

The Hydrogen Sulfide Bands at 10,200 cm^{-1} *

HAROLD R. GRADY** AND PAUL C. CROSS
Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island

AND
 GILBERT W. KING
Arthur D. Little, Inc., Cambridge, Massachusetts
 March 22, 1949

APPROXIMATELY ninety absorption lines have been measured in the region 10,070 cm^{-1} to 10,270 cm^{-1} using a 21-foot grating (15,000 lines per inch) and a path of 220 ft. of H_2S at 0.75 atmosphere pressure. The high frequency portion of this region also contains a number of atmospheric water vapor lines.

Essentially all these lines are assigned as water lines or as transitions in one (or both) of two bands at $\nu_0 = 10,194.48 \text{ cm}^{-1}$ and $\nu_0 = 10,188.25 \text{ cm}^{-1}$, respectively. The selection rules correspond in the first band to the electric moment along the axis of least inertia, perpendicular to the symmetry axis and, in the second band, along the axis of intermediate inertia, parallel to the symmetry axis. The constants are tabulated (see Table I)

TABLE I. Constants for the H_2S molecule.

| | 0.00 | 9911.05 | 10188.25 | 10194.48 cm^{-1} |
|----------|--------|---------|----------|--|
| ν_0 | 10.373 | 9.883 | 9.605 | 9.698 |
| a | 8.991 | 8.340 | 8.560 | 8.466 |
| b | 4.732 | 4.474 | 4.477 | 4.490 |
| c | 2.698 | 2.832 | 2.914 | $2.886 \times 10^{-40} \text{ g cm}^2$ |
| I_a | 3.113 | 3.356 | 3.269 | 3.306 |
| I_b | 5.914 | 6.255 | 6.251 | 6.233 |
| I_c | 0.103 | 0.067 | 0.068 | 0.041 |
| Δ | | | | |

together with those derived from the 9911.05 cm^{-1} band,^{1,2} recalculated using $h/8\pi^2c = 27.9865 \times 10^{-40} \text{ g cm}^2$.

In the table, $\Delta = I_c - I_a - I_b$ and the inertial constants a, b, c were determined by least squares after applying a first-order classical correction for centrifugal distortion.¹ The 9911 and 10,194 bands are probably the ($\nu_a\nu_b\nu_c$) = (130) and (310) bands, considerably mixed by resonance.³ The 10,188 band is believed to correspond approximately to the (400) band, also possibly involved in resonance. Since the absorption in this band is much weaker than in the other band, the upper state constants are not as well established as are those given for the 10,194 band.

The previous report¹ of a new band at about 10,100 cm^{-1} was an erroneous conclusion based on the observed spacing in this region as about that expected in an R -branch near the band center. This spacing is now established as due to the interspersed P -branches of the two new bands reported here.

* This work was supported in part by the Office of Naval Research Contract N6ori-88 Task I.

** Arthur D. Little Fellow in chemistry.

¹ P. C. Cross, *Phys. Rev.* **47**, 7 (1935).

² B. L. Crawford and P. C. Cross, *J. Chem. Phys.* **5**, 621 (1937).

³ B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).

simple permanent dipole interaction of two ammonia molecules, without bringing in the complicated effects suggested by some authors.^{1,2,4}

We limit ourselves to the statistical type of theory, in which the perturbed energy of the levels of interest for two molecules fixed relative to each other is computed as a function of the intermolecular distance r , and then suitably averaged over all r to obtain the line-shape. One can think of our results in terms of a single molecule in a varying electric field. In weak fields the "proper linear combinations" of wave functions are $\psi_+ = (\psi_{+K} + \psi_{-K})/(\sqrt{2})$ and $\psi_- = (\psi_{+K} - \psi_{-K})/(\sqrt{2})$, where ψ_{+K} and ψ_{-K} are the "single-ended" wave functions in which the N atom is thought of as on one side or the other of the potential barrier formed by the triangle of H atoms. The perturbation is second order and small (not true in the case of two atoms), and the selection rule is $\psi_+ \leftrightarrow \psi_-$ only.

On the other hand, under a strong electric field, such that the perturbation, $\mathbf{p} \cdot \mathbf{E}$, is greater than the inversion splitting ΔE , the inversion is completely broken down by the external perturbation, and the right linear combinations are ψ_{+K} and ψ_{-K} . Here the selection rule is $+K \leftrightarrow -K$, so that the only allowed radiation is composed of jumps in magnetic quantum number of one, small in frequency relative to the $\pm K$ splitting. It seems clear that such a change in selection rules can account both for the shift and the narrowing of the observed line.

An exact solution of the secular equation, simplified by ignoring the m -dependence of all quantities, and thus by using an unperturbed wave functions the products $\psi_{\pm}(1)\psi_{\pm}(2)$, shows that the same considerations apply in this more complicated case, except that the degenerate pair of levels $\psi_+(1)\psi_-(2)$ and $\psi_-(1)\psi_+(2)$ always undergo a first-order perturbation. The perturbing energy is the simple first-order interaction of two dipoles

$$H = \frac{1}{r^3} \left[\mathbf{p}_1 \cdot \mathbf{p}_2 - \frac{3(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^2} \right].$$

The observed anomaly has become pronounced at atmospheric pressure. At this pressure it is easy to show that the molecules are within distances such that $H(r) \geq \Delta E$ for a large percentage (perhaps 50 percent) of the time. In this case one would suspect that the effect here discussed is quite strong since the molecules spend a large percentage of their time in the region where the strong field solution has some validity. Then one would expect a shift toward zero frequency and a narrowing of the line of much the same order of magnitude as is observed. A quantitative check must, of course, await a theory which reconciles the impact theory with the statistical theory used here, and in addition a complete statistical theory which sets up the rigorous secular equation and averages the result properly over all r , taking into account selection rules.

* Now at Bell Telephone Laboratories, Inc.

** National Research Council Predoctoral Fellow.

¹ Bleaney and Penrose, *Proc. Phys. Soc. (London)* **60**, 83 (1948).

² Bleaney and Loubser, *Nature* **161**, 523 (1948).

³ DeForest F. Smith, *Phys. Rev.* **74**, 506 (1948).

⁴ I. Weingarten, unpublished Thesis, Columbia University, New York, 1948.

On the Anomalous Line-Shapes in the Ammonia Inversion Spectrum at High Pressures

P. W. ANDERSON*, **
Harvard University, Cambridge, Massachusetts
 March 17, 1949

THE purpose of this letter is to suggest a qualitative, rather than rigorous, explanation of the magnitude and direction of the observed anomalies in line-shapes in the ammonia inversion spectrum.¹⁻⁴ At high pressures the line is found to be much narrower than would be expected on the standard theory, and is shifted strongly to lower frequencies. It appears that these effects can be explained on the basis of

Interaction Hamiltonian for Photon, Meson, and Nucleon Fields

GEORGE J. YEVICK
Stevens Institute of Technology, Hoboken, New Jersey
 January 10, 1949

USING the methods developed by Tomonaga and collaborators, we have obtained the Hamiltonian for vector mesons interacting simultaneously with nucleons and with the electromagnetic field. The method is the same as that of