Vibrationally elastic and inelastic scattering of electrons by hydrogen sulphide molecules

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Abstract. Vibrationally elastic and inelastic cross sections (differential and integral ones) are calculated for electron scattering from hydrogen sulphide (H$_2$S) at the collision energies 3–30 eV. Vibrational excitation of all three fundamental modes is considered. The calculation is based on the rotationally sudden and a vibrationally close-coupling method using an ab initio electrostatic potential. The effects of electron exchange and target polarization are taken into account approximately. The resulting cross sections are compared with the experimental data available. The present differential cross sections (DCS) for the elastic scattering reproduce the experimental data well. For the inelastic scattering, the present DCS is too small at 3 eV, compared with the experimental data. This is probably due to a shape resonance, which the present calculation would not be sufficiently accurate to produce. In the higher energy region (i.e. above about 10 eV), the present vibrational cross section should be more reliable, but no experimental data are available so far.

1. Introduction

Cross sections for electron scattering by molecules play an important role in many fundamental areas of research such as radiation science, astrophysics, plasma processes and so on (Christophorou 1984). This paper is an extension of our previous work on the H$_2$O molecule (Okamoto et al 1993, Nishimura and Itikawa 1995) to hydrogen sulphide (H$_2$S), which has molecular structure similar to H$_2$O. H$_2$S is another example of a typical polar molecule, for which a large cross section can be expected in the electron scattering. In addition, H$_2$S is one of the molecules of astrophysical interest. While several calculations have been carried out for the vibrationally elastic scattering, there have been very few calculations for vibrationally inelastic scattering so far. The main purpose of the present work, therefore, is the calculation of the cross sections for the vibrational excitation of H$_2$S. A H$_2$S molecule has three normal modes of vibration. Here cross sections are calculated for the excitation of the lowest excited state of each mode: symmetric stretching (100), bending (010) and antisymmetric stretching (001) modes.

First of all, we take a look at the history of the research on the e + H$_2$S collision. Gianturco and Thompson (1980) first calculated the elastic cross sections by solving coupled equations for partial waves. Taking account of the electron exchange and target polarization effects through a simple procedure, they studied the process only in the resonance region. Making use of the local model potentials, i.e. the Hara version of the free-electron gas model (Hara 1967) for the electron-exchange, and the parameter-free polarization potential obtained by the method of Temkin (Jain and Thompson 1982)
for the target polarization, Jain and Thompson (1984) calculated both the vibrationally elastic and inelastic cross sections in the energy range of 1–10 eV. They used the adiabatic nuclei approximation for the calculation of the vibrational excitation cross section. They calculated the cross sections for the (100) and the (010) modes, but not for the (001) mode. Since then, no theoretical study of vibrational excitation has been reported. Gianturco (1991) obtained the elastic cross section using a semiclassical exchange and other parameter-free correlation-polarization potentials. He reported differential cross sections (DCS) at 1–25 eV. Yuan and Zhang (1993) also reported the elastic cross section (at 0.1–50 eV). They calculated the cross sections taking only the spherical part of the potential with an addition of the contribution of the dipole interaction through the Born approximation. Recently, Greer and Thompson (1994) improved the calculation of elastic cross section of Jain and Thompson (1984) by treating the electron-exchange effect exactly by an iterative technique. There are two sets of calculations based on the variational approach. Lengsfield et al (1992) reported the elastic cross sections using the complex Kohn method. They included polarization for energies less than 10 eV, but not in the higher energy region (for details, see Rescigno et al 1995). Machado et al (1995) calculated the elastic cross sections by using the Schwinger method, but including no polarization.

As for the experiment, two groups have reported their results so far (Rohr 1978, 1983, Gulley et al 1993). Rohr obtained his cross sections in absolute magnitude by comparing the elastic scattering rates in H$_2$S with those for He known at that time. The resulting absolute scale was estimated to have a considerable ambiguity (about a factor of two). Therefore we compare our results with only the recent experiment by Gulley et al (1993). They measured the vibrationally elastic cross sections at 1–30 eV and the inelastic ones at 2 and 3 eV. No experimental integral cross section (ICS) has been reported for the vibrational excitation. Experimentally the two stretching modes, (100) and (001), cannot be separated with the present technique. All the experimental papers therefore report only the combined cross section for the two stretching modes. We represent the combined one as (100,001) hereafter. The present cross sections for the (100) and the (001) are added together, when compared with the experimental data.

The present calculation of H$_2$S is based on the rotationally sudden (i.e. the fixed nuclear orientation) approximation. The vibrational transition is treated in a (two-state) close-coupling method. The electrostatic potential is calculated from an ab initio target wavefunction. The effects of electron exchange and target polarization are taken into account approximately through a model potential. The DCSs and ICSs are calculated at 3–30 eV. At the collision energies around and below 3 eV, the present method of calculation cannot be expected to be very reliable. In that region, the effects of electron exchange and target polarization become more significant than in the higher energy region. The present model potentials to include those effects are probably too crude to give a reliable cross section at those low energies, particularly for vibrational excitation. Since any comparison with experiment for the vibrational excitation of H$_2$S can only be made at 2 and 3 eV, we calculate the cross section at energies as low as 3 eV. The main emphasis of the present paper, however, is placed on the region of the collision energy around and above 10 eV, for which there is no quantitative information reported so far on the vibrational excitation of H$_2$S. The present work gives not only a detailed insight into electron scattering from H$_2$S, but also quantitative information about the vibrational excitation of the three fundamental modes of H$_2$S.
2. Theory

Here we consider vibrationally elastic and inelastic scattering of electrons from H$_2$S molecules. Details of the basic theory have been already presented (Okamoto et al 1993, Nishimura and Itikawa 1995). We therefore describe briefly the outline of the theory. The present calculation is based on the fixed-nuclear orientation approximation. For vibrational motion, the three normal modes of H$_2$S are treated as uncoupled and harmonic. The interaction potential ($V$) is expanded in terms of the nuclear coordinates ($\xi$) around their equilibrium values ($\xi^e$). When considering an excitation of lower excited states, terms of higher than first-order have only a small contribution to the vibrational matrix element and we ignore them. The matrix element of the interaction potential is then derived as follows:

$$
\langle n| V | n' \rangle = V(\xi^e, r)\delta_{nn'} + \frac{1}{\sqrt{2}} \sum_i \frac{\partial V(\xi^e_i, r)}{\partial \xi_i} \{\sqrt{n_i + 1}\delta_{n'_i,n_i+1} + \sqrt{n_i}\delta_{n'_i,n_i-1}\} \prod_{j(i\neq i)} \delta_{n'_j,n_j} \tag{1}
$$

where $n \equiv (n_1, n_2, n_3)$ denotes the vibrational quantum number collectively for the three vibrational modes and $r$ is the position vector of the incident electron from the centre of gravity of the molecule. Here atomic units are used unless otherwise stated.

We adopt three types of interaction potentials: electrostatic, electron exchange and correlation-polarization. The electrostatic potential is obtained with an $ab$ initio multicentred target wavefunction. The effects of electron exchange and target polarization are approximately taken into account through the Hara version of the free-electron gas exchange (Hara 1967) and the parameter-free correlation-polarization (Padial and Norcross 1984) model potentials, respectively. The whole potential is expanded in terms of the symmetry-adapted angular basis functions $X^v_\lambda$ (Burke et al 1972) as follows:

$$
V(\xi, r) = \sum_{\lambda v} V_{\lambda v}(\xi, r)X^v_\lambda(\hat{r}). \tag{2}
$$

Here $v$ collectively denotes the indices specifying the irreducible representation and those distinguishing the degenerated members.

The wavefunction of the collision system is expanded as

$$
F(\xi, r) = \frac{1}{r} \sum_{lvn} f_{lvn}(r)X^v_\lambda(\hat{r})\chi_n(\xi) \tag{3}
$$

where $\chi_n$ is the vibrational wavefunction of the molecule. The radial part of the scattering wavefunction, $f_{lvn}(r)$, then satisfies a set of coupled differential equations,

$$
\left\{ \frac{d^2}{dr^2} - \frac{l(l + 1)}{r^2} + k_n^2 \right\} f_{lvn}(r) = 2 \sum_{l'v'n'} \langle lvn| V | l'v'n' \rangle f_{l'v'n'}(r) \tag{4}
$$

where $k_n$ is the wavenumber of the scattered electron in the channel ($lvn$), and

$$
\langle lvn| V | l'v'n' \rangle = \int d\hat{r} X^{v'}_l(\hat{r})\langle n| V | n' \rangle X^v_l. \tag{5}
$$

When solving equation (4) for each mode of vibrational excitation, we retain only the initial and the final vibrational states. This is, in essence, the same as the so-called ‘hybrid theory’ proposed by Temkin and his group for a diatomic molecule (Chandra and Temkin 1976a, b). The validity of this (i.e. two-state close-coupling) approximation has been discussed in our previous paper (Nishimura and Itikawa 1995).

From equation (4), the DCSs and the ICSs are calculated in a standard way (Okamoto et al 1993). Since H$_2$S has a permanent dipole moment, high partial waves contribute significantly to the cross section. We use the Born approximation to evaluate such a
contribution. In the calculation of elastic cross section, use is also made of the Born-closure formula (Gianturco and Scialla 1987) to obtain the converged cross sections, as in the case of H2O (Okamoto et al 1993). The elastic cross sections, thus obtained, depend on the rotational state of the target molecule.

3. Numerical calculation

The wavefunction of H2S in its electronic ground state is obtained with an ab initio molecular orbital code GAMESS (Schmidt et al 1993) in the SCF approximation. At the equilibrium geometry of H2S, the H–S distance and the H–S–H angle are taken to be 2.5251 au and 92.06°, respectively. The molecule is placed in the yz plane. The origin of the coordinates is taken at the centre of gravity of the molecule and the z axis along the molecular symmetry axis with the S atom on the negative side. A GTO basis set (12s8p) contracted to [6s4p] (Dunning and Hay 1977), is used with three d functions (exponents: 0.52, 0.15 and 0.05) for sulphur. For hydrogen, the same basis set (Huzinaga 1965) contracted by Dunning (1970) with p functions (Werner and Meyer 1976), is used as those employed in Martin et al (1979).

The total energy obtained is \(-398.673\,\text{893 au.}\) The wavefunction gives the dipole (\(µα\)) and the quadrupole (\(θαβ\)) moments as \(µ_z = 0.431, θ_{zz} = 0.708\) and \(θ_{xz} − θ_{yz} = -4.71\,\text{au}\). The experimental value of the dipole moment is 0.385 au (Landolt-Börnstein 1992). For the long-range part of the polarization potential, the experimental values of the polarizability (Bogaard et al 1982) are adopted (i.e. \(α_{xx} = 25.92, α_{yy} = 25.21\) and \(α_{zz} = 25.30\) au).

To evaluate the potential derivative in equation (1), we use the method of numerical differentiation with respect to the symmetry coordinates (Emerson and Eggers 1962). The method needs much less computing time than the CPHF (coupled perturbed Hartree–Fock) method, which provides the derivative more directly. Furthermore, no serious difference has been found in the results of the two methods. Table 1 shows the derivatives of the dipole and the quadrupole moments for each vibrational mode, derived from the present electrostatic potential. For the derivative of the long-range part of the polarization potential, use is made of the derivatives of the polarizability calculated at the SCF level (Martin et al 1979). The frequencies of the normal vibrations are taken from experiment (i.e. 2615, 1183 and 2626 cm\(^{-1}\) for the (100), (010) and (001) modes, respectively).

In equation (2), we retain the terms up to \(λ = 8\). The coupled equations (4) are solved

<table>
<thead>
<tr>
<th>Derivative of multipole(^a)</th>
<th>Present</th>
<th>Experiment(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(∂µ_z/∂ξ_1)</td>
<td>(-2.279 \times 10^{-3})</td>
<td>(-1.64 \times 10^{-3})</td>
</tr>
<tr>
<td>(∂µ_z/∂ξ_2)</td>
<td>(1.038 \times 10^{-2})</td>
<td>(5.48 \times 10^{-3})</td>
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<tr>
<td>(∂µ_z/∂ξ_3)</td>
<td>(7.540 \times 10^{-3})</td>
<td>(1.19 \times 10^{-4})</td>
</tr>
<tr>
<td>(∂θ_{zz}/∂ξ_1)</td>
<td>(8.301 \times 10^{-2})</td>
<td></td>
</tr>
<tr>
<td>(∂θ_{zz}/∂ξ_2)</td>
<td>(-0.5087)</td>
<td></td>
</tr>
<tr>
<td>(∂θ_{zz}/∂ξ_3)</td>
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<td></td>
</tr>
<tr>
<td>(∂(θ_{xx} − θ_{yy})/∂ξ_1)</td>
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<td></td>
</tr>
<tr>
<td>(∂(θ_{xx} − θ_{yy})/∂ξ_2)</td>
<td>(-0.5403)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \(ξ_1, ξ_2\) and \(ξ_3\) denote the nuclear coordinates for the symmetric stretching, bending and antisymmetric stretching normal modes, respectively.

\(^b\) Dipole derivatives derived from the experimental IR intensities by Lechuga-Fossat et al (1984) for the (100) and (001) modes and Emerson and Eggers (1962) for the (010) one.
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with the partial waves up to $l = 8$ in each irreducible representation. For the partial waves higher than that, the Born approximation with the asymptotic part of the dipole, quadrupole and polarization (only for the elastic scattering) interactions is used to obtain the relevant $T$-matrix elements. The rotational energy and transition dipole matrix which are necessary to obtain converged cross sections for the elastic scattering are derived from Townes and Schawlow (1955).

4. Results and discussion

4.1. Differential cross section

Figures 1–3 show the vibrationally elastic DCSs at collision energies of 3, 5 and 15 eV, respectively. These DCS have been calculated for H$_2$S in its ground rotational state. As is shown in the previous paper (Okamoto et al 1993), the DCS depends on the rotational state only in the vicinity of the forward direction. The present values shown in figures 1–3, therefore, are independent of the rotational state and can be compared, for instance, with the experimental data obtained at room temperature. The present DCSs reproduce the experimental data (Gulley et al 1993) generally well. In those figures, the present cross sections are compared with several other calculations. There is an overall agreement among the results of the different calculations, except in a few cases. The calculation by Gianturco (1991) follows almost the same procedure as the present one. However, the results of

![Figure 1](image)

**Figure 1.** Differential (DCS) cross section (in cm$^2$ sr$^{-1}$) for the elastic scattering of electrons from H$_2$S at 3 eV. The present calculation (full curve) is compared with the experiment by Gulley et al (1993) (full circles) and the calculations by Jain and Thompson (1984) (diamonds), Gianturco (1991) (open circles) and Lengsfield et al (1992) (squares). A comparison is also made with the Born calculation with the dipole interaction (chain curve).
Figure 2. Same as figure 1, but at 5 eV. A comparison is also made with the calculation by Greer and Thompson (1994) (triangles).

Figure 3. Same as figure 2, but at 15 eV.
the two calculations are in considerable disagreement with each other at scattering angles larger than 60°. This may be attributed to the difference in the target wavefunctions used. Another significant difference is seen at 15 eV. The calculation by Greer and Thompson (1994) clearly gives DCS larger than the others. This is ascribed to the polarization potential they employed, which, the authors say, is too strong. To see this, we calculated our DCS without a polarization potential and compared the result with the static-exchange calculation of Greer and Thompson. The agreement of the two sets of static-exchange results was good. This comparison endorses not only the above statement of the polarization potential of Greer and Thompson, but also the adequacy of the exchange model potential of the present calculation. Figure 1 also shows the Born DCS with a point dipole interaction. In the range of scattering angles less than 10°, the dipole interaction dominates considerably and even the Born calculation gives a good result. As the collision energy increases, the validity of the Born cross section becomes limited into the very vicinity of the forward scattering.

Figure 4. DCS for the vibrational excitation of the (010) mode at 3 eV. The present calculation (full curve) and the Born one with the dipole and quadrupole interactions (chain curve) are compared with the experiment by Gulley et al. (1993) (full circles with error bars).

Figures 4–9 show the vibrationally inelastic DCSs at electron energies of 3, 5 and 15 eV for the bending mode (figures 4–6) and the two stretching ones (figures 7–9). Since it is impossible at present to measure the cross sections for the two stretching modes (100) and (001) separately, we show the sum of these two cross sections together with the individual ones. No calculation has been reported so far for the (001) mode. At 3 eV, our DCSs are too small compared with the experimental data for both the (010) and the (100, 001) modes (see figures 4 and 7). Rohr (1978) found a broad shape resonance in the vibrational cross section at about 2.3 eV. The DCS at 3 eV must be greatly influenced by the resonance. Any calculation of resonance is very sensitive to the interaction potential employed. Probably
Figure 5. Same as figure 4, but at 5 eV. No experimental data have been reported at this energy.

Figure 6. Same as figure 5, but at 15 eV.
the model potentials used for the electron exchange and correlation-polarization, particularly their nuclear-coordinate dependence, are not sufficiently accurate to reproduce the resonance. Moreover, the close-coupling equations would need to include more vibrational states to describe the proper behaviour of the resonance cross section (Schneider 1976). Figure 7 also shows a comparison with the calculation by Jain and Thompson (1984) for the (100) excitation. The basic principle of their calculation is not much different from ours. The resulting cross sections, however, show a large discrepancy from each other. This is again probably due to the sensitivity of the cross section at resonance to the detail of the interaction potential. Unfortunately, no comparison can be made between theory and experiment in the energy region outside the resonance.

To see the effect of the long-range part of the electrostatic interaction on the vibrational excitation, we calculated the vibrational cross section in the Born approximation taking the dipole and quadrupole moment of the molecule into account. The results are shown in figures 4–9. The Born cross sections are far less than the corresponding ones of the close-coupling calculation, except in the close vicinity of the forward direction for the (010) mode. In that case, the molecular dipole dominates even in the vibrational excitation near the scattering angle $\theta = 0^\circ$ and the Born approximation gives a satisfactory result. In the case of the (100, 001) modes, the contribution of the molecular dipole is relatively small at the lower energies (i.e. 3 and 5 eV). Instead, the polarization interaction dominates in the forward direction at those energies.
Figure 8. Same as figure 7, but at 5 eV. Neither experimental nor other theoretical data are available at this energy.

Figure 9. Same as figure 8, but at 15 eV.
4.2. Integral cross section

Figure 10 shows the vibrationally elastic ICSs. To compare with the experimental data, the present values of the elastic ICS have been averaged over the distribution of initial rotational states at the gas temperature of 300 K. It is noted that the corresponding cross section for the ground rotational state is larger by about 6% than the one shown in the figure 10 at 3 eV. The difference comes only from the DCS in the vicinity of the forward direction and becomes smaller with increasing energy. When compared with the experimental values (with an uncertainty of about 20% in absolute magnitude) obtained by Gulley et al (1993), the present ICSs are too large. In general, an ICS derived from experimental DCS includes some ambiguities because of an extrapolation of the measured DCS into the region where no measurement is possible. Particularly for a polar molecule, this ambiguity may become considerable because its dipole produces a very large, sharp forward peak in DCS (Okamoto et al 1993). In the present case, however, the magnitude of the dipole moment is so small that the contribution of the forward peak is moderate. The uncertainty from the extrapolation in the small-angle region would be within the experimental uncertainty quoted by the authors. (In the present ICS, the contribution of the DCS at the angles less than 10° is 14–18%, except at 3 eV, where it amounts to 26%.) The present ICSs are also compared with the ones obtained in other calculations. Again the present ICS is too large. It should be noted that, when we calculated the cross section without including the correlation-polarization potential, our result at the energies above 10 eV becomes closer to the values obtained by Lengsfield et al (1992) and Machado et al (1995). The latter two calculations also include
no polarization in that range of energy. This suggests that the discrepancy of the present calculation with the experimental data, particularly in the region above 10 eV, comes mainly from the inadequacy of the present model potential for the correlation-polarization effect.

Figures 11 and 12 show the vibrationally inelastic ICSs for the bending mode and the two stretching modes, respectively. For the latter, the sum of the cross sections for the two stretching modes (100) and (001), is presented together with individual ones. There are no experimental data comparable to theory. (Gulley et al. and Rohr reported only DCSs at a limited range of scattering angles.) In the figures, we compare our result with the ICS calculated by Jain and Thompson (1984). They are the only data available for comparison. It should be noted that Jain and Thompson obtained no cross section for the (001) mode. Their ICSs are larger than the present ones, except for the (100) mode at the energies larger than 5 eV. The difference between the two calculations is probably attributed to the difference in the target wavefunctions and the model potentials for the polarization effect. If judged from the total energy of the molecule obtained, the quality of the present wavefunction is better than that of Jain and Thompson. From the comparison of DCS (see Gulley et al. 1993), the calculation of Jain and Thompson gives too large cross sections in the energy range 2–3 eV. As is shown in figures 4 and 7, the present calculation gives too small values of DCS at 3 eV. Estimated from this comparison of DCS, an experimental ICS at 3 eV would be by a factor of about two larger than the present value of ICS there. In the higher energy range (i.e. above 10 eV), the present calculation is expected to be more reliable from the experience in the previous calculation for H$_2$O (Nishimura and Itikawa 1995). No definite conclusion, however, can be drawn until any further experimental study is made at the higher energy region.

![Graph](Image)

**Figure 11.** ICS for the vibrational excitation of the (010) mode. The present calculation (full curve) is compared with the calculation by Jain and Thompson (1984) (full curve through diamonds).
5. Conclusion

Vibrationally elastic and inelastic electron scattering of H₂S has been studied theoretically. The calculation is based on the rotationally sudden and vibrational close-coupling method. The dependence of the interaction potential on the nuclear coordinates is considered only through the linear term in the expansion with respect to the displacement from the equilibrium geometry. Differential (DCS) and integral (ICS) cross sections have been calculated at the collision energies 3–30 eV and compared with the experimental and theoretical data available.

As for the vibrationally elastic process, the present DCSs reproduce the angular distribution of the experimental data reasonably well over all the energies considered. For the inelastic process, a comparison with experimental data can be made only at 3 eV. At this energy, the present DCS is too small in comparison with the experiment. It has been suggested that a shape resonance occurs at around 2–3 eV (see, for example, Gulley et al 1993). Generally speaking, cross sections at a resonance are very sensitive to the details of the interaction potential. Probably the present model of interaction is not sufficiently accurate to produce the resonance. In the energy region above the resonance (\( E \geq 5 \) eV, for example), the present vibrational cross section can be expected to be more reliable. This could be confirmed with further experimental data.

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