

Total cross sections for electron scattering on NO₂, OCS, SO₂ at intermediate energies

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Abstract. Total cross sections for electron scattering on SO₂, NO₂, OCS have been measured in the energy range from 90 to 4000 eV. Our data extrapolated to low energies match other experiments on OCS and NO₂; for SO₂ discrepancies amount to as much as 20%. The experimental values for these gases and for CO₂ (the latter measured previously in our laboratory) have been fitted with a Born-like formula. Two parameters are sufficient to reproduce the SO₂, NO₂ and CO₂ cross sections from 20 to 4000 eV within the experimental errors. A double Yukawa potential with four parameters is needed to reproduce the OCS cross sections over the same energy interval

1. Introduction

In the laboratory at Trento University a systematic investigation of total cross sections for electron–molecule scattering in the intermediate (80–4000 eV) range is under way. This range is particularly interesting because above 100 eV total (and also elastic) cross sections are slowly varying, monotonic functions of energy. This could facilitate the search for systematic relations between the cross section values and molecular parameters of targets. This strategy has already produced a few preliminary results.

For simple hydrides ('almost spherical' molecules) we noticed (Zecca *et al* 1992a) that the total cross sections are well approximated by a Born-like formula with two adjustable parameters. At high energies, the relative differences in TCS for these targets reflect the geometrical dimensions of molecules. Subsequently, a similar approximation has been established at high energies for the chlorofluoromethanes series (CF₄ to CCl₄) (Zecca *et al* 1992b). Contrary to hydrides, it has been found that inclusion of another term into the approximation was needed to fit experimental points at energies below 200 eV, for chlorinated molecules. The inclusion of this term corresponds to the scattering from a weaker and longer range potential. The phenomenological conclusion has been drawn that the presence of chlorine atoms in those molecules reflects in a rise of the low energy cross section.

Recently, the one-term approximation was used to fit TCS for the two-atom molecules N₂ and CO (Karwasz *et al* 1993) and SF₆ (Zecca *et al* 1992c) between 30 and 4000 eV. In the present study, triatomic linear (OCS, CO₂) and almost linear (NO₂, SO₂), nearly homonuclear molecules are compared. (CO₂ has been measured previously in this laboratory (Szmytkowski *et al* 1987).)

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2. Targets

The three investigated molecules are atmospheric pollutants. SO_2 and to a minor extent NO_2 are the agents of acid rain. Recent papers (Wigley 1989, Zecca and Brusa 1991) have shown that SO_2 has an important role in determining the climate of the Earth: SO_2 and its aerosols have a cooling effect which is of the same order of magnitude of the warming effect of CO_2 . SO_2 has structural similarities with O_3 (Jones 1985). Electron scattering experiments on O_3 are tedious (Davies *et al* 1993) and this makes SO_2 a test molecule also for understanding the dynamics of ozone production and decomposition in the Earth's atmosphere.

SO_2 has been found to be a main constituent of the atmosphere of Jupiter's satellite Io; it is also abundant in the Venus atmosphere. OCS molecules have been detected as a constituent of interstellar clouds (Jefferts *et al* 1971). Electron impact cross sections are needed in modelling the energy decomposition processes in astrophysical environments and in the optimization of electrical-discharge-based devices for the removal of pollutants from industrial fumes.

The triatomic molecules studied here show large similarities with the CO_2 molecule. NO_2 and SO_2 are oxides in which carbon is substituted by heavier elements. In the OCS molecule one oxygen atom is substituted by its heavier chemical analogue. CO_2 and OCS are linear and have the same number of valence electrons; OCS possesses a permanent dipole moment. SO_2 and NO_2 are bent molecules and consequently also polar. A few parameters of these molecules are summarized in table 1.

Table 1. Some physical parameters of the studied molecules. If not stated differently, the data are taken from Lide (1990).

	Number of electrons	Valence electrons	Bond length (Å)	Bond angle (deg)	Dipole moment (debye)
CO_2	22	14	1.162 ^a	180 ^a	0
NO_2	23	15	1.195 ^b	134 ^b	0.316
OCS	30	14	1.162 ^a /1.588	180 ^a	0.712
SO_2	32	18	1.432	119	1.63

^a Herzberg (1966), see also Lynch *et al* (1979).

^b Hardwick and Brand (1976).

The presently studied molecules, in spite of their practical importance, have received little experimental and theoretical attention. For NO_2 the low energy absolute total cross section has been measured by Szmytkowski *et al* (1992). Relative, partial ionization cross sections were measured by Stephan *et al* (1980). To our knowledge, no data exist for absolute elastic, excitation and ionization cross sections for this molecule. OCS total cross sections were measured by Szmytkowski *et al* (1984, 1989), and Dababneh *et al* (1986). Sohn *et al* (1987) have given experimental elastic integral cross sections from 0.3 to 5 eV.

SO_2 has been studied more extensively; this can be attributed to the already mentioned vast technological importance. The total cross sections have been measured by Sokolov and Sokolova (1981), and by Zubek *et al* (1981) up to 10 eV, by Dababneh *et al* up to 50 eV and by Szmytkowski and Maciąg (1986) up to 100 eV. Differential and total elastic cross sections were given by Trajmar and Shyn (1989), Orient *et al* (1982) and recently by Gulley and Buckman (1994). Ionization cross sections were measured in beam experiments

by Orient and Srivastava (1984) and Čadež *et al* (1983) and by a flowing plasma method by Smith and Stephenson (1981).

To our knowledge, theoretical work for these molecules is limited to that of Lynch *et al* (1979) on elastic scattering by OCS from 0 to 100 eV and recent calculations of total cross sections in NO_2 (and also N_2O , CO_2 and O_3) between 100 and 1000 eV (Joshiyura and Patel 1994). In this latter work the optical model has been used to obtain the cross section for single atoms constituting the given molecule and then the additivity rule has been applied.

3. Experimental set-up

The apparatus used in these measurements has been utilized in several previous experiments. Therefore, only a short description will be given here, referring the reader to other published papers (Zecca *et al* 1992a and references therein) for further details.

The experimental method relies on attenuation measurements in a Ramsauer-type apparatus. The cross section was obtained from simultaneous measurements of the transmitted current (I_c); the current intercepted at the scattering chamber walls (I_s); and the gas density (N) in the interaction region. The modified de Beers formula yields:

$$I_{ci}/(I_{ci} + I_{si}) = I_{cj}/(I_{cj} + I_{sj}) \exp[-\sigma L(N_i - N_j)]. \quad (1)$$

The suffixes i, j refer to two differential pressures and L is the length of the interaction region. In the present apparatus L was relatively large (143.2mm): this decreases the influence of end effects. The gas region was followed by a pumped region electrically connected with the previous one: this allows an average angular acceptance at the detector of 3.4×10^{-4} sr. A last important detail regards the electronic system which allows the capacitance manometer head to track the gas chamber temperature within ± 0.1 °C. This feature hinders any thermal transpiration error.

The overall systematic uncertainty (apart from the angular resolution error) was estimated as in previous works (Zecca *et al* 1992a). If the various contributions are added quadratically, we end up with systematic error of $\pm 3\%$.

It has not been possible to evaluate the angular resolution error due to the lack of appropriate differential cross section measurements (or calculations) for scattering into near-zero angles. The three molecules studied here are polar and therefore the angular cross sections are forward peaked (compare for example Bromberg 1970). On this basis we can expect an angular resolution error higher than the value (0.5% at 3000 eV) evaluated for CO_2 (Szymkowski *et al* 1987).

The statistical error was within $\pm 4\%$ at energies between 80 and 150 eV; $\pm 3\%$ up to 1000 eV and increasing up to 5% at 4000 eV. The most critical among these gases was OCS, with statistical errors closer to the upper limit given above; this gas produces emission instability of the oxide coated cathode and decomposes to CO (as observed in the present experiment and by Szymkowski *et al* (1984) when exposed to copper.

The gas purity was 99.8% for SO_2 (Alphagas, Italy), 99.5% for NO_2 (Matheson, USA) and 97.5% for OCS (Merck, Germany), the main contaminants for the latter being CO (1%), N_2 (0.5%), CO_2 (0.4%).

4. Results

The results of the present experiment are presented in table 2 and compared with other measurements in figures 1 and 2. Unfortunately, there are no other experimental results which cover our energy range and the only overlap is with the measurements of Szmytkowski *et al* (1992) for NO₂ up to 200 eV. Therefore, for SO₂ and OCS the comparison can be made only by extrapolating the slopes of the curves at the closest energy points.

Table 2. Absolute total cross sections for electron scattering on OCS, SO₂ and NO₂ in 10⁻²⁰m² units. Statistical errors (one standard deviation of the mean value) are also given in per cent.

Energy	OCS	Error	SO ₂	Error	NO ₂	Error
90	21.6	3.9	16.0	1.3		
100	19.9	3.1	15.2	2.0	11.9	5.5
110	19.4	4.1	15.0	1.8	11.3	3.9
121	18.0	2.1	14.7	0.7	10.5	5.5
132	17.2	0.8				
144	16.5	0.8	14.3	2.4	9.84	2.5
156	15.3	2.7				
169	14.7	1.2	12.9	2.0	9.28	2.2
180	13.9	0.6				
200	13.6	4.4	12.4	2.9	8.52	2.7
220	12.5	1.9				
225			11.6	2.8	7.70	1.1
250	12.1	3.6				
256			11.0	2.3	7.49	0.2
289	11.6	2.4	10.1	1.8	7.22	0.7
324	10.8	3.7	9.54	2.8	6.70	3.0
361	10.2	3.4	8.96	2.5	6.69	1.9
400	9.40	3.2	8.55	1.1	6.00	0.9
484	7.75	1.3	7.50	0.9	5.28	5.7
576	6.98	0.2	6.66	0.6	4.72	1.5
676	6.27	1.0	5.94	0.9	4.15	4.6
785	5.48	0.4	5.56	0.2	3.77	5.6
900	5.06	1.0	4.90	0.7	3.34	1.6
1000	4.43	1.4			3.11	4.1
1025	4.57	0.7	4.37	1.9	3.00	2.6
1150	4.14	0.1	4.05	2.0	2.75	3.7
1300	3.68	3.0	3.72	2.0	2.48	1.9
1450	3.27	0.2	3.27	3.7	2.22	1.2
1600	3.05	0.8	3.17	2.9	2.08	2.2
1770	2.80	3.3	2.82	3.9	1.88	1.3
1940	2.60	0.4	2.55	7.3	1.73	2.4
2000	2.44	1.9			1.68	0.2
2120			2.36	1.1	1.62	3.6
2150	2.35	2.9				
2300	2.21	3.1	2.17	1.2	1.48	2.6
2500	1.97	3.7	2.01	1.4	1.37	0.2
2750	1.87	1.7	1.81	3.0	1.29	2.6
3000	1.73	1.5	1.71	2.4	1.17	2.8
3250	1.55	4.4	1.65	5.5	1.10	4.5
3500	1.47	2.4	1.48	1.2	1.03	3.2
4000	1.29	1.6	1.32	1.5	0.915	1.4

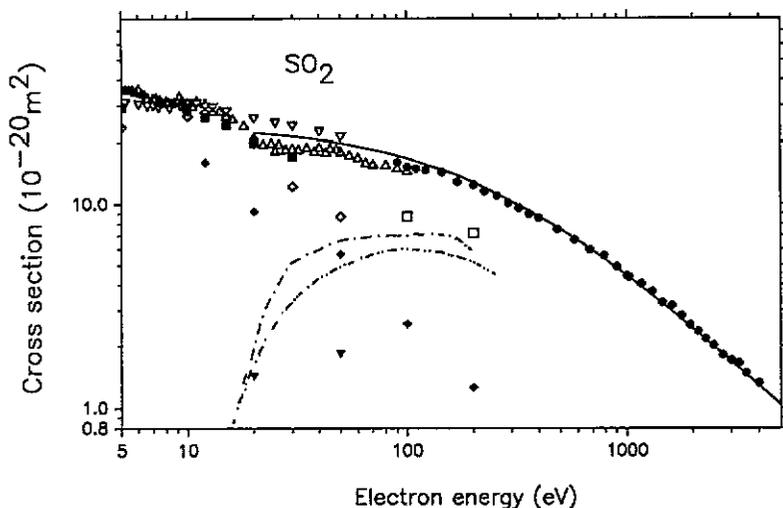


Figure 1. Cross sections for electron scattering on SO_2 molecules. Total absolute: present (\bullet), Dababneh *et al* (∇), Szymtkowski and Maciąg (Δ), present semiempirical fit (—); total ionization: Orient and Srivastava (---), Čadež *et al* (- · - ·); elastic: Orient *et al* (\diamond), Trajmar and Shyn (\diamond), Gulley and Buckman (\blacksquare), present semiempirical (\square), electronic excitation: Vušković and Trajmar (\blacktriangledown).

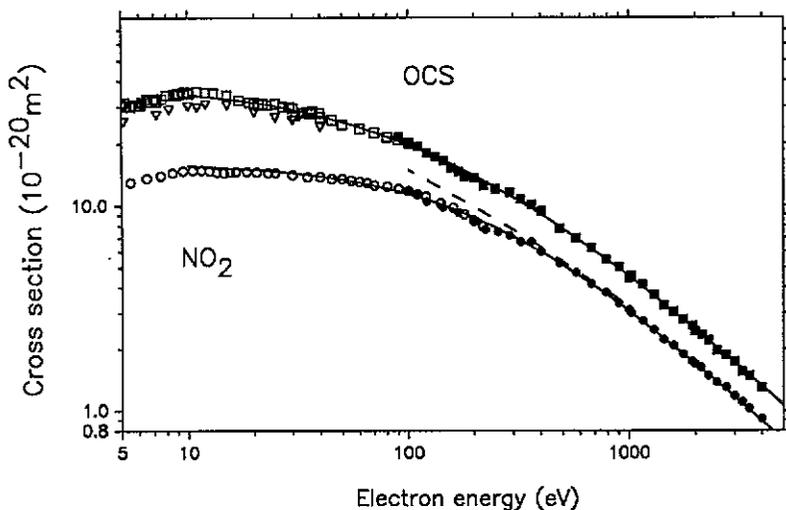


Figure 2. Total cross sections for electron scattering on NO_2 and OCS. NO_2 : present (\bullet), Szymtkowski *et al* (1992) (\circ), Joshipura and Patel (---); OCS: present (\blacksquare), Dababneh *et al* (∇), Szymtkowski *et al* (1984 and 1989) (\square); present semiempirical fit (—).

For OCS and NO_2 the present results agree very well, within the declared error bars, with the data of Szymtkowski *et al* (1984, 1989, 1992). For OCS they also merge well with the data of Dababneh *et al* (1986), which are slightly (about 10%) lower than those of Szymtkowski *et al* (1989). This discrepancy is similar to the one found in measurements on other gases, like N_2 (see Karwasz *et al* 1993) or SF_6 (see Zecca *et al* 1992c). A part of this discrepancy could be attributed to the longitudinal guiding magnetic field used in the

Detroit apparatus. Due to this field, a fraction of the scattered electrons can be guided to the detector, causing underestimation of the total cross section (Kauppila *et al* 1981).

The discrepancies are somewhat bigger for SO₂, where the highest-energy points measured by Szmytkowski and Maciąg (1986) depart down by 10% from the merging line between the two sets of data (see figure 1). Our SO₂ results seem to merge better with the data of Dababneh *et al* (1986). Also the recent measurements of the total elastic cross sections by Gulley and Buckman (1994) would indicate that the data of Szmytkowski and Maciąg (1986) are underestimated in their high energy limit. Probably this is due to the fact that SO₂ was measured by Szmytkowski and Maciąg with a worse (2×10^{-3} sr) angular resolution than NO₂ and OCS. A higher dipole moment of SO₂, comparing with NO₂ and OCS, causes additional rise in the angular resolution error, as explained before.

The recent calculations of Joshipura and Patel (1994) for NO₂ agree well with the present data at 1000 eV, while they overestimate the experimental results by 25% at 100 eV.

For SO₂, according to the absolute data of Čadež *et al* (1983) and Orient and Srivastava (1984), the ionization contributes about 40–45% of the total cross section at 100 eV and about 41–43% at 200 eV. The measurements of the excitation cross section by Vušković and Trajmar (1982) indicate that the remaining part of the total cross section should be attributed to the elastic scattering. In figure 1, open squares at 100 eV and 200 eV mark the elastic cross section resulting from subtraction of the averaged cross section from our total value. Obtained in this way, the elastic cross section merges well with recent absolute measurements of Gulley and Buckman (1994) at lower energies. The agreement is somehow poorer with the previous data of Trajmar and Shyn (1989). The discrepancy of our elastic cross section values with the results of Orient *et al* (1982) is outside the combined error of the two determinations.

Due to the lack of experimental total elastic and ionization cross sections it is not possible to perform the analysis of the partitioning scheme for NO₂ and OCS.

5. Comparison of cross sections for triatomic molecules

In figure 3 the total cross sections of the studied molecules and CO₂ from our previous measurements (Szmytkowski *et al* 1987) are compared in a wide energy range (only selected data are presented for the low energy part).

This figure clearly shows that the CO₂ and OCS total cross sections have similarities in the low energy range. Both molecules exhibit a sharp resonant peak: centred at about 1.2 eV for OCS and at about 3.2 eV for CO₂. These structures (shape resonances) are due to the capture of the incoming electron into an unoccupied molecular orbital of the target in its ground electronic state. The temporary negative ion has configurations $^2\Pi_u$ for CO₂ (Claydon *et al* 1970) and $^2\Pi$ for OCS (Szmytkowski *et al* 1984). The resonance is shifted to lower energies for OCS, probably due to the permanent dipole moment of the molecule. At the lowest energies, both molecules exhibit a rise of the total cross section, which in the case of CO₂ has been attributed to a virtual-state zero-energy resonance (Estrada and Domcke 1985). The similarity of the low energy $\sigma(E)$ functions for CO₂ and OCS could be attributed to their analogue chemical structure and/or the same number of valence electrons.

No sharp structures are observed for NO₂ and SO₂ in the presented energy range although the occurrence of resonant scattering has been observed in studies of vibrational excitation (Andrić *et al* 1983, Benoit and Abouaf 1991). Probably, for SO₂ and NO₂, the resonances are too weak to be seen in the total cross section curves.

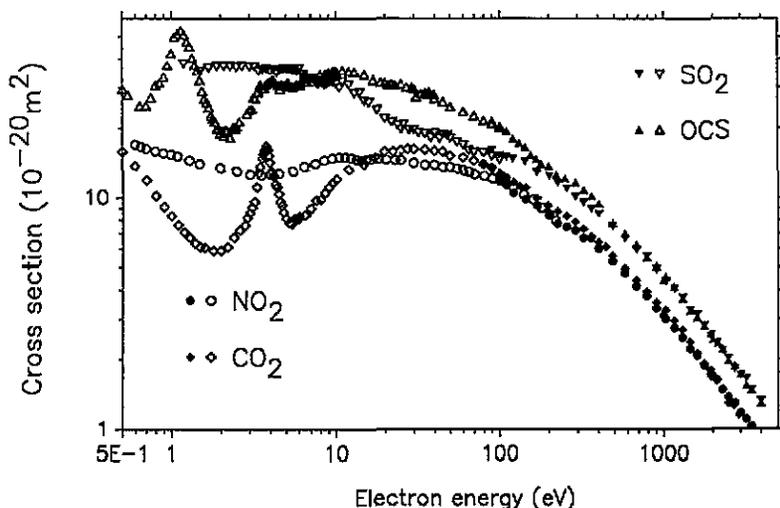


Figure 3. Total cross sections for electron scattering on NO_2 , OCS , SO_2 and CO_2 molecules from 0.5 to 4000 eV. Full symbols correspond to results from Trento laboratory: present data, and Szmytkowski *et al* (1987)— CO_2 ; open symbols are the results from the Gdansk laboratory: Szmytkowski *et al* (1984 and 1989)— OCS (Δ), Szmytkowski and Maciąg— SO_2 (∇); Szmytkowski *et al* (1992)— NO_2 (\circ).

In the high energy range the presented molecules tend to form groups according to the total number of electrons: above 300 eV the total cross sections are almost equal to CO_2 (22 electrons) and NO_2 (23 electrons) and for OCS (30 electrons) and SO_2 (32 electrons). To quantify this observation, the measured data were fitted with a Born-like formula, corresponding to elastic scattering from a double Yukawa potential:

$$V(r) = \frac{V_1}{r} \exp(-r/a_1) + \frac{V_2}{r} \exp(-r/a_2) \quad (2)$$

where V_i and a_i are parameters describing the depth and the radial extension of the Yukawa well. In this approximation, the total cross section is given by (see Zecca *et al* 1992b):

$$\sigma = \frac{1}{A_1 + B_1 E} + \frac{1}{A_2 + B_2 E} + \frac{2}{E} \frac{\sqrt{A_1 A_2}}{A_2 B_1 - A_1 B_2} \ln \frac{(1 + B_1 E/A_1)}{(1 + B_2 E/A_2)} \quad (3)$$

where

$$A_i = \frac{\hbar^4}{16\pi m^2 V_i^2 a_i^4} \quad \text{and} \quad B_i = \frac{\hbar^2}{2\pi m V_i^2 a_i^2} \quad (4)$$

In the above equations, setting $V_2 = 0$ yields the results for the scattering on a single Yukawa well. The cross section reduces to:

$$\sigma(E) = \frac{1}{A_1 + B_1 E} \quad (5)$$

Equations (3) and (4) were used to fit the present experimental data. In order to cover the region below 90 eV, the measured data of Szmytkowski *et al* (1984, 1989, 1992),

Szmytkowski and Maciąg (1986) and Dababneh *et al* (1986), were used. The best fitting parameters are given in table 3. The corresponding curves are given in figure 1 for SO₂ and in figure 2 for NO₂ and OCS, as full curves. The fitted curves reproduce the measured NO₂ and OCS data within the experimental error from 20 eV up to 4000 eV. The same positive result (not shown in the figures) is obtained for our CO₂ data (Szmytkowski *et al* 1987) from 30 to 3000 eV. The situation is less clear for SO₂ in the region from 20 to 100 eV; this is due to the fact that the available data have a discrepancy of the order 15–20% in the energy range of overlap (20 to 50 eV). In spite of this, equation (4) reproduces the present measurements from 90 to 4000 eV, within the error bars.

Table 3. Parameters of the semiempirical fit for the triatomic molecules. Parameter A is given in \AA^{-2} , parameter B in $\text{\AA}^{-2}\text{keV}$. The amplitude V and the range a of the Yukawa potential are given in atomic units.

Gas	A_1	B_1	A_2	B_2	V_1	a_1	V_2	a_2
CO ₂	0.0528	0.262			139	0.068		
NO ₂	0.0612	0.265			146	0.064		
SO ₂	0.0415	0.184			173	0.065		
OCS	0.0317	0.188			147	0.075		
OCS	0.157	0.420	0.0749	1.27	147	0.050	33.7	0.126

Table 3 gives the best fit parameters of the four molecules. The CO₂ and NO₂ total cross sections are described by a single Yukawa formula (equation (4)). The SO₂ cross section is probably also reproduced by a single Yukawa formula. The uncertainty is connected with the discrepancy between the low energy data used in the fitting procedure. The weak Yukawa is mostly determined by the low energy data and therefore, no precise assessment can be made until new measurements of the SO₂ cross section are available. The OCS cross section is better reproduced by a double Yukawa formula (equation (3)) down to 10 eV. However, it is meaningless to compare directly the parameters of the single (equation (4)) and of the double (equation (3)) fit. Willing to do this, we stress that in the limit of high energies equation (3) can be approximated by equation (4). On this basis, a single-Yukawa fit for OCS is also given in table 3.

The single Yukawa fits parametrize the observation from figure 3 that at high energy the studied molecules can be grouped according to the total number of electrons: parameters B_1 of NO₂ and CO₂ differ by merely 1.5% and those of SO₂ and OCS by 2%. However, the proportionality of the cross section to the total number of electrons, as observed by Floeder *et al* (1985) for the hydrocarbon series, is not valid for the triatomic molecules. On the contrary, the CO₂ cross section above 20 eV is slightly, but systematically higher than that for the NO₂ molecule with more electrons. A similar observation holds for OCS and SO₂.

We do not have a phenomenological explanation for this regularity: we can only recall that similar occurrences have been observed in the hydride series studied in our previous work (Zecca *et al* 1992a). There, it has been found that the CH₄ cross section is slightly higher than that for NH₃. An analogy can be set to the CO₂–NO₂ case by hypothesizing that the substitution of a given central atom of the molecule with a heavier one in the same row of the periodic table produces a tiny decrease in the total cross section. Recent theoretical results of Joshipura and Patel (1994) for CO₂, NO₂ and O₃ total cross sections between 100 and 1000 eV, although not reproducing exactly the absolute values, confirm the above noted tendency.

The parameters of the phenomenological total scattering potential are compared in the last column of table 3. The three molecules CO_2 , NO_2 and OCS, with the central atom belonging to the second row of the periodic table, exhibit essentially the same (about 140 ± 4 au) amplitude V_1 of the single centre, single-range potential. The range of this potential is larger for OCS, which reflects the presence of the heavier atom of sulphur (on the periphery of the molecule). On the other hand, the substitution of the central atom with a heavier one (NO_2 , SO_2) does not change the range but increases the amplitude of the potential. Parametrization of the potentials used for *ab initio* calculations would shed more light on the physical significance of the observed phenomenological relations.

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