# Nuclear Isotope Shift in the Spectrum of ZnH

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The structure of the lines in the (0,0) band of the band system $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$ of zinc hydride has been studied by means of a Fabry-Perot etalon. The spectrum was excited in a hollow cathode tube. A structure caused by the isotopic constitution of zinc was observed for the lines near the head of the branch $^0P_{12}$. The measured shifts are larger than those calculated by the usual formulas for the vibrational and rotational isotope effects, thus showing the presence of an additional shift at least partly of nuclear origin, amounting to about 0.007 $\text{cm}^{-1}$ for the consecutive isotopes of zinc of even mass. This case is quite similar to that of the nuclear shifts in HgH, the chief differences being that they are about 10 times smaller in absolute value and in the opposite direction.

A NUCLEAR isotope effect was found by the author some years ago in the spectra of HgH and HgD and an explanation of its dependence on the vibrational, and possibly also rotational, energy of the molecule has been given by Bohr.[1, 2] Recently analogous shifts were found in the spectra of $\text{HgH}^+$ and $\text{HgD}^+$.[3] The author[2] has previously given some explanation of why nuclear isotope shifts have not been heretofore observed in spectra of other molecules. Nevertheless the molecule of HgH cannot in principle represent a unique case in this respect. Therefore it seemed important to find this effect in the spectrum of another molecule, and thus to show its generality and at the same time to furnish a new contribution to the problem of nuclear isotope shifts in band spectra and their correlation with the effects in the respective atomic spectra.

The recently discovered spectra of the hydrides of thallium and lead would be very promising in this respect, but unfortunately they can be excited only in presence of a high pressure of hydrogen, thus making impossible their study with instruments of very high resolving power, because of pressure broadening. Therefore an attempt has been made to investigate the spectrum of zinc hydride, although it was clear from the beginning that the nuclear isotope shift in this case should be much smaller than in mercury hydride and that exceptional sharpness of the lines would be required. The experiments originated from an observation made during investigations of the spectra of Be and B. The hollow cathode of the discharge tube (see detailed description of this tube in a recent paper[3]) in these latest experiments was made of brass. When even a very small amount of hydrogen was present in the tube a strong spectrum of $\text{ZnH}(^2\Pi \rightarrow {}^2\Sigma)$ was observed in the visible and near ultraviolet. By increasing the pressure of hydrogen to the point where the H$\alpha$ line became almost as intense as the red He line,[4] the intensity of these bands was further increased. In this discharge the ultraviolet bands of $\text{ZnH}^+$ are also emitted, although considerably weaker. The bands (0,1), (0,2), (1,3), (2,4), (3,5), (0,3) and (1,4) of the $^1\Sigma^* \rightarrow {}^1\Sigma$ system of the ion were found. Because of lack of time only the long wave-length bands of ZnH were analyzed with high resolving power, and the measurements were limited to some lines in the (0,0) band of the $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$ system near 4300A. This band is the most suitable for detection of a nuclear isotope shift. Stenvinkel[5] has shown that in the spectrum of ZnH the separations of components corresponding to different isotopes of Zn follow the formulas for the normal mass isotope shift almost exactly, the differences not exceeding the limits of error, estimated at about $\pm 0.02$ $\text{cm}^{-1}$. The nuclear isotope shift is then probably still smaller and in order to obtain clear evidence of the existence of such a small shift a band with the smallest

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

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

[3] S. Mrozowski, Phys. Rev. **58**, 332 (1940).

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

[5] G. Stenvinkel, *Das Bandenspektrum des Zinkhydrides* (Stockholm 1936), p. 96.

possible separation of the isotopic components has to be chosen, so that the effect looked for constitutes not too small a part of the total isotope splitting.

The spectrographic apparatus was the same as that described in a former paper,[3] with the sole difference that instead of the quartz optical system a very fast glass system was used in the spectrograph. It gave a dispersion of about 7A/mm in the neighborhood of 4300A. For high resolving power the Fabry-Perot etalon with plates covered with Hochheim alloy and with a separation of 27.2 mm was used. The exposures lasted about a half an hour with a discharge current of 0.3 amp. Although the hollow cathode was cooled only by running water, the lines appeared to be quite sharp, having a half-width of about 0.035 $\mathrm{cm}^{-1}$. The band investigated has a relatively complicated structure—lines belonging to several branches lie close together, giving rise to considerable overlapping. Only the lines of the long wave-length branch $^0P_{12}$ are entirely clear, because they fall outside of the strong band head and only the lines of low quantum number have appreciable intensity. The maximum of the intensity distribution occurs between $^0P_{12}(4\frac{1}{2})$ and $^0P_{12}(5\frac{1}{2})$ and the intensity decreases sufficiently before reaching the long wave-length edge of this branch so that the higher lines beyond the turning point do not interfere. Therefore the structure of lines lying quite close to the head of the branch could be investigated. These lines show a complex structure, which is certainly due to the isotopic constitution of zinc. The observed structure corresponds exactly to the expected distribution shown in Fig. 1. The separation of the components of the isotopes 64 and 66 was impossible to measure, because there is no minimum of intensity between them. The separation of the components 64 and 68 was measured for two lines, $^0P_{12}(10\frac{1}{2})$ and $^0P_{12}(9\frac{1}{2})$, giving 0.066 and 0.058 $\mathrm{cm}^{-1}$. Traces of structure were also detected in the line $^0P_{12}(8\frac{1}{2})$, but no reliable measurements could be made. The normal isotope effect was computed from the data given by Stenvinkel.[5] From the band constants the position of the zero line of the band system was found to be 23099.0 $\mathrm{cm}^{-1}$ and taking the value $\rho_{64,66}-1=0{,}000226$ from the mass-spectrographic data the mass isotope shifts between components of consecutive even isotopes of zinc were found to be 0.0255 $\mathrm{cm}^{-1}$ and 0.0225 $\mathrm{cm}^{-1}$ for these lines. The two corresponding experimental values 0.033 $\mathrm{cm}^{-1}$ and 0.029 $\mathrm{cm}^{-1}$ are larger, showing without question the presence of a nuclear isotope shift of about 0.007 $\mathrm{cm}^{-1}$. The smallness of these nuclear shifts is in excellent agreement with Stenvinkel's measurements.[5]

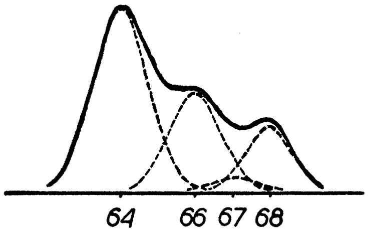

FIG. 1. Structure of lines from ZnH.

The smallness of this nuclear shift, as well as the smallness and relatively low precision of the measured splittings, might cast some doubt upon the reality of the effect found. Fortunately one can check this result in a different way by observing the width of the consecutive band lines. The rotational part of the isotope effect produces a linear change of isotope splitting with frequency. The sign and magnitude of the vibrational effect for this band are such that the total isotope effect changes sign in the region of the $^0P_{12}$ branch. Thus a minimum of the width is produced at a point where the total isotope effect vanishes (exact overlapping of all isotope components). It was easy to see by inspection that the minimum width falls between $^0P_{12}(3\frac{1}{2})$ and $^0P_{12}(4\frac{1}{2})$, rather closer to the former. From this one can calculate the nuclear shift, because at the minimum it is exactly compensated by the normal isotope effect. In the absence of any nuclear shift, the minimum where the rotational effect exactly compensates the vibrational effect should lie between the next pair, $^0P_{12}(4\frac{1}{2})$ and $^0P_{12}(5\frac{1}{2})$, which is certainly not the case. Thus the presence of a nuclear shift of about 0.007 $\mathrm{cm}^{-1}$ is independently confirmed. This convenient method of measuring the nuclear shift could not be applied to the (0,0) bands in $\mathrm{HgH}^+$ and $\mathrm{HgD}^+$,[3] because even for the highest rotational lines the minimum width is not reached in these bands.

The nuclear shift in ZnH is about one-tenth of the shifts previously reported in the analogous bands of HgH and HgD (0.06 cm$^{-1}$). Furthermore it has the opposite sign. The correlation of this effect in the ZnH molecule with the same effect in the Zn atom is at first somewhat disturbing. Billeter[6] has shown that the resonance line of Zn $4^3P_1 \rightarrow 4^1S_0$ at 3076A is anomalously broadened, which he explained as due to an isotope shift of about 0.0185 cm$^{-1}$ between the lines of the even isotopes. He assumed the sign of the shift to be the same as in the resonance line of Hg at 2537A. If the directions of the shifts in both Zn and Hg are the same why should they be opposite in the hydride spectra when the electron configurations in both molecules are analogous? The argument given by Billeter[6] for the signs adopted is misleading, because the sign cannot be inferred directly from the shifts observed by Schüler and Westmeyer[7] in some lines of ZnII. One must consider the shifts of *levels*. In a paper published shortly afterwards, Schüler and Westmeyer[8] showed that for ZnII, just as for CuI, the direction of the nuclear shift is opposite to that in heavier atoms like Cd and Hg, the levels of the heavier isotopes lying lower. It should be remarked that the order of the isotopic levels thus disagrees with the current theory of nuclear isotope shifts. There is every reason to expect that this same inversion holds for the levels of ZnI and that Billeter's assumption is wrong. Then it is clear that the nuclear shift found in ZnH and its correlation with the corresponding atomic spectrum present exact analogs of the effects previously found in HgH, except for reversed directions and the much smaller magnitude.

It must be emphasized, however, that for ZnH it is not certain whether the whole shift of about $-0.007$ cm$^{-1}$ is to be explained as pure nuclear effect, because in this case the shift is much smaller than in HgH and the correction terms[9] to be applied to the usual isotope mass formula are much greater than for HgH. Hence a part of the effect found may represent a mass effect. Nevertheless this effect certainly cannot be large enough to explain more than half of the shift found in the spectrum of ZnH. On the other side the true nuclear isotope shift in the line 3076A of ZnI is different from the value found by Billeter.[6] For such a relatively light element a correction for the mass effect has to be applied, which in this case makes the nuclear isotope shift probably considerably smaller. (In the case of the lines in ZnII investigated by Schüler and Westmeyer,[7] the true nuclear shifts are bigger than the measured ones, but the correction is relatively very small.) The normal mass shift amounts to about 0.008 cm$^{-1}$ and the specific shift has probably the same sign but is comparatively much smaller (compare for instance the calculations of Vinti[10] for MgI).

As to other possible cases of nuclear isotope shifts the author suggested some years ago[2] that the shift of 0.33 cm$^{-1}$ found by Jenkins and McKellar[11] in the system origins in the spectra of $B^{10}O$ and $B^{11}O$ may have a nuclear origin. It was recently shown by Opechowski and de Vries[12] that the observed shifts in the spectrum of boron are pure mass shifts. Therefore a possible nuclear origin of the shift in BO is excluded and the whole effect must be explained as due to mass correction terms. The order of magnitude seems to be in agreement with formulas for these terms.[9] Thus no indications of the presence of a nuclear isotope shift in other spectra than the cases mentioned above—namely HgH(HgD), $HgH^+$-($HgD^+$) and ZnH—have been found up to the present.

I wish to express my sincere thanks to Professor C. Bialobrzeski for his kind interest in this experiment. 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 in English 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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[6] W. Billeter, Helv. Phys. Acta **7**, 524 (1934).

[7] H. Schüler and H. Westmeyer, Zeits. f. Physik **81**, 565 (1933).

[8] H. Schüler and H. Westmeyer, Zeits. f. Physik **82**, 685 (1933).

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

[10] J. P. Vinti, Phys. Rev. **56**, 1120 (1939).

[11] F. A. Jenkins and A. McKellar, Phys. Rev. **42**, 464 (1932).

[12] W. Opechowski and D. A. de Vries, Physica **6**, 913 (1939).