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BENCHMARK CALCULATIONS OF FIRST PRINCIPLES ROTATIONAL AND RO-VIBRATIONAL LINE STRENGTHS

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Benchmark first principles calculations of the pure rotational and ro-vibrational transition frequencies and line strengths are presented, using two independent program suites. Both sets of calculations were performed using the same potential energy and dipole surfaces. Our example calculations use recently calculated surfaces for H_2S which have been shown to give good agreement with experimental data. The results, which show perfect agreement for the energy levels, transition frequencies and line strengths, are used as an external check on the two program suites. It is suggested they could provide a standard with which other groups working in this field can compare their calculations.

1. Introduction

In the past few years, it has been shown that it is possible to calculate fully coupled ro-vibrational energy levels of triatomic molecules from first principles with an accuracy that is competitive with experimental data [1–4]. The technique is to use potential energy surfaces calculated either *ab initio* or semi-empirically and to use the variational secular equation method to compute the ro-vibrational eigensolutions.

If suitable dipole surfaces also exist, it is possible to use the above determined ro-vibrational wavefunctions to calculate line strengths for all transitions [2,4–8], including those which are formally "forbidden" by the harmonic-oscillator/rigid-rotor selection rules. Recent developments have been made in this area that have confirmed existing spectral assignments and made predictions of transitions so far undetected, but which could be candidates for laboratory and interstellar observation.

Although the basic ideas of this approach are straight-forward, the algebra and other technical details are non-trivial. The final ro-vibrational wavefunctions may consist of contributions from anything up to 10000 basis functions. Dipole matrix elements must then be calculated between these wavefunctions and there is no immediate check that there are no errors in the programs which carry out this analysis.

As with any large numerical calculation, it is possible to carry out a number of internal checks to eliminate errors. Comparison with known ex-

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perimental spectra is an obvious external check but, when differences show up, it is not always possible to determine whether this is due to errors in the method and execution of the calculations or to deficiencies in the potential energy and/or dipole surfaces employed.

There are two principle source of error in the calculation of ro-vibrational eigenfunctions, energy levels and transition moments. Firstly, neither the form of the kinetic energy operator nor the matrix elements which go into the final secular matrix are easy to determine. Secondly, it is all too easy to use the wrong phase factors in the determining the contributions to the wavefunctions and the resulting transitions. This may have no effect on the ro-vibrational energy levels but it can have a substantial effect on transition intensities.

Experience of calculating ro-vibrational energy levels shows that various systems have been used as benchmarks in developing new methods, involving a considerable amount of duplicated effort. Examples include CH_2^+ [9–13], LiCN [14–16] and H_3^+ [3,17–19].

There are now many scientists who use the variational approach for the calculations of ro-vibrational energy levels for triatomic molecules [16,20,21]. The area of first principles calculation of transition moments and line strengths is, however, still relatively new and we feel it is appropriate to establish a published benchmark against which other workers may compare their results.

Our purposes here is to take the programs developed by two independent groups and use them with identical potential energy and dipole surfaces, to ensure they produce identical results within the accuracy of the programs.

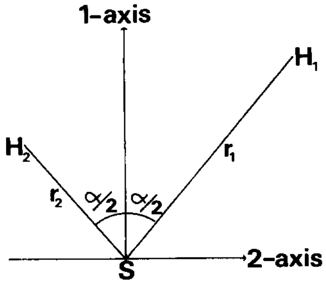

Fig. 1. Definition of axes used in the dipole surface.

In this paper we publish complete details of such a calculation on H_2S, for which a theoretical spectrum has recently been published [2]. Any other workers wishing to test their programs for the calculation of rotational and ro-vibrational energy levels and/or line strengths should then be able simply to input the surface(s) and constants into their code and reproduce the results given here.

2. Computational details

Two independent computer program suites were used to calculate the rotational and ro-vibrational energy levels and transitions of the triatomic molecule H_2S.

(i) Carter and Handy [1] use a variational kinetic energy operator, $\hat{T}_V$, expressed in terms of the two-bondlengths, r_1 and r_2, and the internal angle α. To obtain the ro-vibrational kinetic energy operator $\hat{T}_V + \hat{T}_{VR}$, body-fixed axes must be defined. They are specified in fig. 1, with two of the axes in the plane of the molecule, one of which bisects the angle α. Full details of the kinetic energy operator, the expansion set and matrix element evaluation may be found in ref. [1]. For the dipole transition moments, details of the calculation are described in ref. [5]. Specifically, the programs used are JGE0 [22] and TRANS.

(ii) Tennyson, Sutcliffe and Miller use a program which has greater flexibility in the choice of the two radial coordinates, q_1, q_2 and an included angle θ [24]. One body-fixed axis is embedded along either of the radial coordinates, with the other in-plane axis perpendicular to it. For this study calculations were performed in both scattering coordinates – q_1 is the H–H separation and q_2 is the distance of S from the H–H centre – and bondlength–bondangle coordinates, as in (i). We note that the axis embeddings mean that for rotationally excited calculations the C_{2v} symmetry of the system is not preserved in bondlength–bondangle co-ordinates. This suite of programs is based around the driver program TRIATOM [24]. The suite has been extended recently to include programs DIPOLE and SPECTRA which calculate line strengths and integrated absorption coefficients [23].

Although the two program suites have been developed separately they share a common feature, namely, that the potential energy and dipole surfaces to be used may be supplied in any form. Subroutines which carry out appropriate coordinate transformations are included in the main suite. Note that the ro-vibrational energy levels and transition moments must be independent of the choice of body-fixed axes. The ability to produce identical results using different body-fixed axes systems is thus a good test of the calculations.

The potential energy surface calculated by Senekowitsch et al. [2] has the form

$$V(r_1, r_2, \alpha) = \sum_{klm} f_{klm}(\Delta r_1^V)^k (\Delta r_2^V)^l (\Delta\alpha^V)^m. \tag{1}$$

The transformed coordinates are given by

$$\Delta r_n^V = \frac{(r_n - r_{\mathrm{ref}}^V)}{r_n} \tag{2}$$

and

$$\Delta\alpha^V = (\alpha - \alpha_{\mathrm{ref}}^V) + \beta_2(\alpha - \alpha_{\mathrm{ref}}^V)^2 + \beta_3(\alpha - \alpha_{\mathrm{ref}}^V)^3, \tag{3}$$

where r_{ref}^V and α_{ref}^V are the reference values of the two H–S bonds and the H–S–H angle, respectively, used in the potential energy expansion.

A similar expansion is used to represent the dipole surface components. Thus

$$\mu^{(\lambda)}(r_1, r_2, \alpha) = \sum_{klm} \mu_{klm}^{(\lambda)}(\Delta r_1^\mu)^k (\Delta r_2^\mu)^l (\Delta\alpha^\mu)^m, \tag{4}$$

where λ labels the axes, 1 and 2. In this case, the transformed coordinates are given by

$$\Delta r_n^\mu = (r_n - r_{\mathrm{ref}}^\mu); \tag{5}$$

and

$$\Delta\alpha^\mu = (\alpha - \alpha_{\mathrm{ref}}^\mu), \tag{6}$$

where r_{ref}^μ and $\alpha_{\mathrm{ref}}^\mu$ are the reference values of the two H–S bonds and the H–S–H angle, respectively, used in the dipole expansion.

Table 1
Expansion parameters for the potential energy surface of H_2S

$k\ l\ m$	f_{klm} [a]	$k\ l\ m$	f_{klm} [a]
0 0 0	0.000000	2 2 0	0.026455
0 0 1	−0.000403	3 0 1	0.004669
0 2 0	0.886280	0 3 1	0.004669
0 0 2	0.087964	0 2 2	−0.100007
1 2 0	−0.010851	0 0 4	0.021878
1 1 1	−0.077552	0 0 5	0.005135
0 1 2	−0.052780	0 0 6	−0.005423
3 1 0	−0.030729	0 1 0	−0.002782
0 4 0	−0.418121	1 1 0	−0.005510
1 2 1	−0.060572	0 1 1	0.023534
1 1 2	0.098939	2 1 0	−0.010851
0 1 3	0.026950	2 0 1	0.014673
0 5 0	−0.304955	1 0 2	−0.052780
6 0 0	−0.331182	4 0 0	−0.418121
1 0 0	−0.002782	1 3 0	−0.030729
2 0 0	0.886280	2 1 1	−0.060572
1 0 1	0.023534	2 0 2	−0.100007
3 0 0	−0.309955	1 0 3	0.026950
0 3 0	−0.309955	5 0 0	−0.304955
0 2 1	0.014673	0 6 0	−0.331182
0 0 3	−0.006213		

$r_{\mathrm{ref}}^V = 2.523703$ a.u.
$\alpha_{\mathrm{ref}}^V = 1.609659$ radians
$\beta_2 = -0.027215$
$\beta_3 = -0.130193$

[a] Expansion coefficients in atomic units.

The expansion coefficients together with the reference geometries for the potential energy, V, and the two dipole components, $\mu^{(1)}$ and $\mu^{(2)}$, are given in tables 1 and 2. The axes are defined in fig. 1 for an arbitrary H_2S geometry. Table 3 gives the masses and conversion factors used in the programs.

For both sets of calculations, care was taken to ensure that the final energy levels were converged to at least 0.1 cm^{-1} and that line strengths were constant to at least three significant figures with respect to increasing basis sets or integration grids. The calculations were carried out in atomic units and then converted to cm^{-1} and debye. The JGE0 suite calculations used in this paper were performed using the Amdahl 370/V7A computer at Reading University, and those using the TRI-

Table 2
Expansion parameters for the dipole surface of H_2S

$k\ l\ m$	$\mu^{(1)}_{klm}$ [a]	$\mu^{(2)}_{klm}$ [a]
0 0 0	0.387497	0.000000
0 0 1	0.059821	0.000000
0 2 0	−0.025178	0.033777
0 0 2	0.053680	0.000000
1 2 0	0.006169	0.014296
1 1 1	−0.025947	0.000000
0 1 2	−0.030831	−0.043655
3 1 0	−0.001260	0.000715
0 4 0	0.005137	−0.004815
1 2 1	−0.003403	−0.005711
1 1 2	0.029810	0.000000
0 1 3	0.038636	0.017810
1 0 0	−0.007730	−0.009997
2 0 0	−0.025178	−0.033777
1 0 1	−0.092358	−0.157789
3 0 0	−0.012602	−0.010204
0 3 0	−0.012602	0.010204
0 2 1	−0.004742	0.044677
0 0 3	−0.145655	0.000000
2 2 0	0.011762	0.000000
3 0 1	0.007284	−0.030944
0 3 1	0.007284	0.030944
0 2 2	−0.042114	0.020499
0 0 4	0.057108	0.000000
0 1 0	−0.007730	0.009997
1 1 0	−0.021291	0.000000
0 1 1	−0.092358	−0.157789
2 1 0	0.006169	−0.014296
2 0 1	−0.004742	−0.044677
1 0 2	−0.030831	−0.043655
4 0 0	0.005137	0.004815
1 3 0	−0.001260	−0.000715
2 1 1	−0.003403	0.005711
2 0 2	−0.042114	−0.020499
1 0 3	0.038636	−0.017810

$r^{\mu}_{ref} = 2.520000$ a.u.
$\alpha^{\mu}_{ref} = 1.605703$ radians

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[a] Dipole in atomic units.

Table 3
Masses and conversion factors used in the calculations

Parameter	Value
mass of hydrogen atom	1.007825 a.m.u.
mass of sulphur atom	31.972071 a.m.u.
atomic mass units to atomic units	1 a.m.u. = 1822.84475 m_e
hartree to cm^{-1}	1 a.u. = 2.19474624×10^5 cm^{-1}
atomic units to debye	1 a.u. = 2.5417662 D

Table 4
Energy levels for H_2S relative to $V(r^V_{ref}, r^V_{ref}, \alpha^V_{ref}) = 0$

Vibrational band	J	K_a	K_c	Energy
ground state	0	0	0	3297.5
	1	0	1	3311.2
	1	1	1	3312.5
	1	1	0	3316.8
ν_2	0	0	0	4487.9
	1	0	1	4501.7
	1	1	1	4503.3
	1	1	0	4507.8
$2\nu_2$	0	0	0	5669.5
	1	0	1	5683.5
	1	1	1	5685.2
	1	1	0	5690.0
ν_1	0	0	0	5917.8
	1	0	1	5931.3
	1	1	1	5932.7
	1	1	0	5936.9
ν_3	0	0	0	5928.4
	1	0	1	5942.0
	1	1	1	5943.3
	1	1	0	5947.5

Table 5
Rotational and ro-vibrational transitions in H_2S

Vibrational band	$J'K_a'K_c'$	$J''K_a''K_c''$	ω_{if} (cm^{-1})	$S(f-i)$ [a] (D^2)
ground state	1 1 0	1 0 1	5.6	0.1449(+1)
	1 1 1	0 0 0	15.1	0.9657(+0)
ν_2	0 0 0	1 1 1	1175.4	0.1834(−3)
	1 0 1	1 1 0	1184.9	0.2762(−3)
	1 1 0	1 0 1	1196.6	0.3794(−3)
	1 1 1	0 0 0	1205.8	0.2540(−3)
$2\nu_2$	0 0 0	1 1 1	2356.9	0.1226(−4)
	1 0 1	1 1 0	2366.7	0.1776(−4)
	1 1 0	1 0 1	2378.8	0.2176(−4)
	1 1 1	0 0 0	2387.7	0.1413(−4)
ν_1	0 0 0	1 1 1	2605.3	0.4563(−4)
	1 0 1	1 1 0	2614.5	0.7354(−4)
	1 1 0	1 0 1	2625.7	0.8197(−4)
	1 1 1	0 0 0	2635.2	0.6068(−4)
ν_3	0 0 0	1 0 1	2617.3	0.3613(−4)
	1 1 1	1 1 0	2626.5	0.5437(−4)
	1 1 0	1 1 1	2634.9	0.6593(−4)
	1 0 1	0 0 0	2644.5	0.4064(−4)

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[a] Powers of ten in brackets.

ATOM suite were performed on the Cray XMP-48 at the Rutherford Appleton Laboratory's Atlas Centre.

The line strength for a transition from an initial state $|i\rangle$ to a final state $\langle f|$ is defined by

$$S(f-i)=\sum_{A=X,Y,Z}\ \sum_{M',M''}\langle f|\mu_A|i\rangle^2, \tag{7}$$

where X, Y and Z are the space-fixed axes, and μ_A is the component of the dipole moment along the space-fixed A-axis. The second summation is over the rotational sublevels of the initial and final states, but does not include any weighting factors which may arise from nuclear spin statistics or from the symmetry degeneracy of the levels involved in the transitions, (e.g. 2 for E states, 3 for T states etc.).

The final expression for $S(f-i)$ is given by eq. 16 of ref. [4] and eq. 44 of ref. [8]. $S(f-i)$ is equal to R^2 as defined in eq. 3 and 29 of ref. 5. The relationship between $S(f-i)$ or R^2 and the Herzberg formulation [25] for symmetric top molecules can be found in ref. 5, although this is not applicable in the case of H_2S.

3. Results and discussion

Energy levels for total angular momentum states of $J=0$ and 1 are given in table 4 for the JGE0 and TRIATOM suite calculations. f_{000} was taken to equal zero for numerical convenience so that all energies are relative to $V(r^V_{\mathrm{ref}}, r^V_{\mathrm{ref}}, \alpha^V_{\mathrm{ref}})=0$. Line strengths for the allowed transitions are given in table 5.

Both program suites give identical results for the energy levels, transition frequencies, ω_{if}, and line strengths, $S(f-i)$, to all significant figures shown. Indeed, in almost every case the computed levels and line strengths were the same to at least one further significant figure than given in the tables. In addition, the results from the TRIATOM suite were found to be independent of the coordinate system used to all significant figures given here.

We hope that these results will be of use to other workers in this field as benchmark calculations and would be happy to supply details of other calculations we have made if they would also be helpful.

4. Acknowledgements

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