The Potential Energy Surface of Hydrogen Sulfide

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We report here a refinement of the potential energy surface for the electronic ground state of the $H_2^{32}S$ molecule in a least-squares fit to experimental spectroscopic data. The calculations are carried out by combining an exact kinetic energy (EKE) approach to the calculation of the rotation–vibration energies of a triatomic molecule with the MORBID approach, which employs an approximate kinetic energy operator. The combined method has been described and applied to the water molecule in two previous publications [O. L. Polyansky, P. Jensen, and J. Tennyson, *J. Chem. Phys.* **101,** 7651–7657 (1994); *ibid.,* submitted for publication.]. The input data for the fit of the present work comprised rotation–vibration term values with $J \leq 10$ for the vibrational ground state and the ν_2 state, and with $J \leq 5$ for all other states that have been characterized by high-resolution spectroscopy. In total, we fit data for 31 vibrational states of $H_2^{32}S$. We have obtained a very accurate potential within the framework of the EKE approach. The root-mean-square deviation for the fitted vibrational energies was found to be 0.28 cm^{-1}. The fit to all 450 input data had a standard deviation of 0.17 cm^{-1}. In the final fit, 11 parameters were varied. Our analysis of the residuals (observed − calculated) from the fit provides even stronger evidence than analogous fits for water that we have reached a level of accuracy at which the breakdown of the Born–Oppenheimer approximation becomes the most important reason for the deviation between theory and experiment. In order to improve further the fit, the J, K_a-dependent nonadiabatic corrections to the kinetic energy operator for the nuclear motion must be explicitly considered.   © 1996 Academic Press, Inc.

I. INTRODUCTION

In two previous publications (*1, 2*) we have reported determinations of highly accurate potential energy surfaces for the water molecule by least-squares fitting to experimental spectroscopic data. The calculations were carried out in an approach combining the advantages of the exact kinetic energy (EKE) (*3*) approach to the variational calculation of molecular rotation–vibration energy levels with those of the approximative kinetic energy approach in its particular MORBID (Morse oscillator rigid bender internal dynamics) (*4, 5*) form. In the present work, we report an analogous calculation for the H_2S molecule.

There are a number of reasons for studying hydrogen sulfide. For example, the H_2S and H_2O molecules are obviously similar, but the energy level spectrum of H_2S is in many ways simpler than that of H_2O. Hence, to assess the limitations of present-day theoretical methods for accurately calculating the water spectrum, it is desirable to contrast results obtained for water with those computed for the simpler hydrogen sulfide molecule. Furthermore, H_2S is interesting in itself.

One interesting feature of its rotation–vibration energy

level spectrum is the so-called fourfold cluster effect (see, for example, Refs. (*6, 7*)), i.e., the formation of four-member groups of nearly degenerate energy levels at high rotational excitation. Two types of fourfold energy clusters are known for H_2X molecules (*8, 9*): Type I clusters form in vibrational states with local mode labels (nn^+v_2) (*10*), and Type II clusters form in near-degenerate vibrational states with local mode labels $(n_1 n_3^{\pm} v_2)$, $n_1 \neq n_3$. In the local mode label (*10*), the bending quantum number v_2 has its usual (harmonic oscillator) meaning, whereas the stretching quantum numbers n_1 and n_3 define the number of excited quanta in a Morse oscillator basis. The $\pm$ superscript defines the symmetry in the molecular symmetry group $C_{2v}(M)$ (*11*); + states have A_1 symmetry and − states have B_2 symmetry. A Type I cluster is formed by coalescence of four energies which can all be assigned as belonging to the vibrational state (nn^+v_2), whereas Type II clusters are formed by coalescence of an energy doublet belonging to the $(n_1 n_3^+ v_2)$ vibrational state with one belonging to the $(n_1 n_3^- v_2)$ state.

Type I clusters were observed experimentally for the first time in the vibrational ground state of the H_2Se molecule (*12, 13*). The groups of near-degenerate levels could be followed up to $J = 23$. Recently, the rotational energy structure in the vibrational ground state of $H_2^{32}S$ has been studied experimentally (*14*). The highest energy levels in the J manifolds could be followed up to $J = 15$. It is known from theoretical predictions (see, for example, Fig. 2 of Ref. (*6*))

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that for $H_2^{32}S$, the so-called critical J value, $J_{critical} = 15$. At this J value, the energy difference between the highest two doublets in each J manifold starts decreasing with J, and the cluster formation becomes evident. In Ref. (*14*), transitions to cluster states at $J = 16$ could not be observed since they are obscured by stronger transitions. However, transitions to cluster states with $J = 17$ were tentatively assigned. Type II clusters have been observed experimentally for the ν_1/ν_3 vibrational states of H_2Se (*15*) and, very recently, evidence of Type II cluster formation has been noticed for highly excited stretching states of H_2S (*16*).

Generally, the cluster states have very high values of J and K_a, so that transitions involving them are difficult to observe experimentally. In order to populate the lower states of these cluster transitions, it is desirable to obtain spectra at higher temperatures. Fourfold cluster formation has been established experimentally and theoretically for the molecules H_2S (*6, 16*), H_2Se (*8, 9, 12, 13, 15*), and H_2Te (see Ref. (*7*) and references therein). Initially one would expect that the experimental verification of the cluster effect would be easier for H_2Se and H_2Te since in these molecules, the clusters form at lower J values than in H_2S. However, as mentioned above the observation of transitions involving cluster states is facilitated by heating of the absorption cell, but this is difficult to do for H_2Se and H_2Te since these molecules are unstable at higher temperatures. The H_2Se molecule decomposes at temperatures around 300°C, and H_2Te is unstable even at room temperature so that in a recent measurement of its far infrared spectrum (*17*), the H_2Te sample was cooled to −40°C. In view of these facts, it would appear that high-temperature spectra of H_2S could provide a useful source of information about the fourfold cluster effect: the clusters form at higher J values than in H_2Se and H_2Te, but a H_2S sample could be heated to temperatures sufficiently high that the cluster states could be traced to extremely high J and K_a values. In principle, the same would hold for the water molecule. However, for water it is not certain that cluster formation takes place at all, at least in the form known for the H_2S, H_2Se, and H_2Te molecules, and even if clusters do form, they will be found at prohibitively high J and K_a values, making a laboratory observation of transitions to them virtually impossible (*1, 7*).

Furthermore, there is atmospheric and astrophysical interest in the spectrum and potential energy surface of H_2S. For example, hydrogen sulfide is present as a trace species in the Earth's atmosphere and is believed to be present in the atmospheres of cool stars, so that its absorption contributes to their opacities, and in the atmospheres of the Giant Planets.

Previous determinations of the H_2S potential energy surface from experimental data (*6, 18*) were made with models employing an approximate kinetic energy operator for the nuclear motion. Furthermore, the fit of Ref. (*18*) was based on a very limited input data set of vibrational ($J = 0$) ener-

gies. In the present work, we report the first refinement of the potential energy function for the electronic ground state of $H_2^{32}S$ carried out with a kinetic energy operator exact within the Born–Oppenheimer approximation in a least-squares fit to an extended set ($J \leqslant 10$) of rotation–vibration term values.

II. POTENTIAL ENERGY FUNCTION AND INPUT DATA

In the present work, we use the analytical form of the potential energy function already described in Refs. (*4, 5*). The function is given as

$$
\begin{aligned}
V(\Delta r_1, \Delta r_3, \overline{\rho}) = V_0(\overline{\rho}) &+ \sum_j F_j(\overline{\rho}) y_j \\
&+ \sum_{j \leqslant k} F_{jk}(\overline{\rho}) y_j y_k + \sum_{j \leqslant k \leqslant m} F_{jkm}(\overline{\rho}) y_j y_k y_m \\
&+ \sum_{j \leqslant k \leqslant m \leqslant n} F_{jkmn}(\overline{\rho}) y_j y_k y_m y_n \\
&+ \sum_{j \leqslant k \leqslant m \leqslant n \leqslant o} f^{(0)}_{jkmno} y_j y_k y_m y_n y_o \\
&+ \sum_{j \leqslant k \leqslant m \leqslant n \leqslant o \leqslant p} f^{(0)}_{jkmnop} y_j y_k y_m y_n y_o y_p \\
&+ \sum_{j \leqslant k \leqslant m \leqslant n \leqslant o \leqslant p \leqslant q} f^{(0)}_{jkmnopq} y_j y_k y_m y_n y_o y_p y_q,
\end{aligned}
\tag{1}
$$

where all summation indices j, k, m, n, o, p, and q run over the values 1 and 3, and the quantities $f^{(0)}_{jkm\ldots}$ are expansion coefficients. The Morse-transformed coordinate y_j in Eq. [1] is given by

$$
y_j = 1 - \exp(-a_j \Delta r_j),
\tag{2}
$$

where the a_j are molecular constants and $\Delta r_j = r_j - r_j^e$, $j = 1$ or 3, is the displacement from the equilibrium value r_j^e of the internuclear distance r_j from the ''central'' nucleus 2 to the ''terminal'' nucleus $j = 1$ or 3. The instantaneous value of the bond angle supplement is denoted $\overline{\rho}$ (see Fig. 1 of Ref. (*4*)). The expansion coefficients $F_{jkm\ldots}$ of Eq. [1] depend on $\overline{\rho}$ and are defined as

$$
F_j(\overline{\rho}) = \sum_{i=1}^{4} f_j^{(i)} (\cos \rho_e - \cos \overline{\rho})^i,
\tag{3}
$$

and

$$
F_{jk\ldots}(\overline{\rho}) = f_{jk\ldots}^{(0)} + \sum_{i=1}^{N} f_{jk\ldots}^{(i)} (\cos \rho_e - \cos \overline{\rho})^i,
\tag{4}
$$

where ρ_e is the equilibrium value of $\overline{\rho}$ and the $f_{jk\ldots}^{(i)}$ are expansion coefficients. The function $F_{jk}(\overline{\rho})$ has $N = 3$,

$F_{jkl}(\overline{\rho})$ has $N = 2$, and $F_{jklm}(\overline{\rho})$ has $N = 1$. The function $V_0(\overline{\rho})$ is the potential energy for the molecule bending with bond lengths fixed at their equilibrium values, and we parameterize it as

$$V_0(\overline{\rho}) = \sum_{i=2}^{12} f_0^{(i)}(\cos \rho_e - \cos \overline{\rho})^i, \qquad [5]$$

where the $f_0^{(i)}$ are expansion coefficients.

In our work on the H_2O molecule (*1, 2*), we have shown that in calculations of this type, the accuracy is sufficiently high that the primary cause of model errors becomes the breakdown of the Born–Oppenheimer approximation. Consequently, we fitted only data for the $H_2^{16}O$ isotopomer in Refs. (*1, 2*). For the same reason, we fit in the present work only data for the isotopomer $H_2^{32}S$. The $H_2^{32}S$ input data used for the fit in Ref. (*6*) were taken from Refs. (*19–24*). The data set comprised $J \leq 5$ rotation–vibration term values for all vibrational states which had been studied in high resolution together with a few vibrational ($J = 0$) term values for which no rotational information was available (see Table 1 of Ref. (*6*)). For the fits of the present work, we extended this data set to contain the rotational term values of the vibrational ground state for $J \leq 10$; these data were obtained from the THz-infrared spectrum reported in Ref. (*25*). Further, the data set was supplemented with rotation–vibration term values with $5 < J < 10$ for the $(v_1v_2v_3) = (010)$ vibrational state (*23*), and with eight recently determined vibrational energies extending up to 11 000 cm^{-1} (*26*). These latter data replace old measurements from Ref. (*19*).

III. RESULTS

The fits were carried out using the combined EKE/MORBID approach described in detail in Ref. (*1*). All calculations used atomic masses and, for the EKE calculations, the constants given by Carter *et al.* (*27*). As in Refs. (*1, 2*), the EKE calculations were performed using the DVR3D program suite (*3*). For calculations with $J > 0$, 21 symmetrized DVR grid points in each radial coordinate and 49 angular DVR grid points were used. To ensure convergence of the local mode stretching states $J = 0$ calculations were performed using 28 symmetrized DVR grid points in each radial coordinate. The radial DVR points were based on basis functions optimized for previous calculations (*28*).

The MORBID calculations were done with the basis sets described in Ref. (*6*). The potential of Kozin and Jensen (*6*) was used as a starting point for the fits. The potential energy parameters obtained in the least-squares fit are given in Table 1. The constants in Table 1 are given to more figures than would appear justified from their standard error; however, use of less precisely defined constants leads to

TABLE 1
Fitted Potential Energy Parameters for H_2 ^{32}S.

ρ_e/deg	87.669282	$f_{11}^{(0)}$/cm^{-1}	39228.206(6.2)
r_{12}^e/Å	1.336024(34)	$f_{11}^{(2)}$/cm^{-1}	−3008.372(280)
a_1/Å^{-1}	1.658377	$f_{13}^{(0)}$/cm^{-1}	−375.750(8.5)
$f_0^{(2)}$/cm^{-1}	19293.907(11)	$f_{13}^{(2)}$/cm^{-1}	4426.557(98)
$f_0^{(4)}$/cm^{-1}	4239.022(180)	$f_{111}^{(0)}$/cm^{-1}	−898.485(23)
$f_0^{(5)}$/cm^{-1}	6931.270	$f_{111}^{(2)}$/cm^{-1}	−4720.345
$f_0^{(6)}$/cm^{-1}	4140.373(530)	$f_{113}^{(0)}$/cm^{-1}	−301.103(45)
$f_1^{(1)}$/cm^{-1}	−3670.331	$f_{1111}^{(0)}$/cm^{-1}	850.092
$f_1^{(2)}$/cm^{-1}	−7504.719(240)		

Note. Numbers in parentheses are standard errors in μÅ for r_{12}^e or cm^{-1} for the other constants; constants with no standard error were held fixed in the final iteration of the fit.

significant changes in the resulting potential. This is a common phenomenon in potential fitting and arises from the use of partially correlated constants in the least-squares fitting procedure.

In Table 2 we present observed and calculated values for the vibrational ($J = 0$) term values together with the residuals (observed − calculated). The root-mean-square deviation for the fitted vibrational energies was found to be 0.28 cm^{-1}. The fit to all 450 input data had a standard deviation of 0.17 cm^{-1}. In the final fit, only 11 parameters of the potential energy expansion (Eqs. [1]–[5]) were varied. We have tried to decrease further the standard deviation of the fit by variation of all other parameters currently available in the MORBID program. However, no improvement could be obtained. The situation is more spectacular than that encountered in our fit of the water molecule (*2*), where we determined expansion coefficients involving up to 7 powers of the y_j functions. For water, there would seem to be a remote possibility that the fit could be improved by inclusion of further parameters; this appears impossible for hydrogen sulfide. We conclude that, as in the case of the water molecule, we have reached the limit of accuracy attainable within the Born–Oppenheimer approximation.

Since we have fitted data belonging to the $H_2^{32}S$ isotopomer only, the adiabatic correction to the true Born–Oppenheimer potential energy function has been effectively included in the fitted potential. The calculations of the present work neglect only the nonadiabatic corrections to the kinetic energy operator. It is very difficult to judge from the residuals of the vibrational energies (Table 2) if it would be possible to improve them by inclusion of such nonadiabatic corrections. However, there is some systematic trend in the

TABLE 2
Comparison between Observed and Fitted Values for the Vibrational Band Origins of $H_2\,^{32}S$ (in cm^{-1}).

$(v_1v_2v_3)$	E_{obs}	E_{calc}	Obs.−Calc.
(010)	1182.57	1182.90	−0.33
(020)	2353.96	2354.15	−0.19
(100)	2614.41	2614.39	0.02
(001)	2628.45	2628.79	−0.34
(030)	3513.79	3513.84	0.05
(110)	3779.17	3779.04	0.13
(011)	3789.26	3789.18	0.08
(040)	4661.68	4661.57	0.11
(120)	4932.70	4932.45	0.35
(021)	4939.10	4938.66	0.44
(200)	5144.99	5145.30	−0.31
(101)	5147.22	5147.27	−0.05
(002)	5243.10	5243.53	−0.43
(050)	5797.24	5796.63	0.61[a]
(130)	6074.58	6074.69	−0.11
(031)	6077.60	6077.26	−0.34
(130)	6074.58	6074.69	−0.11
(031)	6077.60	6077.26	−0.34
(210)	6288.15	6287.90	0.25
(111)	6289.17	6288.70	0.47
(121)	7420.09	7419.64	0.45
(102)	7576.38	7576.42	−0.04
(201)	7576.54	7576.48	0.06
(300)	7752.26	7752.65	−0.39
(003)	7779.32	7779.80	−0.48
(112)	8697.14	8696.75	0.39
(211)	8697.15	8696.71	0.44
(202)	9911.02	9910.70	0.32
(301)	9911.02	9910.69	0.33
(400)	10188.30	10189.00	−0.70[a]
(103)	10194.45	10194.15	0.30
(212)	11008.68	11008.86	−0.18
(311)	11008.68	11008.85	−0.17

Note. The observed energy values are from Refs. (20–26). The root-mean-square deviation for all term values in the table is 0.28 cm⁻¹.

[a] Not included in the fit.

residuals of the high-J, high-K_a term values in the vibrational ground state and the (010) state, and we have compared these residuals to estimated nonadiabatic corrections. The order of magnitude and the sign of the residuals can in fact be explained in terms of simple, rigid-rotor nonadiabatic corrections estimated from the theoretical results of Ref. (29). This observation provides strong evidence that in the present fit, we have indeed reached a level of accuracy at which the breakdown of the Born–Oppenheimer approxima-

tion becomes the most important reason for the deviation between theory and experiment. In order to improve further the fit, the J, K_a-dependent nonadiabatic corrections to the kinetic energy operator for the nuclear motion must be explicitly considered. Similar situations have been encountered in *ab initio* calculations for H_3^+ (30) and in our fit of the water potential energy function (2).

IV. SUMMARY AND CONCLUSION

We have used the combined EKE/MORBID approach described previously (1) to refine the potential energy surface for the electronic ground state of the $H_2\,^{32}S$ molecule in a least-squares fit to an extensive set of experimentally derived molecular term values. Relative to previous spectroscopic determinations of this potential energy surface (6, 18), we have significantly extended the input data set while also lowering the standard deviation of the fit. The result is a potential parameterized by only 17 constants which simultaneously reproduces 450 experimentally derived rotation–vibration term values for 31 vibrational states with a standard deviation of only 0.17 cm⁻¹. In order to improve further the potential surface calculated in the present work, it will be necessary to account explicitly for the J, K_a-dependent nonadiabatic corrections to the kinetic energy operator for the nuclear motion.

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