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F and G intensity sum rule applications: the CH_xD_{4-x} molecules

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Numerical analyses based on the *F* and *G* intensity sum rules show that recently published experimental values for the fundamental vibrational intensities of CH₄, CH₃D, CH₂D₂, CHD₃, and CD₄ are internally consistent within experimental errors. Effective charge values for the carbon and hydrogen atoms obtained using the intensity sums for all these isotopically related molecules are almost in exact agreement with reported values obtained from the polar tensors of CH₄ and CD₄. The *G* sum rule allows a determination of the signs of the dipole moment derivatives using the fundamental intensity sum for CH₄ (or CD₄) and the polar tensor values for CD₄ (or CH₄).

In recent articles¹⁻⁴ the authors have suggested that the *F* and *G* intensity sum rules⁵ allow several useful applications in studies involving fundamental vibrational intensities. Most importantly, perhaps, these rules serve as a check on the internal consistency of the experimental intensity results for a series of isotopically related molecules. Also, the *G* sum rule allows a determination of the relative signs of the dipole moment derivatives of those molecules from a knowledge of the individual fundamental intensities of one member of this series and only the *sum* of these intensities for another member. Studies with these objectives can be accomplished without reference to the sum rules. A main advantage in their use, however, is a minimization of the dependence on normal coordinate information which contains experimental errors of varying magnitudes for the different members of the isotopically related family of molecules. In this report the above-mentioned applications are tested for the CH_xD_{4-x} molecules.

For these molecules the *G* intensity sum rule in terms of the carbon and hydrogen effective charges, ξ_C and ξ_H , can be expressed as⁶ ($\xi_H = \xi_D$ and $m_D = 2m_H$)

$$(1/K)\sum A_i = \xi_C^2 m_C + (4+x)\xi_H^2/2m_H,$$

where $\sum A_i$, m_C and m_H are the fundamental intensity sum, and the atomic masses of carbon and hydrogen. A graph of ξ_C^2/m_C against ξ_H^2 leads to *G* sum rule lines with slopes of $-(4+x)/2m_H$ and intercepts of $(1/K)\sum A_i$, where $K = N\pi/3c^2$, N and c being Avogadro's number and the velocity of light.

In Table I fundamental intensity sums and their error limits as calculated from the data of Saëki, Mizuno, and Kondo⁷ are presented for CH₄, CH₃D, CH₂D₂, and CD₄. As their data are incomplete for CHD₃, the intensity sum for this molecule in Table I was taken from Hecklen.⁸ In Fig. 1, the possible ranges in the *G* sum rule lines for CH₄, CH₃D, CH₂D₂, and CD₄, as determined by the $\sum A_i$ values and their errors, are presented in a graph of ξ_C^2/m_C vs ξ_H^2 . Each pair of lines represents the upper and lower limits for the *G* sum rule lines, the lines corresponding to the $\sum A_i$ values in Table I being equidistant between the limiting lines. Clearly, the data of Saëki *et al.*⁷ appear to be quite accurate within their estimated experimental errors as the sets of parallel lines containing the experimentally

allowed *G* sum rule lines converge quite nicely around $\xi_C^2 = 0$ and $\xi_H^2 = 0.026 \underline{e}$.

As the effective charges are real quantities, $\xi_C^2 > 0$. With this limitation the region of common overlap for the experimentally allowable *G* sum rule lines of these four CH_xD_{4-x} molecules corresponds to values of the effective charges within the ranges $0 < \xi_C/m_C < 10^{-4} \underline{e}$ and $0.0261 \underline{e} < \xi_H < 0.0265 \underline{e}$. Assuming that the *G* sum rule line for CHD₃ passes through the point with $\xi_C^2 = 0$ and $\xi_H^2 = 0.0263 \underline{e}^2$ a fundamental intensity sum of 63.6 km mol⁻¹ is predicted for this molecule. This value is in excellent agreement with the intensity sum of 60.8 ± 1.8 km mol⁻¹ calculated from the experimental intensities reported by Hecklen.⁸ Indeed the predicted value is probably too large as it reflects a sum of fundamental intensities which appears to be a bit too high. Clearly, Fig. 1 shows that although the experimentally permissible *G* sum rule lines for CH₃D, CH₂D₂, and CD₄ show a large region of overlap, the ones for CH₄ are just barely in common with this region. A slightly lower value for the CH₄ sum would result in improved convergence of all *G* sum rule lines.

The *F* sum rule also indicates that the intensity sum for CH₄ may be slightly too high. The values for the *F* sum rule invariant, $\sum A_i/\omega_i^2$, for methane and its deuterated derivatives are also given in Table I. These values were calculated using the intensity data in Ref.

TABLE I. *F* and *G* sum rule results for methane and its deuterated analogues.^a

	$\sum A_i$ ^b	$\sum A_i/\omega_i^2$ ^c
CH ₄	104.0 ± 3.0	26.4 ± 0.7
CH ₃ D	86.7 ± 1.9	23.2 ± 0.5
CH ₂ D ₂	73.2 ± 2.2	23.1 ± 0.6
CHD ₃	60.8 ± 1.8	24.0 ± 0.7
CD ₄	49.9 ± 1.3	24.3 ± 0.5

^aThe intensity values are taken from Ref. 7 for all the molecules except for CHD₃, for which data were taken from Ref. 8. The frequency values used to calculate the *F* sum rule invariant were taken from Ref. 9.

^bUnits of km mol⁻¹.

^cUnits of 10⁻¹⁶ km³ mol⁻¹.

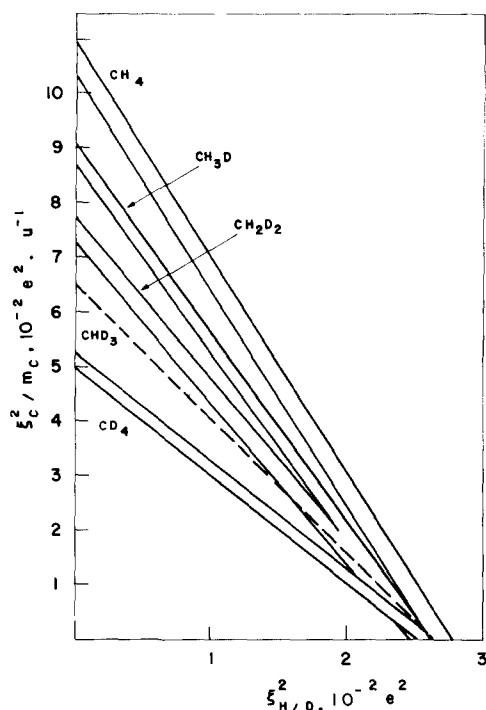


FIG. 1. Ranges due to experimental errors for the *G* sum rule lines of CH_4 , CH_3D , CH_2D_2 , and CD_4 . The dashed line is the predicted *G* sum rule line for CHD_3 based on the region of intersection of the experimentally permissible *G* sum rule lines for the other molecules.

7 except for CHD_3 , where the data of Heicklen⁸ were used. The frequencies were taken from the book by Sverdlov.⁹ Although all the values of $\sum A_i/\omega_i^2$ are in excellent agreement, the value for CH_4 appears to be about $2 \times 10^{-16} \text{ km}^3 \text{ mol}^{-1}$ too high when compared with all of the other *F* sum rule values.

Based on comparisons of experimental intensity data for all the isotopically related methanes⁷ and theoretically (CNDO and *ab initio*) calculated results¹⁰ the signs of $\partial p/\partial Q_3$ and $\partial p/\partial Q_4$ have been found to be identical. The *G* intensity sum rule provides a very straightforward method for verifying this result. Newton and Person¹¹ have calculated average values for the polar tensor of methane and its carbon and hydrogen effective charges using the individual fundamental intensities of CH_4 and CD_4 . For the (– –) sign combination ($\partial p/\partial Q_3$ and $\partial p/\partial Q_4$ both < 0) average values of $\xi_C^2 = 0.0006$ and $\xi_H^2 = 0.027 e^2$ are reported. These values are in excellent agreement with effective charge values corresponding to the region of overlap defined by the experimental ranges in the four *G* sum rule lines

shown in Fig. 1. On the other hand, the alternative sign combination, (+ –), leads to average values of $\xi_C^2 = 0.271$ and $\xi_H^2 = 0.018 e^2$. Reference to Fig. 1 shows that this value of ξ_H^2 corresponds to four different values for ξ_C^2 for the CH_4 , CH_3D , CH_2D_2 , and CD_4 intensity sums. As ξ_C^2 should be invariant for these molecules within the Born–Oppenheimer approximation, the (+ –) sign combination can be confidently eliminated.

Average values of ξ_C^2 and ξ_H^2 have been used here as effective charge values based on only the CH_4 or CD_4 intensity data have not been reported for the two possible sign combinations of the $\partial p/\partial Q_i$'s. However, the effective charge values obtained from either the CH_4 and CD_4 individual intensities, via the polar tensor, must be in reasonable agreement with the average values quoted here. Hence it is easily seen that the relative signs of $\partial p/\partial Q_3$ and $\partial p/\partial Q_4$ can be determined from a knowledge of the polar tensors for CH_4 (or CD_4) and a sum of the fundamental vibrational intensities of CD_4 (or CH_4).

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- ¹R. E. Bruns and B. de Barros Neto, *J. Chem. Phys.* **68**, 847 (1978).
- ²B. de Barros Neto and R. E. Bruns, *J. Chem. Phys.* **68**, 5451 (1978).
- ³R. E. Bruns and A. B. M. S. Bassi, *J. Chem. Phys.* **68**, 5448 (1978).
- ⁴R. E. Bruns and B. de Barros Neto, *J. Chem. Phys.* (to be published).
- ⁵B. L. Crawford, Jr., *J. Chem. Phys.* **20**, 977 (1952).
- ⁶W. T. King, G. B. Mast, and P. P. Blanchette, *J. Chem. Phys.* **56**, 4440 (1972).
- ⁷S. Saëki, M. Mizuno, and S. Kondo, *Spectrochim. Acta A* **32**, 403 (1976).
- ⁸J. Heicklen, *Spectrochim. Acta A* **17**, 201 (1961).
- ⁹L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, *Vibrational Spectra of Polyatomic Molecules* (Wiley, New York, 1974).
- ¹⁰G. A. Segal and M. L. Klein, *J. Chem. Phys.* **47**, 4236 (1967); W. Meyer and P. Pulay, *J. Chem. Phys.* **56**, 2109 (1972).
- ¹¹J. H. Newton and W. B. Person, *J. Phys. Chem.* **82**, 226 (1978).