Extremal Properties of Force Constants of the H₂S Molecule

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The parametric representation of the force constants of a molecule

\[ \mathbf{F} = E L - 1 \mathbf{A} L - 1, \quad L = L_0 \mathbf{C}, \]

in which \( \mathbf{C} \) is any orthogonal matrix of degree \( n \) (\( n \) degree of the \( \mathbf{F} \)-matrix), the force constants depend—besides on the frequencies \( \mathbf{A} \) of normal vibrations—for \( n = 2 \) on a parameter \( \psi \). It may be defined by

\[ \mathbf{C} = \{ c_{ij} \}, \quad c_{11} = c_{22} = \cos \psi, \quad c_{12} = -c_{21} = \sin \psi, \]

see Ref.\(^1\). When the force constants of the totally symmetric species of the \( \text{O}_2 \) molecule are plotted versus \( \psi \), the correct force constants of this molecule correspond within the limits of accuracy to that value of the parameter \( \psi \), for which the force constant \( F_{14} = F_{24} + F_{24} \) has a maximum. In Ref.\(^1\) the same extremal property was found for the molecules \( \text{H}_2 \text{~S} \) and \( \text{H}_2 \text{Se} \), though the correspondence of extremal and correct force constants is not so striking as for the \( \text{H}_2 \text{O} \) molecule. But in \( \psi \) relatively inaccurate \((\pm 3 \text{ cm}^{-1})\) harmonic wavenumbers \( \omega_i \) of the \( \text{D}_2 \text{~S} \) molecule were used for calculating the correct force constants of the \( \text{H}_2 \text{~S} \) molecule. These harmonic wavenumbers were based on observed wavenumbers of \( \text{Allen}, \text{Plyler}, \) and \( \text{Blaine} \)\(^2\), see Table 1, line 2. Recently the vibrational spectrum of \( \text{D}_2 \text{~S} \), which is entered in Table 1, line 3. We have calculated the harmonic wavenumbers \( \omega_i \) of \( \text{D}_2 \text{~S} \) using these data, the harmonic wavenumbers \( \omega_i \) and anharmonicity constants \( x_{ij} \) of the \( \text{H}_2 \text{~S} \) molecule of \( \text{Allen} \) and \( \text{Plyler} \)\(^3\), and the assumption \( x_{ij}' = \omega_{ij} / \omega_i \). The results are listed in Table 1, line 3. The following quantities were used: \( z = 92.12 \), \( m_2 = 1.008145 \text{ a. u.}, \)

\[ m_D = 2.014744 \text{ a. u. and } m_S = 31.892196 \text{ a. u.} \]

The product rule yields \((\omega_1 \omega_2)/(\omega_1 \omega_2) = 1.9427\) compared with 1.941798 from theory. \( \text{Miller}, \text{Leboi}, \) and \( \text{Eggers} \)\(^5\) have calculated the harmonic wavenumbers \( \omega_1 \) and \( \omega_2 \) of \( \text{D}_2 \text{~S} \) from the observed wavenumbers \( v_1 \) and \( v_2 \) of \( \text{Miller} \) and \( \text{Eggers} \)\(^5\), the anharmonicity constants \( x_{ij}' \) of \( \text{D}_2 \text{~S} \) of \( \text{Allen} \)\(^6\) and with the aid of the Eqs. II.270 of \( \text{Henzarcc} \)\(^7\). They get somewhat different results (see Table 1, line 4) which very well satisfy the product rule. Finally \( \text{Gamo} \)\(^8\) has computed \( \omega_1 \) and \( \omega_2 \) of \( \text{D}_2 \text{~S} \) by means of two combination frequencies to be

\[ \omega_1 = 1952.08 \text{ cm}^{-1} \quad \text{and } \omega_2 = 872.12 \text{ cm}^{-1}. \]

Therefore the harmonic wavenumbers of vibrations \( \omega_1 \) and \( \omega_2 \) now have a greater degree of accuracy than in Ref.\(^1\), so that in Table 2 again a comparison can be made between extremal and correct force constants of the \( \text{H}_2 \text{~S} \) molecule. In column 1 is specified, which data were used for calculating the force constants. For example: \((1+2)\) means, that the harmonic wavenumbers of the first and second line of Table 1 were taken for iterative computation of the force constants. Hence line 1 of Table 2 contains force constants, which are

\begin{align*}
\text{Correct} & \quad \text{Extremal} \\
\text{force constants} & \quad \text{force constants} \\
(1+2)^a & \quad \text{(1+2)}^a \\
4.271 & \quad 4.271 \\
0.409 & \quad 0.409 \\
-0.235 & \quad -0.235 \\
0.219 & \quad 0.219 \\
(1+3) & \quad (1+3) \\
4.284 & \quad 4.284 \\
0.462 & \quad 0.462 \\
-0.111 & \quad -0.111 \\
0.062 & \quad 0.062 \\
(1+4) & \quad (1+4) \\
4.284 & \quad 4.284 \\
0.425 & \quad 0.425 \\
-0.011 & \quad -0.011 \\
0.039 & \quad 0.039 \\
\end{align*}

Table 2. Comparison of correct and extremal force constants (mdyn/Å) of the \( \text{H}_2 \text{~S} \) molecule, calculated with the harmonic wavenumbers of Table 1. \( a \) The numbers in brackets signify the lines in Table 1. The force constants are calculated with the wavenumbers of these lines.

The same as in Ref.\(^1\). A comparison of the force constants obtained by the new more accurate wavenumbers with extremal ones shows an essentially better agreement than before. Now the agreement between correct and extremal force constants is within the limits of accuracy of the data as good as in the case of the \( \text{H}_2 \text{O} \) molecule.

\begin{table} \[ \begin{array}{cccc} \hline \text{v}_1 & \text{v}_2 & \text{Ref} & \text{\omega}_1 & \text{\omega}_2 & \text{\omega}_3 & \text{Ref} \\
\hline 1 & \text{H}_2 \text{~S} & 2614.56 & 1182.68 & 2627.48 & 2721.92 & 1214.51 & 2733.36 & 9 \\
2 & \text{D}_2 \text{~S} & 1892 \pm 3 & 855 \pm 3 & 1947 \pm 3 & 874 \pm 3 & 1963.87 & 1 \\
3 & \text{D}_2 \text{~S} & 1896.38 & 855.5 & 1951.6 & 871.9 & 1963.87 & 5 \\
4 & \text{D}_2 \text{~S} & 1896.38 & 855.5 & 1952.84 & 871.78 & 1963.86 & 5 \\
\hline \end{array} \] \end{table}

Table 1. Observed \((\text{v})\) and harmonic \((\omega)\) wavenumbers of the vibrations of \( \text{H}_2 \text{~S} \) and \( \text{D}_2 \text{~S}\). \( a \) own calculation.

1. G. Strej, J. Mol. Spectrosc. 24, 87 [1968].