Moment of Inertia of Hydrogen from Raman Effect.

F. RASETTI (*Phys. Rev.*, **34**, 367; 1929) has recently obtained accurate data on the Raman effect for gaseous hydrogen. From his data it is possible to calculate extremely precise values of B_0 and B_1. This is very fortunate, for it is now possible, from band spectra, to obtain an accurate value of B_0 only by extrapolation, as has been shown in the preceding letter by Hyman and Jeppesen. Because of the importance of this constant, it has seemed advisable to make a searching analysis of Rasetti's data, using all known theoretical relations.

We have expressed the rotational energy as $E_m = B_v m^2 + D_v m^4 + F_v m^6$, where m is a half-integer for the actual rotational levels. We have calculated values of D_v from the theoretical relations derived by Kemble. The only value of F which is known theoretically is F_e, but this can be used safely for F_v, when v is small. We have also paid scrupulous regard to the difference between derivatives and finite central differences. For most molecules the distinction can be ignored, but this is not at all the case for hydrogen. Rasetti, in his calculations, omitted the $F_e m^6$ term, although his data clearly require it. He also used D_v as constant, $= D_e$. Besides the rotational constants for $v = 0$ and 1, his data also evaluate $\omega_{1/2}$, the separation of these two vibrational levels, for zero rotation ($m = 0$). Using all of his data, we get $\omega_{1/2} = 4161 \cdot 70$ cm.$^{-1}$. Rasetti's value of $4161 \cdot 8$ is based on a single line.

This value of $\omega_{1/2}$ is most interesting, for it lies definitely *off* the smooth $\omega_v : v$ curve. Hyman's new data have not yet been analysed for ω_v values, but the older data lead to $\omega_{1/2} = 4146$ cm.$^{-1}$, with a probable error not greater than 2 cm.$^{-1}$, so far as the extrapolation is concerned. The discrepancy of 16 cm.$^{-1}$, or $0 \cdot 38$ per cent, is therefore real. Such a *vibrational* perturbation seems to be quite unprecedented, and obviously cannot be explained as due to the crossing of two sets of rotational levels. Such a crossing, in any case, affects only certain *lines* of a band, and not the entire band. Even the older data give 4159 cm.$^{-1}$ for $\omega_{1/2}$, as one of us noticed several years ago, but Rasetti's work is the first to establish definitely the existence of this irregularity. One disturbing consequence of the irregularity is that one cannot be certain of the value of ω_e, the frequency of vibration for infinitesimal amplitude. In calculating D_v values, we have used $\omega_e = 4371$, as derived from a *smooth* ω_v curve, ignoring $\omega_{1/2}$. The resulting uncertainty in D_v is negligible, in any case.

Our final calculated values of B_0 and B_1, from Rasetti's data, are $59 \cdot 354$ cm.$^{-1}$ and $56 \cdot 4035$ cm.$^{-1}$, respectively, as compared with Rasetti's published $59 \cdot 40 \pm 0 \cdot 03$, and $56 \cdot 47$. So far as the consistency of the data is concerned, our own calculated values have a probable error of less than $0 \cdot 01$ cm.$^{-1}$, but the real probable error is doubtless several times as large. Using all our derived constants, Rasetti's sixteen measured lines are represented with an average residual of $0 \cdot 24$ cm.$^{-1}$. His own average residual is $0 \cdot 36$ cm.$^{-1}$. The agreement with theory is remarkably close in every detail, and this is especially gratifying, since the hydrogen molecule provides the most severe test of any theory of band spectra.

The equation for B_v, derived by Hyman and Jeppesen from band spectra data *only*, gives $B_1 = 56 \cdot 4115$ cm.$^{-1}$. This agrees with our value from Raman effect to *one part in seven thousand*. It is the most accurate check between Raman effect and band spectra data that has yet been found, and is again a most satisfactory confirmation of theory. On the other hand, the Raman effect value of B_0 is $0 \cdot 27$ per cent greater than the *extrapolated* band spectrum value. The agreement of the B_1 values shows that the B_v equation given by Hyman and Jeppesen is entirely correct at $v = 1$, and hence its extrapolation to $v = 0$ is certainly correct to $0 \cdot 1$ per cent or less. We therefore have a *perturbation* in the moment of inertia of the *lowest* vibrational state of hydrogen. Since the separation of vibrational levels is assumed to measure an average value of the classical frequency of vibration in the two levels concerned, the conclusion seems almost inevitable that in the lowest vibrational level of hydrogen the frequency of vibration is *greater* and the moment of inertia *less* than the values to be expected from the constants for the other vibrational levels.

The essential correctness of the value of B_0, as derived from Raman effect, cannot be questioned. Hence the true I_0 for hydrogen is $0 \cdot 46602 \times 10^{-40}$ gm.cm.^{2}, $r_0 = 0 \cdot 74891 \times 10^{-8}$ cm. These constants are given to five significant figures, like B_0, but it should be remembered that the conversion factor has itself a probable error of one part in seven hundred. As noted by Hyman and Jeppesen, the value of B_e now becomes indefinite, due to the irregularity in B_0, but in the absence of contrary evidence, it seems best to use, for both B_e and ω_e, when calculating derived constants, the smooth extrapolated values already given.

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Raman Spectra of Crystalline Powders.

IN a recent communication (NATURE, Nov. 2, 1929) Prof. R. Bär of Zurich has shown that it is possible in many cases to photograph the Raman effect with solids in a state of powder. The difficulty encountered by him, and also by Dr. A. C. Menzies (see NATURE, Oct. 5, 1929), of the continuous background in the spectrum which overpowers all but the strongest Raman lines, is, however, serious, as it interferes with the general utility of the method. During the past two months I have been engaged in an attempt to overcome this difficulty, and have found that it may practically be avoided by running the mercury arc at a lower temperature, and, where necessary, also by interposing a suitable light filter between the arc and the illuminated substance. A concentrated solution of didymium chloride proved especially useful for this purpose. Thus, for example, all the four lines obtained by Schaefer with a large single crystal of sodium nitrate may, with equal success, be photographed in about half an hour by using an irregular aggregate of small crystals placed within a small triangular-shaped cell with mirrored walls.

Prof. Bär has found that in the case of naphthalene the Raman lines appear in the same position in the crystal powder as in the liquid. My results with benzophenone crystals and liquid show that a marked change in the position of some of the Raman lines occurs on fusion of this substance; this is best seen with the line usually attributed to the ketonic group, which gives a shift of 1657 wave numbers in the liquid and 1650 in the solid, and is also noticeably sharper in the latter. It is clear that a promising field of research offers itself in the comparative study of the Raman spectra in the liquid and solid states.

About eighteen inorganic nitrates have also been examined by this method, some anhydrous and the others as hydrates. It was noticed by Schaefer and by Bär that the inactive frequency of the NO_3 group in $NaNO_3$ crystals differed appreciably from the value in its aqueous solution. In the present investigation, the largest shifts corresponding to the inactive frequency were given by lithium, sodium, and mag-