Extremal Properties of Force Constants of the H_2S Molecule

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In the parametric representation of the force constants of a molecule

$$\boldsymbol{F} = \tilde{\boldsymbol{L}}^{-1} \boldsymbol{\Lambda} \boldsymbol{L}^{-1}, \quad \boldsymbol{L} = \boldsymbol{L}_0 \boldsymbol{C},$$

in which $\boldsymbol{C}$ is any orthogonal matrix of degree n (n degree of the $\boldsymbol{F}$-matrix), the force constants depend — besides on the frequencies $\boldsymbol{\Lambda}$ of normal vibrations — for $n=2$ on a parameter φ. It may be defined by $\boldsymbol{C} = \{c_{ij}\}$, $c_{11}=c_{22}=\cos\varphi$, $c_{21}=-c_{12}=\sin\varphi$, see Ref. [1].

When the force constants of the totally symmetric species of the H_2O molecule are plotted versus φ, the correct force constants of this molecule correspond within the limits of accuracy to that value of the parameter φ, for which the force constant $F_{11}=f_{\mathrm{r}}+f_{\mathrm{rr}}$ 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 ($\pm 3\ \mathrm{cm}^{-1}$) harmonic wavenumbers ω_i' of the D_2S molecule were used 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 ν_i' of D_2S, which are entered in Table 1, line 3. We have calculated the harmonic wavenumbers ω_i' of D_2S using these data, the harmonic wavenumbers ω_i and anharmonicity constants x_{ij} of the H_2S molecule of Allen and Plyler [4], and the assumption $x'_{ij} = \dfrac{\omega_i'\,\omega_j'}{\omega_i\,\omega_j}\,x_{ij}$. The results are listed in Table 1, line 3. The following quantities were used: $\alpha = 92.12°$, $m_{\mathrm{H}} = 1.008145$ a. u., $m_{\mathrm{D}} = 2.014744$ a. u. and $m_{\mathrm{S}} = 31.892196$ a. u. The product rule yields $(\omega_1\,\omega_2)/(\omega_1'\,\omega_2') = 1.9427$ compared with 1.941798 from theory. Miller, Leroi, and Eggers [5] have calculated the harmonic wavenumbers ω_1' and ω_2' of D_2S from the observed wavenumbers ν_1' and ν_2' of Miller and Eggers [3], the anharmonicity constants x'_{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 ω_1' and ω_2' of D_2S by means of two combination frequencies to be

$$\omega_1' = 1952.08\ \mathrm{cm}^{-1} \quad \text{and} \quad \omega_2' = 872.12\ \mathrm{cm}^{-1}.$$

Therefore the harmonic wavenumbers of vibrations ω_1' and ω_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 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 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 H_2O molecule.

	f_{r}	f_{α}	f_{rr}	f_{r}
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 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.

		ν_1	ν_2	ν_3	Ref.	ω_1	ω_2	ω_3	Ref.
1	H_2S	2614.56	1182.68	2627.48	9	2721.92	1214.51	2733.36	9
2	D_2S	1892 ± 3	858 ± 3		2	1947 ± 3	874 ± 3	1963.87	1
3	D_2S	1896.38	855.5		3	1951.6	871.9	1963.87	a
4	D_2S	1896.38	855.5		3	1952.84	871.78	1963.86	5

Table 1. Observed (ν_i) and harmonic (ω_i) wavenumbers of the vibrations of H_2S and D_2S. [a] — own calculation.

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