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Ab initio Molecular Orbital Studies of the Vibrational Spectra of some van der Waals Complexes. Part 4. Complexes of Sulphur Dioxide with Carbon Dioxide, Carbonyl Sulphide, Carbon Disulphide and Nitrous Oxide

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ABSTRACT

The binary complexes formed between sulphur dioxide, as electron donor, and the series carbon dioxide, carbonyl sulphide and carbon disulphide, as electron acceptors, have been studied by means of *ab initio* molecular orbital theory. The optimized structures, the interaction energies and the vibrational spectra have been determined, and the effect of successive substitution of sulphur for oxygen atoms in the electron acceptor molecules has been established. Nitrous oxide, which is isoelectronic with carbon dioxide, has also been included among the electron acceptors, but the properties of the complex formed between sulphur dioxide and nitrous oxide are substantially different from those of the other three complexes.

KEYWORDS

***Ab initio* calculations, molecular complexes, sulphur dioxide, carbon dioxide, carbonyl sulphide, carbon disulphide, nitrous oxide, molecular structures, interaction energies, vibrational spectra.**

1. Introduction

We have reported a series of *ab initio* studies of a variety of molecular complexes containing the family of Lewis acids carbon dioxide, carbonyl sulphide and carbon disulphide, with the aim of determining the effect of successively substituting sulphur for oxygen atoms in the electron acceptor molecules. The range of electron donors examined in these studies includes dinitrogen,[1] carbon monoxide,[2] ozone,[3] water and hydrogen sulphide.[4,5] The corresponding complexes containing sulphur dioxide as the electron donor have been studied experimentally, by Fourier transform microwave spectroscopy.[6–8] Nitrous oxide, being isoelectronic with carbon dioxide, might be expected to form a complex with sulphur dioxide whose properties were similar to those of the three main subjects of this work. However, our studies have shown that the N_2.N_2O complex exhibited quite different properties from those of the N_2.CO_2, N_2.OCS and N_2.CS_2 analogues, and this was interpreted as being due to the fundamentally different electronic structures of N_2O and the other three acceptor monomer species.[1] The SO_2.N_2O complex, investigated by Fourier transform microwave spectroscopy,[9] was found to have a different structure from those between SO_2 and CO_2,[6] OCS[7] and CS_2,[8] determined by the same group of workers under comparable conditions. To the best of our knowledge, among the complexes of SO_2 considered here, only SO_2.N_2O has been subjected to an *ab initio* treatment.[10] In this paper we describe the results of our computational studies of the complexes SO_2.CO_2, SO_2.OCS and SO_2.CS_2, and attempt to rationalize the similarities and differences among their properties, and then go on to present the corresponding results obtained for the anomalous SO_2.N_2O adduct and discuss the reasons for the different nature of this species.

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2. Computational Methods

The calculations were performed using the Gaussian-98 computer program.[11] The level of treatment employed was second order Møller-Plesset perturbation theory (MP2),[12] and the basis set used was the 6-311+G(d) basis set of Pople[13] and Schleyer.[14] The structures were optimized, initially using the experimentally-determined symmetries[6–9] and then, when those structures were found not to be genuine minima, by successively relaxing the geometrical constraints. The VERYTIGHT convergence criterion[11] was used, in order to ensure as close an approach to the real minimum energy structures as possible. The interaction energies were computed from the energies of the complexes and of the relaxed monomers, in their structures as found in the complexes, and were corrected for basis set superposition error (BSSE),[15] using the full counterpoise technique of Boys and Bernardi,[16] and for zero-point energy differences.

3. Results and Discussion

3.1. Molecular Structures

The geometries of the SO_2.CO_2 and SO_2.CS_2 complexes were first optimized under C_{2v} symmetry, in accordance with the symmetry of the former species determined experimentally by Kuczkowski *et al.*[6] However, these structures were found to be first-order (SO_2.CO_2) and second-order (SO_2.CS_2) saddle points. The symmetries were then reduced to C_s, and the optimizations repeated. Although an energy saving was achieved in each case, SO_2.CO_2 was still found to be a first-order saddle point, while SO_2.CS_2 changed to a first-order transition state. Finally, both structures were re-optimized with all symmetry constraints removed, and both species converged with no imaginary modes. The SO_2.OCS and SO_2.N_2O complexes were optimized, starting with C_s symmetry,[7,9] with the SO_2 molecule straddling

Table 1 Energies (in Hartree) and Hessian indices (in brackets) of the complexes.

Complex	C_{2v}	C_s	C_1
$SO_2.CO_2$	–735.99842846 (1)	–735.99860971 (1)	–735.99891746 (0)
$SO_2.OCS$ (structure 1)	–	–1058.56470338 (1)	–1058.56488105 (0)
$SO_2.OCS$ (structure 2)	–	– [a]	–1058.56421514 (0)
$SO_2.CS_2$	–1381.13099425 (2)	–1381.13200018 (1)	–1381.13224863 (0)
$SO_2.N_2O$ (structure 1)	–	–732.08245668 (1)	–732.08266382 (0)
$SO_2.N_2O$ (structure 2)	–	–732.08254352 (0)	–732.08264767 (0)

[a] Relaxed to structure 1.

the plane containing the S (SO_2), O, C and S (OCS), or S (SO_2), N, N and O (N_2O) atoms. Two isomers were considered, in which the S atom of SO_2 approached the O (structure 1) and the S atom of OCS (structure 2), or the terminal N (structure 1) and the O atom of N_2O (structure 2). Structure 1 of $SO_2.OCS$ was the preferred experimental structure,[7] while in the case of $SO_2.N_2O$ the observed structure lacked a symmetry plane.[9] In our calculations, structure 1 of $SO_2.OCS$ optimized with one imaginary vibrational mode, while structure 2 relaxed to structure 1. For $SO_2.N_2O$, structure 1 was found to be a first-order saddle point, while structure 2, which was slightly lower in energy, was a true minimum. Finally, optimization under C_1 symmetry resulted in all modes being real, with an energy saving in each case. These results are collected in Table 1.

The barrier heights to interconversion among the various isomers are given in Table 2. These barriers imply that in most cases the wavenumber of the interconversion mode is of the order of 50 cm^{-1}, except for the $C_{2v} \rightarrow C_s$ mode of $SO_2.CS_2$, where it is about 220 cm^{-1}. Structure 1 of $SO_2.OCS$, which, for want of a better description, we shall call the S…O bonded species, and structure 1 of $SO_2.N_2O$ (the S…N bonded species) are clearly the most stable structures of these two complexes, and further discussion will be confined to these isomers. The preferred minimum energy structures of all four complexes are illustrated in Fig. 1, and the Cartesian coordinates are available as Supplementary Material.

While Kuczkowski *et al.* identified the symmetry of $SO_2.CO_2$ as C_{2v}, they conceded that, due to the large uncertainty in their determination of the *A* rotational constant, they could not confirm this structure unequivocally.[6] We interpret our finding that the true symmetry is C_1 by proposing that the experimentally observed structure is a vibrationally-averaged one; the C_{2v} structure is a saddle point connecting two equivalent C_s structures in which the C_2 axis of the SO_2 molecule is tilted slightly relative to the S…C axis. The two C_s structures are interconverted by a SO_2 wagging vibration, coupled with an in-plane OCO libration. The form of this imaginary vibrational mode is illustrated in Fig. 2. Moreover, the C_s structure is also a saddle point, linking two equivalent C_1 forms which are interconverted

Table 2 Barrier heights to interconversion among the various isomers of the complexes.

Complex	Interconversion	Barrier height/kJ mol^{-1}
$SO_2.CO_2$	$C_{2v} \rightarrow C_s$	0.476
	$C_s \rightarrow C_1$	0.808
$SO_2.OCS$	$C_s \rightarrow C_1$	0.466
$SO_2.CS_2$	$C_{2v} \rightarrow C_s$	2.641
	$C_s \rightarrow C_1$	0.652
$SO_2.N_2O$ (structure 1)	$C_s \rightarrow C_1$	0.544
$SO_2.N_2O$ (structure 2)	$C_s \rightarrow C_1$	0.273

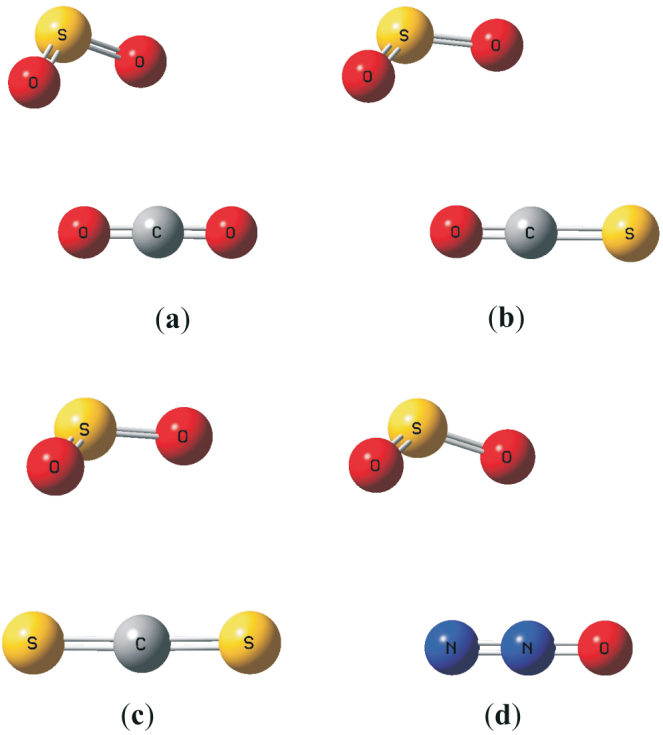

Figure 1 The optimized structures of the C_1 complexes of SO_2 with (**a**) CO_2, (**b**) OCS, (**c**) CS_2 and (**d**) N_2O.

through a SO_2 rocking mode, coupled with an out-of-plane OCO libration, as shown in Fig. 3.

A potential surface scan of the OS…CO dihedral angle confirms the presence of an energy barrier at the C_{2v} structure (see

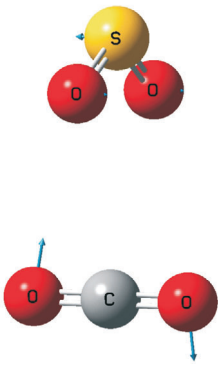

Figure 2. The form of the imaginary mode of the C_{2v} structure of the $SO_2.CO_2$ complex.

Fig. 4). A scan of the OSO…C dihedral angle revealed that a similar barrier exists, for interconversion of the two C_1 species, as illustrated in Fig. 5. For the $SO_2.CS_2$ C_{2v} complex the two imaginary modes are the counterparts of those represented in Figs 2 and 3.

In the case of $SO_2.CS_2$, Kuczkowski *et al.* determined a C_s structure, with two alternative orientations fitting the experimental spectrum equally well.[8] Our interpretation of the true structure involving interconversion of two C_1 species through a small C_s barrier holds here too. The experimental structure of SO_2.OCS is C_s, with the C_2 axis of SO_2 almost parallel to the OCS molecule, and with their dipole moments opposed.[7] For $SO_2.N_2O$ the experimental symmetry is C_1, as evidenced by the splitting of some of the rotational transitions into doublets, arising from a tunnelling motion.[9] As a result the complex lacks a symmetry plane, in agreement with our calculated structure. The authors

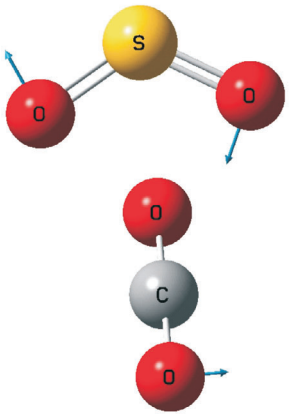

Figure 3 The imaginary mode of the C_s structure of the $SO_2.CO_2$ complex.

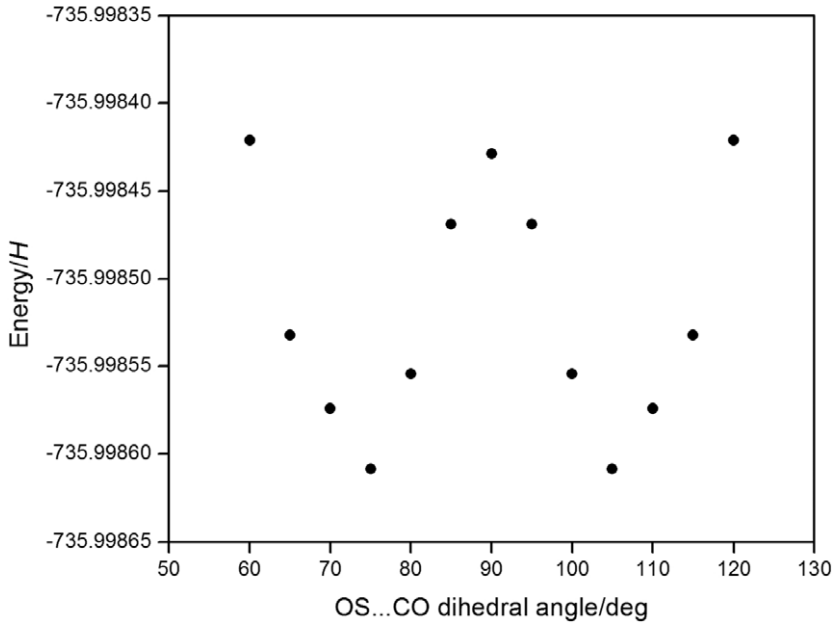

Figure 4 Potential surface scan of the OS…CO dihedral angle of the $SO_2.CO_2$ complex of C_s symmetry.

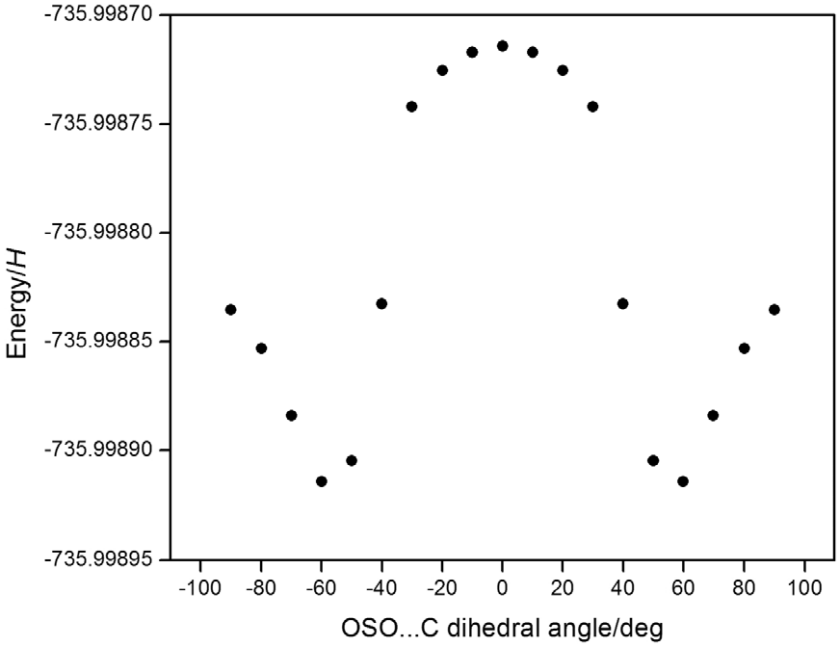

Figure 5 Potential surface scan of the OSO…C dihedral angle of the $SO_2.CO_2$ complex of C_1 symmetry.

Table 3 Natural bond orbital charges of the interacting monomers.

Complex	Charge/e	
	SO_2 fragment	Partner fragment
$SO_2.CO_2$	0.0025	–0.0025
$SO_2.OCS$	0.0020	–0.0020
$SO_2.CS_2$	–0.0071	0.0071
$SO_2.N_2O$	0.0007	–0.0007

Table 4 Primary and secondary orbital interactions of the complexes.

Complex	Primary interaction	Secondary interaction
$SO_2.CO_2$	SO_2 n(O) → CO_2 σ^*(CO)	CO_2 π(nb) → SO_2 π^*(SO)
$SO_2.OCS$	SO_2 n(O) → OCS σ^*(CS)	OCS π(CS) → SO_2 π^*(SO)
$SO_2.CS_2$	CS_2 π(nb) → SO_2 π^*(SO)	SO_2 n(O) → CS_2 π^*(CS)
$SO_2.N_2O$	SO_2 n(O) → N_2O σ^*(NO)	N_2O π(NN) → SO_2 π^*(SO)

failed to observe any such splittings in the other three complexes; this is clearly associated with the lower symmetry of $SO_2.N_2O$. In $SO_2.OCS$ and $SO_2.N_2O$ also, we envisage the tunnelling to involve mainly a SO_2 rocking motion, interconverting two equivalent C_1 structures. Valdes and Sordo have also computed the structure of the $SO_2.N_2O$ complex.[10] They examined six separate models and observed that all six were close in energy, with a very flat potential energy surface, and also invoked dynamic structure averaging to explain their results.

The interactions responsible for the stabilization of the four complexes may be pictured as an interplay between a primary donation of charge from an oxygen lone pair orbital associated with the SO_2 sub-molecule to a σ^* orbital located mainly on the central atom of the electron acceptor, and a secondary back-donation from a π type orbital associated with the closer terminal atom of the acceptor to the π^* orbital of the SO_2 molecule, which projects essentially normally to the SO_2 molecular plane. However, while a natural bond order (NBO)[17] charge analysis indicates that SO_2 is a net electron donor to CO_2 and OCS, the reverse is true for $SO_2.CS_2$, and the charge transfer in the case of $SO_2.N_2O$ is negligible (see Table 3).

The reversal of behaviour between CO_2 and OCS as electron acceptors on the one hand and CS_2 as a net donor on the other may be traced to the change of sign of the molecular quadrupole moment on progressing from CO_2 through OCS to CS_2 (-14.3×10^{-40} C m^2 for CO_2, -3.0×10^{-40} C m^2 for OCS and 11.5×10^{-40} C m^2 for CS_2).[18,19] The virtual lack of charge transfer in the case of $SO_2.N_2O$ can be attributed to the unfavourable alignment of the axes of the terminal nitrogen lone pair of N_2O (along the molecular axis) and of the π^* orbital of SO_2. The orbital interactions are summarized in Table 4.

Table 5 Intramolecular structural parameters of the complexes, and their changes relative to those of the monomers.

Complex	Parameter	Value	Difference
$SO_2.CO_2$	r(CO)/pm	117.11	0.11
		116.85	–0.15
	r(SO)/pm	146.83	0.09
		146.94	–0.03
	∠OSO/deg	118.88	–0.38
$SO_2.OCS$	r(CO)/pm	117.23	0.18
	r(CS)/pm	155.96	–0.32
	r(SO)/pm	146.92	0.06
		146.85	–0.01
	∠OSO/deg	118.96	–0.30
$SO_2.CS_2$	r(CS)/pm	156.54	0.38
		155.83	–0.34
	r(SO)/pm	147.06	0.20
		146.89	0.03
	∠OSO/deg	118.89	–0.36
$SO_2.N_2O$	r(NN)/pm	116.35	0.06
	r(NO)/pm	117.89	–0.22
	r(SO)/pm	146.99	0.13
		146.84	–0.02
	∠OSO/deg	118.88	–0.38

The changes to the intramolecular structural parameters on complexation are reported in Table 5. While the changes are minimal, in general the SO bond lying in the pseudoplane containing the linear acceptor molecule and the S atom of SO_2 lengthens slightly while the SO bond which projects out of the pseudoplane shortens. The OSO angle consistently reduces by about a third of a degree. The bond of the electron acceptor closer to the S atom of SO_2 lengthens in each case and the bond remote from the interaction shortens, indicating a weakening of the intramolecular bond associated with the interaction and a strengthening of the more remote intramolecular bond.

Table 6 lists the computed intermolecular structural properties of the complexes. The most characteristic of these properties is the separation of the O atom of the SO_2 molecule lying in the pseudoplane and the central atom of the electron acceptor. In the series CO_2 – OCS – CS_2 this distance increases regularly, indicating a successively weaker interaction along the series. For $SO_2.N_2O$ the N…O distance is similar to the C…O separation in $SO_2.CO_2$, suggesting a similarity in the properties of these two

Table 6 Intermolecular structural parameters of the complexes.

Complex	Parameter	Value	Complex	Parameter	Value
$SO_2.CO_2$	R(S…O)/pm	355.21	$SO_2.CS_2$	R(S…S)/pm	363.04
	R(C…O^i)/pm [a]	290.42		R(C…O^i)/pm [a]	330.55
	∠OC…O^i/deg [a]	83.45		∠SC…O^i/deg [a]	101.64
	∠O^iS…O/deg [a]	56.60		∠O^iS…S/deg [a]	90.66
	∠O^oS…O/deg [b]	86.75		∠O^oS…S/deg [b]	94.45
$SO_2.OCS$	R(S…O)/pm	333.04	$SO_2.N_2O$	R(S…N)/pm	350.15
	R(C…O^i)/pm [a]	305.93		R(N…O^i)/pm [a]	293.54
	∠OC…O^i/deg [a]	79.78		∠NN…O^i/deg [a]	85.31
	∠O^iS…O/deg [a]	67.22		∠O^iS…N/deg [a]	60.88
	∠O^oS…O/deg [b]	85.62		∠O^oS…N/deg [b]	86.91

[a] O^i – O atom of SO_2 lying in the pseudoplane.
[b] O^o – O atom of SO_2 out of the pseudoplane.

Table 7 Comparison of computed and experimental intermolecular structures of the complexes.

Complex	Parameter	Computed	Experimental [a]
$SO_2.CO_2$	R_{cm}/pm [b]	362.23	329
	∠O1C…X1/deg [c]	66.96	
	∠C…X1…S/deg [c]	129.83	
$SO_2.OCS$	R_{cm}/pm [b]	384.56	374.71
	∠S1…X2…X3/deg [d]	115.81	123.8
	∠X2…X3…S2/deg [d]	152.79	142
$SO_2.CS_2$	R_{cm}/pm [b]	354.26	342.87
	∠S3C…X4/deg [e]	96.22	92.7
	∠C…X4…S4/deg [e]	96.65	102.5
$SO_2.N_2O$	R_{cm}/pm [b]	358.39	333.06
	∠N1…X5…X6/deg [f]	76.25	111.1
	∠X5…X6…S/deg [f]	118.16	156.9

[a] See refs. 6–9.
[b] R_{cm} = centre of mass separation.
[c] O1 = O atom of CO_2 closer to S atom, X1 = centre of mass of SO_2.
[d] S1 = S atom of OCS, S2 = S atom of SO_2, X2 = centre of mass of OCS, X3 = centre of mass of SO_2.
[e] S3 = S atom of CS_2 farther from S atom of SO_2, X4 = centre of mass of SO_2, S4 = S atom of SO_2.
[f] N1 = terminal N atom of N_2O, X5 = centre of mass of N_2O, X6 = centre of mass of SO_2.

Table 8 Interaction energies of the complexes, corrected for basis set superposition error (BSSE) and for zero-point energy differences.

Complex	Interaction energy/kJ mol^{-1}	
	Corrected for BSSE only	Corrected for BSSE and ΔE_o
$SO_2.CO_2$	–4.119	–2.375
$SO_2.OCS$	–3.207	–1.643
$SO_2.CS_2$	–2.650	–1.142
$SO_2.N_2O$	–4.799	–3.025

complexes, but implying a significant difference in the natures of the CO_2 – OCS – CS_2 set on one hand and the N_2O species on the other. The data presented in Table 6 are not directly comparable with the reported experimental intermolecular geometrical properties,[6–9] and our distances and angles have therefore been used to calculate the centre-of-mass separations and some of the angles which may be more sensibly compared with the experimental counterparts, as shown in Table 7. Because of the different symmetries of our computed structures and those (with the exception of $SO_2.N_2O$) observed experimentally, the results shown in Table 7 understandably do not exhibit close agreement. Generally, our centre-of-mass separations overestimate the experimental values by between 2 and 11 %, but the intermolecular angles show no such consistency.

3.2. Interaction Energies

Table 8 presents the interaction energies of all four complexes, corrected for BSSE and also for zero-point energy differences. The counterpoise corrections were applied to the energies of the optimized structure complexes only, and no attempt was made to include such corrections in the optimization process. Both sets of energies indicate that all the complexes are bound, although only very weakly. The interaction energies decrease in the order N_2O > CO_2 > OCS > CS_2. In common with our observations regarding other complexes containing CO_2, OCS and CS_2,[1–5] our interaction energies are found to be directly proportional to the ionization energy,[20a] the absolute electronegativity[21] and the hardness[21] of the electron acceptor, and inversely proportional to the electron affinity,[20b,22] the mean polarizability[20c] and the molecular quadrupole moment.[18,19]

Table 9 Intramolecular vibrational wavenumbers of the complexes and their shifts relative to those of the monomers. All modes are of *a* symmetry.

Complex	Mode	Wavenumber /cm^{-1}	Wavenumber shift/cm^{-1}	Approximate description
$SO_2.CO_2$	ν_1	2434.9	2.1	$\nu_a(CO_2)$
	ν_2	1337.4	1.9	$\nu_s(CO_2)$
	ν_3	1285.3	–0.3	$\nu_a(SO_2)$
	ν_4	1075.3	2.5	$\nu_s(SO_2)$
	ν_5	656.2	1.0	$\gamma(CO_2)$
	ν_6	648.2	–7.0	$\delta(CO_2)$
	ν_7	490.9	1.6	$\delta(SO_2)$
$SO_2.OCS$	ν_1	2100.7	0.0	ν(CO)
	ν_2	1285.9	0.3	$\nu_a(SO_2)$
	ν_3	1074.8	2.0	$\nu_s(SO_2)$
	ν_4	906.8	5.8	ν(CS)
	ν_5	497.1	2.2	δ(OCS)
	ν_6	495.9	1.0	γ(OCS)
	ν_7	488.8	–0.5	$\delta(SO_2)$
$SO_2.CS_2$	ν_1	1636.3	–1.0	$\nu_a(CS_2)$
	ν_2	1280.7	–4.9	$\nu_a(SO_2)$
	ν_3	1070.8	–2.0	$\nu_s(SO_2)$
	ν_4	683.6	–0.5	$\nu_s(CS_2)$
	ν_5	489.5	0.2	$\delta(SO_2)$
	ν_6	374.5	3.4	$\delta(CS_2)$
	ν_7	367.6	–3.5	$\gamma(CS_2)$
$SO_2.N_2O$	ν_1	2261.7	18.5	ν(NN)
	ν_2	1289.7	3.6	ν(NO)
	ν_3	1283.6	–2.0	$\nu_a(SO_2)$
	ν_4	1073.9	1.1	$\nu_s(SO_2)$
	ν_5	539.7	1.9	δ(NNO)
	ν_6	538.9	1.1	γ(NNO)
	ν_7	490.2	0.9	$\delta(SO_2)$

In each case, the datum for the $SO_2.N_2O$ adduct is an outlier, which is not consistent with those for the other three complexes. The anomalous position of $SO_2.N_2O$ in these relationships has been alluded to above, in connection with the essentially zero charge transfer in this complex, and is related to the differences in the type of intramolecular bonding in N_2O compared with the three carbon-containing molecules, which lead to a different mode of intermolecular binding from that in the remaining three species. The interaction energies of intermolecular complexes may be partitioned into contributions from the attractive charge transfer, electrostatic, polarization and dispersion components and a repulsive Coulomb exchange term, and the net interaction energy can result from a complex interplay among these components. The partitioning into these five terms is clearly quite different for the $SO_2.N_2O$ complex from those in the carbon-containing adducts, and an analysis of the decomposition of these interaction energies will be the subject of a future extension of this work.

3.3. Vibrational Spectra

Our observations concerning the computed wavenumber shifts of relatively strongly bound molecular complexes, compared with the wavenumbers of the monomers, have been that these shifts are directly proportional to the interaction energies.[23] In the case of more weakly bound complexes, however, the wavenumber shifts are more erratic, and any dependence on the strength of interaction is determined by the extent to

Table 10 Intermolecular vibrational wavenumbers of the complexes. All modes are of *a* symmetry.

Complex	Mode	Wavenumber/cm^{-1}	Approximate description [a]
$SO_2.CO_2$	ν_8	119.7	$\omega(SO_2)(54) + l(CO_2)(47)$ (antigeared)
	ν_9	69.5	ν(C…O)
	ν_{10}	51.1	$\omega(SO_2)(56) + l(CO_2)(44)$ (geared)
	ν_{11}	29.7	$l(CO_2)(57)$ (antigeared) + tw$(SO_2)(42)$
	ν_{12}	19.5	$\rho(SO_2)(70) + l(CO_2)(29)$ (antigeared)
$SO_2.OCS$	ν_8	100.1	l(OCS)(53) (antigeared) + $\omega(SO_2)(47)$
	ν_9	53.6	ν(C…O)
	ν_{10}	42.5	$\omega(SO_2)(53) + l$(OCS)(46) (geared)
	ν_{11}	35.3	tw$(SO_2)(61) + l$(OCS)(40) (antigeared)
	ν_{12}	19.1	$\rho(SO_2)(77) + l(CO_2)(23)$ (antigeared)
$SO_2.CS_2$	ν_8	94.4	$\omega(SO_2)(95)$
	ν_9	66.6	ν(C…O)
	ν_{10}	53.9	$l(CS_2)(63)$ (antigeared) + $\omega(SO_2)(37)$
	ν_{11}	27.1	$\rho(SO_2)(85)$
	ν_{12}	18.3	tw$(SO_2)(88)$
$SO_2.N_2O$	ν_8	114.4	l(NNO)(52) (antigeared) + $\omega(SO_2)(48)$
	ν_9	60.0	ν(N…S)
	ν_{10}	44.6	l(NNO)(53) (geared)+ $\omega(SO_2)(48)$
	ν_{11}	36.4	l(NNO)(61) (antigeared) + tw$(SO_2)(39)$
	ν_{12}	15.7	$\rho(SO_2)(72) + l$(NNO)(28) (antigeared)

[a] Numbers in parentheses are the approximate potential energy distribution contributions of each monomer unit.

which the particular vibrational mode is localized in one monomer or the other.[23] Table 9 shows the intramolecular wavenumbers of the four complexes, with approximate descriptions of the modes, and the shifts relative to the monomers. With the exception of ν_7 of SO_2.OCS, where the SO_2 bending vibration has only an 82 % potential energy distribution, with an 18 % contribution from the OCS bending mode of the OCS sub-molecule, all the modes listed in Table 9 are almost totally localized in one or other of the monomers. The wavenumber shifts of the SO_2 fragments are all less than 5 cm^{-1}, consistent with the weakness of the interactions indicated in Table 8. Since these shifts are all so small, there is no apparent trend in their values, or even their signs, which might be correlated with the interaction energies. The shifts of the modes of the partner molecules are similarly insubstantial, with the exception of the NN stretching mode of N_2O in $SO_2.N_2O$. Here, too, the signs are irregular, and the spectra of the linear molecules are quite insensitive to the strength of interaction.

The wavenumbers of the intermolecular modes of the complexes are given in Table 10. The intermonomer stretching mode wavenumbers are remarkably constant, at 62 ± 8 cm^{-1}. The hindered rotational vibrations of the SO_2 moiety are coupled to varying degrees with the librational motions of the partner molecules, therefore comparison of the wavenumbers of those modes most closely associated with the SO_2 fragment is not strictly valid. Nevertheless, these mode wavenumbers decrease fairly uniformly in the order wagging > twisting > rocking. Clearly, the perturbations of the spectra of the interacting molecules are minimal, confirming the low interaction energies with which each pair of molecules binds.

4. Conclusions

The molecular complexes formed between sulphur dioxide on one hand, and carbon dioxide, carbonyl sulphide, carbon disulphide and nitrous oxide on the other, each optimize with structures of C_1 symmetry, which are interpreted as being one of a pair of equivalent structures with one SO bond projecting out of the pseudoplane formed by the second SO bond and the partner molecule. These equivalent structures interconvert through small energy barriers at the C_s positions. The experimentally observed C_{2v} ($SO_2.CO_2$[6]), C_s ($SO_2.OCS$[7] and $SO_2.CS_2$[8]) and C_1 ($SO_2.N_2O$[9]) structures may be accommodated by our non-symmetrical models by invoking a tunnelling motion, which is manifested in the experimental rotational spectra of $SO_2.N_2O$ by the splitting of some of the lines. The interaction energies of the complexes involving the carbon-containing molecules are very small, and are proportional to their molecular quadrupole moments, among other properties, while the complex with nitrous oxide exhibits quite anomalous properties. The perturbations of the vibrational spectra of each partner molecule in the complexes are minimal.

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