensities and appearance potentials, which are really upper limits, are measured; (3) these data are combined with all available thermochemical and band spectroscopic data in an effort to ascertain the processes occurring and to estimate various bond energies.

While both the H_2O and NH_3 molecules have been investigated previously,[5–7] lack of high resolving power, on the one hand, and relatively low sensitivity of the instruments on the other, have left the data on these molecules in a somewhat uncertain state. Further, more recent but incomplete data[8, 9] obtained at various times have not been in agreement with the earlier work. It appeared justifiable to presume, therefore, that a thorough investigation of the two molecules with the present apparatus might yield consistent and more complete information.

APPARATUS

The mass spectrometer which was used in the present investigation was employed previously in a study of the dissociation products of C_6H_6, C_2H_4, and HCN.[4, 10] The differential pumping system has been improved in order to make more certain that products of thermal dissociation do

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