Extremal Properties of Force Constants of the H₂S Molecule

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In the parametric representation of the force constants of a molecule

\[ F = L^{-1} \Delta L^{-1}, \quad L = L_0 C, \]

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

\[ C = (c_{ij}), \quad c_{11} = c_{22} = \cos q, \quad c_{21} = -c_{12} = \sin q, \]

as Ref. 1.

When the force constants of the totally symmetric species of the \( H_2O \) molecule are plotted versus \( q \), the correct force constants of this molecule correspond within the limits of accuracy to that value of the parameter \( q \), for which the force constant \( F_{11} = F_{12} + F_{13} \) has a maximum. In Ref. 1 the same extremal property was found for the molecules \( H_2S \) and \( H_2Se \), though the correspondence of extremal and correct force constants is not so striking as for the \( H_2O \) molecule. But in 1 relatively inaccurate (\( \pm 3 \text{ cm}^{-1} \)) harmonic wavenumbers \( \omega_{ij}^0 \) of the \( D_2S \) molecule were calculated for calculating the correct force constants of the \( H_2S \) molecule. These harmonic wavenumbers were based on observed wavenumbers of ALLEN, PLYLER, and BLAINE 2, see Table 1, line 2. Recently the vibrational spectrum of \( D_2S \) was remeasured and analysed by several authors. MILLER and EGGERS 3 evaluate observed wavenumbers \( v_i^0 \) of \( D_2S \), which are entered in Table 1, line 3. We have calculated the harmonic wavenumbers \( \omega_{ij} \) of \( D_2S \) using these data, the harmonic wavenumbers \( \omega_{ij} \) and anharmonicity constants \( \chi_{ij} \) of the \( H_2S \) molecule of ALLEN and PLYLER 4, and the assumption \( \chi_{ij}^{\alpha} = \frac{\omega_{ij}^{\alpha}}{\omega_{ij}} \chi_{ij} \).

The results are listed in Table 1, line 3. The following quantities were used: \( \alpha = 92.12^\circ \), \( m_{ij} = 1.008145 \text{ a.u.}, \)

\( \beta = 2.014744 \text{ a.u. and } m_S = 31.892196 \text{ a.u.} \) The product rule yields \( (\omega_{ij} \omega_{k})^{1/2} = 1.9427 \) compared with 1.941798 from theory. MILLER, LEROI, and EGGERS 5 have calculated the harmonic wavenumbers \( \omega_{ij} \) and \( \omega_{ij}^0 \) of \( D_2S \) from the observed wavenumbers \( v_i \) and \( v_i^0 \) of MILLER and EGGERS 3, the anharmonicity constants \( \chi_{ij} \) of \( D_2S \) of ALLEN 6 and with the aid of the Eqs. II.270 of HERZBERG 7. They get somewhat different results (see Table 1, line 4) which very well satisfy the product rule. Finally GAMO 8 has computed \( \omega_{1} \) and \( \omega_{2} \) of \( D_2S \) by means of two combination frequencies to be

\[ \omega_{1} = 1952.08 \text{ cm}^{-1} \text{ and } \omega_{2} = 872.12 \text{ cm}^{-1}. \]

Therefore the harmonic wavenumbers of vibrations \( \omega_{ij}^0 \) and \( \omega_{ij} \) 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 \( H_2S \) 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

\[ f_t \quad f_a \quad f_T \quad f_T \]

Correct force constants

\((1+2)^a \) 4.271 0.049 -0.025 0.219

\((1+3) \) 4.284 0.462 -0.011 0.062

\((1+4) \) 4.284 0.425 -0.011 0.039

Extremal force constants of \( H_2S \)

4.284 0.426 -0.011 0.065

Table 1. Observed \((v_i)\) and harmonic \((\omega_i)\) wavenumbers of the vibrations of \( H_2S \) and \( D_2S \).

Table 2. Comparison of correct and extremal force constants (mdyn/Å) of the \( H_2S \) 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.

<table>
<thead>
<tr>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_3 )</th>
<th>Ref.</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_3 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( H_2S )</td>
<td>2146.54</td>
<td>1182.68</td>
<td>2627.48</td>
<td>2721.92</td>
<td>1214.51</td>
<td>2733.36</td>
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</tr>
<tr>
<td>2 ( D_2S )</td>
<td>1892.53</td>
<td>858.45</td>
<td>874.43</td>
<td>879.07</td>
<td>1963.87</td>
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<td></td>
</tr>
<tr>
<td>3 ( D_2S )</td>
<td>1896.38</td>
<td>855.55</td>
<td>552.45</td>
<td>871.9</td>
<td>1963.87</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>4 ( D_2S )</td>
<td>1896.38</td>
<td>855.55</td>
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<td>871.78</td>
<td>1963.86</td>
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<td></td>
</tr>
</tbody>
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1 G. STREY, J. Mol. Spectry. 24, 87 [1968].
6 H. C. ALLEN, Jr., Dissertation, University of Washington 1951.