Radial functions of SiS X $^{1}\Sigma$ from vibration-rotational spectra

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The radial functions for the potential energy and the adiabatic and nonadiabatic effects have been determined in the range $1.72 \le R/10^{-10} \text{ m} \le 2.25$ for the molecule SiS in the electronic ground state X¹ Σ directly from the published frequencies and wavenumbers of pure rotational and vibration-rotational transitions. Only twelve independent parameters were required to fit 3025 data with an (unweighted) standard deviation 0.236 m⁻¹.

1. Introduction

The ultimate objective of spectral analysis is to reduce the numerous spectral data to the fundamental molecular properties expressed to that relatively few parameters having a well defined physical meaning reproduce the measurements within experimental error. In the case of diatomic molecules, the internuclear distance R is the particular variable upon which the observable properties are taken to depend within the Born-Oppenheimer approximation. The process of spectral reduction leads then to the determination of the parameters in the radial functions pertaining to the applicable properties. For data in the form of the frequencies or wavenumbers of spectral lines due to vibration-rotational transitions in the absence of electromagnetic fields (other than that due to the radiant energy required for the observations), the applicable properties are the potential energy and certain auxiliary radial functions related to the adiabatic and nonadiabatic effects that govern collectively how the total energy of the molecule within a particular electronic state varies as a function of the internuclear distance. The adiabatic effects arise essentially from the fact that the nuclear masses are finite, whereas the nonadiabatic effects result from coupling between electronic states induced by the rotational and vibrational motions. Therefore the ultimate reduction of frequency data from vibration-rotational spectra yields the values of the parameters in these radial functions, which have been assigned some assumed forms [1].

We have developed a new algorithm to determine the parameters in the applicable radial functions directly from the frequencies and wavenumbers of pure rotational and vibration-rotational transitions of diatomic molecules within an electronic state of type ¹ Σ [2]. The method makes use of all such available data for any known isotopic variants; in fact the existence of data for sufficiently many isotopically substituted species, relative to the most abundant set of nuclides, of both atomic types if the molecule is heteronuclear, is important for the complete determination of the applicable functions within some finite range of internuclear distance. Extensive and precise data for the vibration-rotational spectra in absorption of SiS have recently been reported for four variants, 28Si32S, 29Si32S, 30Si32S and 28Si34S [3,4], complementing the previously compiled pure rotational transitions for not only these variants but also ²⁸Si³³S [5]; the vibrational states are sampled up to v=10and the rotational states up to J=150. These data provide an excellent opportunity to exploit our algorithm; by its use we have determined three radial functions that reproduce satisfactorily the measured spectra within the precision of the measurements with no systematic deviations.

2. The method

The effective potential energy governing the in-

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ternuclear vibration and rotation (about the centre of molecular mass) of a diatomic molecule within a particular electronic state of type Σ we suppose to have the form [2]

$$V_{eff} = c_0 z^2 \left(1 + \sum_{j=1}^{\infty} c_j z^j \right) + \sum_{j=1}^{\infty} \frac{m_e h_j^a z^j}{M_a} + \sum_{j=1}^{\infty} \frac{m_e h_j^b z^j}{M_b} + B_e J (J+1) \times \left(1 + \sum_{j=0}^{\infty} \frac{m_e g_j^a z^j}{M_a} + \sum_{j=0}^{\infty} \frac{m_e g_j^b z^j}{M_b} \right) \frac{R_e^2}{R^2}, \qquad (1)$$

in which m_e is the electronic rest mass, M_a and M_b are the masses of the separate atoms of types a and b, and the reduced variable z for displacement of internuclear distance R from equilibrium at R_e is defined as [6,7]

$$z \equiv \frac{2(R-R_c)}{R+R_c}.$$
 (2)

The functions involving the coefficients $h_i^{a,b}$ take empirically into account mostly the adiabatic effects and the nonadiabatic effects related to the vibrational inertia of the electrons, because other effects have different dependences on atomic mass which makes them currently negligible with respect to the experimental error of frequency measurements [2]. The functions involving the coefficients $g_i^{a,b}$ take empirically into account predominantly the nonadiabatic effects of the rotational inertia of the electrons [2]. Defined according to eq. (1), all coefficients $c_i, g_i^{a,b}$ and $h_i^{a,b}$ are formally independent of mass, and dimensionless except for c_0 and $h_i^{a,b}$. As a consequence of the various contributions to the effective potential energy, the vibration-rotational terms consist of several contributions; the expression for these terms is an extension of Dunham's form [8-10]:

$$E_{\nu J} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \left(Y_{kl} + Z_{kl}^{h,a} + Z_{kl}^{h,b} + Z_{kl}^{g,a} + Z_{kl}^{g,b} \right)$$
$$\times \left(v + \frac{1}{2} \right)^{k} (J^{2} + J)^{l}.$$
(3)

In this equation the coefficients Y_{kl} are supposed to result from the purely mechanical motions of the nuclei and the associated electrons, in the sense that one is able according to classical mechanics to provide an at least semiquantitative treatment of these mo-

tions for the purpose of spectral analysis [11]; the remaining coefficients, the four components of Z_{kl} , reflect respectively the obviously corresponding terms that may be considered perturbations separately additive in the effective potential energy according to eq. (1). We have published in machine-readable form analytic expressions [12] of the coefficients Y_{kl} as functions of the harmonic coefficient $k_{\rm e}$ (implicitly contained within $U_{1,0}$ or ω_e), the equilibrium separation R_e (implicitly contained within $U_{0,1}$ or B_e), the potential-energy coefficients c_i complete up to i=10 and implicitly the reduced mass [13]; further expressions containing coefficients up to i=16 have been generated according to hypervirial perturbation theory [14]. The coefficient c_0 in eq. (1) is defined in terms either of $U_{1,0}$ and $U_{0,1}$, $c_0 = U_{1,0}^2 / 4U_{0,1}$, or equivalently of k_e and R_e , $c_0 = k_e R_e^2/2ch$; the fundamental physical constants c and h enter because E_{kl} , Y_{kl} and Z_{kl} are all expressed in units of wavenumber for spectroscopic applications. Each term coefficient Y_{kl} and Z_{kl} consists of contributions in the series [15],

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \dots,$$
(4)

$$Z_{kl} = Z_{kl}^{(0)} + Z_{kl}^{(2)} + \dots,$$
(5)

independently of either the method of generation of the expressions or the notation used to distinguish the contributions. Because the coefficients $Y_{kl}^{(0)}$ are expressed as a product with the reduced (atomic) mass $\mu = M_a M_b / (M_a + M_b)$,

$$Y_{kl}^{(0)} = U_{kl} \mu^{[(1/2)k+l]}, \tag{6}$$

the coefficients U_{kl} become formally independent of mass. Although we have generated some expressions of the contributions $Y_{kl}^{(6)}$ and $Y_{kl}^{(8)}$ containing coefficients c_j up to j=16, only the leading terms $Y_{kl}^{(0)}$ and the first two corrections $Y_{kl}^{(2)}$ and $Y_{kl}^{(4)}$ are required at present because the effects of experimental error of wavenumber measurement exceed the magnitudes of further corrections. For each of the four components of Z_{kl} even the first correction $Z_{kl}^{(2)}$ is negligible for the same reason; additional terms cannot be included consistently without account being taken of the interaction of the various effects. Each auxiliary set of coefficients Z_{kl} is a function of both the potential-energy coefficients c_j and the respective coefficients either g_i or h_i for either nucleus a or nucleus b, in addition to μ , k_c and R_c . A few expressions for Z_{kl}^h in terms of c_j and h_j have already been published in a slightly different form [15], which are however readily converted to be consistent with the present definition according to eq. (1); a larger collection containing h_j up to j=10 will be published with the extended set of expressions for Y_{kl} . Likewise a few expressions for Z_{kl}^g in terms of c_j and g_j have been reported [2]; a larger collection containing g_j up to j=10 will also be published in machine-readable form.

As we have described elsewhere [2], the method of nonlinear parameter estimation has been applied to determine the applicable coefficients c_i , $g_i^{a,b}$ and $h_i^{a,b}$ directly from the frequencies ν or wavenumbers \tilde{v} of the pure rotational and vibration-rotational transitions. The transition wavenumbers \tilde{v} are of course the difference of two terms E_{uk} the criterion of the best fit is that the sum of the squares of the residuals between the measured and calculated values, $\tilde{\nu}_{obs} - \tilde{\nu}_{calc}$, is a minimum, hopefully the global minimum (apart from possibly the united atom). The algorithm of the fitting process employs the analytic expressions for not only the term coefficients Y_{kl} and the various components of Z_{kl} but also the first (partial) derivatives of Y_{kl} and Z_{kl} with respect to the parameters, for instance $\partial Y_{kl}/\partial c_i$, $\partial Y_{kl}/\partial U_{1,0}$ and $\partial Z_{kl} / \partial h_{l}$. The analytic expressions for the former derivatives up to j = 10 have already been published in machine-readable form [13]: expressions for further derivatives of Y_{kl} and for the derivatives $\partial Z_{kl}^{\epsilon}/\partial g_i$ and $\partial Z_{kl}^{h}/\partial h_i$ will form part of the large collection to be published subsequently. The different dependences of the residuals on the masses $M_{\rm a}$, $M_{\rm b}$ and J make possible the determination of the coefficients g_i^a, g_i^b, h_i^a and h_i^b .

3. Application to SiS

Table 1 indicates the significant parameters of the radial functions of SiS pertaining to eq. (1). By means of nonzero values of these twelve independent parameters, specifically R_e , k_e , c_j with $1 \le j \le 6$, and both h_j^{Si} and h_j^S with $1 \le j \le 2$, we are able to reproduce 532 infrared data [4] within two standard deviations (0.164 m^{-1}) of the fit; the other five lines were within four standard deviations (0.33 m^{-1}) ,

and of these two had values of J>100. Most other lines corresponding to values of J>100 fitted well within one standard deviation, as did all the 33 lines of the pure rotational transitions within their nominal uncertainties [5].

We compare these results with those of Birk and Jones [4]. They fitted the lines due to each of four isotopic species to separate sets of only the coefficients Y_{kl} , however constraining some values of Y_{kl} of ²⁹Si³²S, ³⁰Si³²S and ²⁸Si³⁴S to those calculated on the basis of the results for ²⁸Si³²S because fewer lines were measured for those naturally less abundant isotopic species; by this means they achieved standard deviations of the fits in the range 0.078-0.089 m^{-1} using 23 coefficients in total. The latter range straddles the value of the standard deviation that we obtained with only twelve parameters. When Birk and Jones fitted all the 569 lines (i.e. excluding the pure rotational line of ²⁸Si³³S), they required nine coefficients U_{kl} and four associated parameters $\Delta_{kl}^{Si,S}$ (related to the Z_{kl}^{h} parameters in eq. (3) but achieved a standard derivation 0.45 m^{-1} of their fit, more than five times as large as our standard deviation. Furthermore they reported that transitions with J > 100were consistently poorly reproduced. For this reason we expected that inclusion of the parameters $g_i^{si,s}$ would promote convergence to a smaller standard deviation; this procedure was effective in the case of LiH [16], for which three coefficients g_1^H, g_2^H and g_1^{Li} were significantly determined, and by this means the systematic discrepancies at relatively large values of J noted previously for LiH [17] were eliminated. However the inclusion in our fitting model of either g_1^{Si} and g_1^{S} separately or both together, or indeed any combination of further coefficients $g_i^{si,s}$, led neither to their values being significantly determined nor to the standard deviation of the fit being significantly improved relative to what was attained in their absence. The values of our parameters $h_i^{si,s}$ are in fact determined predominantly by the microwave data; in the lack of the latter, these four parameters which are the precursors in the Hamiltonian to the spectral coefficients either Z_{kl}^{h} here or Δ_{kl} in the previous work [4] are all poorly defined.

Instead we discovered that potential-energy coefficients c_j beyond j=4, implied by the presence of $U_{3,0}$ as the coefficient U_{kl} of greatest order in the analysis of Birk and Jones [4], provided a signifi-

j	C _j	g _j Si	g;	$h_j^{\rm Si}$ (10 ⁶ m ⁻¹)	$h_j^{\rm S}$ (10 ⁶ m ⁻¹)
0	46282417.5±9.3 m ⁻¹	0	0		-
1	-1.9976202 ± 0.0000119	0	0	-61.72 ± 3.0	-88.0 ± 3.3
2	1.805728 ± 0.000065	0	0	327.9±12.0	333.9±13.5
3	-0.924150 ± 0.00166				
4	-0.22381 ± 0.0124				
5	1.0551±0.066				
6	1.351 ± 0.79				
$U_{1,0} = U_{0,1} =$	289563.998±0.242 m ⁻¹ amu ^{1/2} k 452.91124±0.00085 m ⁻¹ amu k	$c_{e} = 494.01446 \pm 0$ $c_{e} = (1.92926429)$.00087 N m ⁻ ±0.00000243	ı 3)×10 ^{−10} m	

Table 1 Coefficients of the radial functions and other molecular properties of SiS X $^{1}\Sigma$

cant improvement in the fit. The value of c_5 was well defined, but $c_6 = -3.0 \pm 2.0$ less so; the latter coefficient is nevertheless essential to an adequate description of the data according to this model based on the radial functions. For a data set containing transitions up to v = 10, certainly the prospective inclusion of c_6 in the potential-energy function is justifiable. The coefficient c_5 provides directly additional rotational dependence through its relation to $Y_{3,1}$, $Y_{2,3}$, $Y_{1,5}$ and $Y_{0,7}$; even though c_6 may be considered primarily to reflect vibrational effects through $Y_{4,0}$, it also enters the rotational dependence through $Y_{3,2}$, $Y_{2,4}$, $Y_{1,6}$ and $Y_{0,8}$ although the latter coefficients contain the expansion parameter y [2] $(\approx 0.003 \text{ for SiS})$ to successively greater powers. The values of the potential-energy coefficients c_i corresponding to the values of the coefficients a_i determined by Birk and Jones are $c_1 = -1.9974764 \pm$ $0.000047, c_2 = 1.80658 \pm 0.00025, c_3 = -1.0302 \pm$ 0.0033 and $c_4 = 0.334 \pm 0.017$; of these the first two values agree closely with those in table 1 whereas the subsequent values deviate progressively further. The latter behaviour is consistent with the differing degrees of truncation of the polynomials and with the fact that the values of the coefficients a_i presented by Birk and Jones were based on transitions with J < 100, whereas we used all the available data to determine our values of the coefficients c_i in the absence of any systematic deviations. The signs of the values of $\Delta_{kl}^{Si,S}$ [4] are essentially consistent with those of our coefficients $h_i^{Si,S}$, but the differences in the magnitudes of the coefficients $h_i^{Si,S}$ corresponding to $\Delta_{kl}^{Si,S}$ relative to our values again reflect the different truncations of the data set and effectively of the polynomial V(z). Our values of the radial coefficients $h_j^{\text{si},\text{s}}$ are relatively more significant than the values of the spectral parameters $\Delta_{kl}^{\text{si},\text{s}}$ that Birk and Jones determined [4].

When the calculations were repeated with the data set containing 2465 lines measured by Frum et al. [3] in addition to the microwave transitions [5], the values of the parameters were similar – almost all agreed within two standard errors – to those determined from the data of Birk and Jones [4], except that $c_6 = -7.68 \pm 1.3$. The standard deviation of this fit is 0.257 m⁻¹, significantly larger than that of the less numerous data of Birk and Jones [4].

The statistically most justifiable treatment includes all the applicable data. Before we combined the two sets [3,4] of infrared data (with the microwave data [5]), we tested for the existence of a systematic shift of one set with respect to the other. For one set of data an absolute accuracy 0.1 m^{-1} of wavenumber measurement is claimed [4], whereas for the more numerous data 0.01 m⁻¹ is claimed [3]. We found that for 254 lines measured by both groups with the maximum relative precision the average shift is 0.005 ± 0.013 m⁻¹, in other words entirely negligible. This result testifies not only to the careful measurements by the two independent groups by means of different techniques, by interferometry [3] or by tunable laser diodes [4], but also to the great reproducibility that is practicable by means of diverse modern methods and the quality of the prevailing standards of calibration.

The data sets [3-5] thus combined with each datum having its applicable weight produced the final set of parameters stated in table 1. Although the

standard deviation (without inclusion of the statistical weights) of the combined fit was 0.236 m^{-1} . that value is mostly due to the data with relatively small weights (i.e. given relatively large standard deviations) by Frum et al. [3]. In fact, in either the fit of only the data of Frum et al. [3] (with the microwave transitions [5]) or the combined fit of all the infrared and microwave transitions, the estimated standard errors of the parameters in table 1 were as little as one fifth those from the fit of the fewer data of Birk and Jones [4] (including the microwave data). That the value $c_6 = 1.35 \pm 0.79$ from the combined fit remains poorly defined is indicated by its relatively large standard error; that the exclusion of c_6 from the parameter set led to a significantly worse fit, just as also from the fit of the data of Birk and Jones [4], means that this parameter remains nevertheless a necessary component of the final set. Even with the much more numerous vibration-rotational transitions in the data set of Frum et al. [3], to define significant values of any coefficients $g_i^{Si,S}$ remains impracticable,

All the uncertainties in table 1 represent one estimated standard error, and the uncertainties in k_e and R_e also take into account the error in the appropriate fundamental constants [18]. The range of validity of the radial functions defined by the coefficients in the table corresponds approximately to that $(1.72-2.25) \times 10^{-10}$ m between the classical turning points for the highest vibrational state v=10 to which transitions are measured.

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References

- [1] J.F. Ogilvie, Spectrochim. Acta 46 A (1990) 43.
- [2] J.F. Ogilvie, to be published.
- [3] C.I. Frum, R. Engleman and P.F. Bernath, J. Chem. Phys. 93 (1990) 5457.
- [4] H. Birk and H. Jones, Chem. Phys. Letters 175 (1990) 536.
- [5] E. Tiemann, J. Phys. Chem. Ref. Data 5 (1976) 1147.
- [6] J.F. Ogilvie, Proc. Roy. Soc. A 378 (1981) 287; A 381 (1982) 479.
- [7] J.F. Ogilvie, J. Chem. Phys. 88 (1988) 2804.
- [8] J.L. Dunham, Phys. Rev. 41 (1932) 721.
- [9] C. Schlier, Z. Physik 154 (1959) 460.
- [10] R.M. Herman and S. Short, J. Chem. Phys. 48 (1968) 1266; 50 (1969) 572.
- [11] R.H. Tipping and J.F. Ogilvie, Chinese J. Phys. 28 (1990) 281.
- [12] J.F. Ogilvic and R.H. Tipping, J. Symbol. Comput. 3 (1987) 277.
- [13] J.F. Ogilvie, Computer Phys. Commun. 30 (1983) 101.
- [14] F.M. Fernandez and J.F. Ogilvie, Phys. Rev. A 42 (1990) 4001.
- [15] J.F. Ogilvie, Chem. Phys. Letters 140 (1987) 506.
- [16] J.F. Ogilvie, J. Mol. Spectry., in press.
- [17] A.G. Maki, W.B. Olson and G. Thompson, J. Mol. Spectry. 144 (1990) 257.
- [18] E.R. Cohen and B.N. Taylor, Rev. Mod. Phys. 59 (1987) 1121.