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Ab initio molecular orbital studies of the vibrational spectra of some van der Waals complexes. Part 3: Complexes of carbon monoxide with carbon dioxide, nitrous oxide, carbonyl sulphide and carbon disulphide

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Abstract

The properties of the molecular electron donor–acceptor complexes formed between carbon monoxide, as the electron donor, and the linear triatomic molecules carbon dioxide, nitrous oxide, carbonyl sulphide and carbon disulphide as the electron acceptors, have been studied. These properties include their structures, interaction energies and vibrational spectra. The studies were performed using the Gaussian 98 computer program, at the second order level of Møller-Plesset perturbation theory (MP2) with the 6-311+G(d) basis set. The interaction energies are inversely dependent on the absolute electronegativities, mean polarizabilities and quadrupole moments of the electron acceptors, at least for CO_2, OCS and CS_2, while the CO stretching wavenumber shifts generally become more positive with increasing interaction energy. The results obtained will be useful in further studies of these complexes using the matrix isolation infrared spectroscopic technique.

Keywords: Ab initio; Molecular complexes; Structures; Interaction energies; Vibrational spectra

1. Introduction

We have published an ab initio study of the properties of the complexes formed between dinitrogen and the four linear triatomic molecules CO_2, N_2O, OCS and CS_2 [1]. The structures of $N_2\cdot CO_2$, $N_2\cdot N_2O$ and $N_2\cdot OCS$ were predicted to be T-shaped, consistent with those obtained experimentally in the gas phase [2–4], and the same general structure was also found for $N_2\cdot CS_2$. We have now investigated the complexes formed between the isoelectronic electron donor molecule, carbon monoxide, and the same four linear triatomic molecules as electron acceptors. Gas phase diode laser infrared spectroscopic studies, using pulsed molecular beams [5–10], and pulsed supersonic nozzle Fourier transform microwave investigations [5,8] of the $CO\cdot CO_2$ [5,6], $CO\cdot N_2O$ [7,9] and $CO\cdot OCS$ [8,10] complexes have been carried out by other workers, and these species were also found to have T-shaped geometries, similar to those of the dinitrogen complexes. Unlike the dinitrogen complexes, however, where the electron donor monomer has no permanent dipole moment, and thus the major source of attraction is a dipole-quadrupole ($N_2\cdot N_2O$ and $N_2\cdot OCS$) or quadrupole–quadrupole ($N_2\cdot CO_2$ and $N_2\cdot CS_2$) interaction [1], in the carbon monoxide complexes dipole–dipole interactions are also possible, depending on the nature of the electron acceptor (as in $CO\cdot N_2O$ and $CO\cdot OCS$).

Matrix isolation studies of the $CO\cdot CO_2$ complex revealed the existence of two conformations which underwent interconversion in argon matrices [11,12]. It was confirmed that this interconversion was not photoinduced, but that it was more likely to be due to a spontaneous reorientation of the CO molecule in the complex, resulting in a complete rotation of the CO moiety, giving rise to two types of CO complex, a C-bound and an O-bound. In this

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work, both the C-bound and O-bound complexes of CO with CO_2, N_2O and OCS were investigated, and the results are reported here. In addition, the novel analogous complexes formed between carbon monoxide and carbon disulphide were investigated, as these species were expected to have similar properties to those of the $CO\cdot CO_2$, $CO\cdot N_2O$ and $CO\cdot OCS$ adducts.

2. Computational methodology

The calculations were performed using the Gaussian 98 program [13], installed on Silicon Graphics Indy and Compaq DS20 computer systems. The calculations were carried out at the second order level of Møller-Plesset perturbation theory [14], using the 6-311+G(d) basis set [15,16]. Geometry optimizations of the monomers and of all eight complexes were carried out using the Berny [17] or Murtagh–Sargent [18] algorithms, as appropriate, and with the VERYTIGHT convergence criterion [13]. The interaction energies were computed and corrected for basis set superposition error (BSSE) [19], using the full counterpoise correction technique of Boys and Bernardi [20]. The wavenumbers and infrared intensities of all the species studied were obtained using the FREQ option [13]. Further details are as reported in our previous publication [1].

3. Results and discussion

3.1. Structures

All eight C-bound and O-bound CO complexes investigated in this work were found to have planar T-shaped structures, with the sole exception of C-bound $CO\cdot CS_2$. The optimized structures are shown in Figs. 1 and 2. Some tilting of the electron acceptor with respect to the CO molecular axis occurs in $CO\cdot N_2O$ and $CO\cdot OCS$, as these species lack a C_2 axis, unlike the two complexes with CO_2 and the O-bound complex with CS_2. The tilting of the NNO fragment of the $CO\cdot N_2O$ complexes brings the O atom of N_2O closer to the CO molecule by almost 7 and 2° in the C-bound and O-bound adducts, respectively. Tilting of the OCS species in the $CO\cdot OCS$ complexes causes the O atom of OCS to bend towards the CO molecule by about 21 and 22° in C-bound and O-bound $CO\cdot OCS$, respectively. In each case, therefore, the more negatively charged pole of the electron acceptor is preferentially attracted to the more positive atom of the CO sub-molecule. In contrast, the C-bound $CO\cdot CS_2$ complex was found to be non-planar, with the CO axis making an angle of about 31° with the line joining the centres of mass. In the case of this species, the initial optimization, with the complex constrained to be planar, resulted in the appearance of a single imaginary eigenvalue, corresponding to the out-of-plane libration of the CO sub-molecule. A second optimization, with the planarity constraint removed, yielded a full set of positive frequencies. This non-planar structure was more stable than the planar species by about 77 J mol^{-1}.

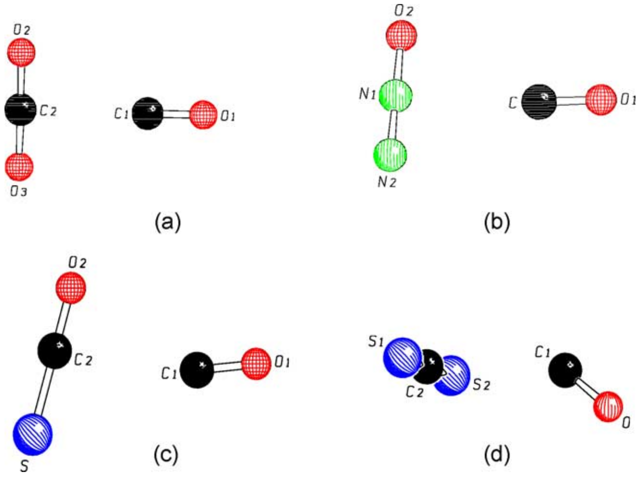

Fig. 1. Optimized structures of the C-bound complexes: (a) $CO\cdot CO_2$, (b) $CO\cdot N_2O$, (c) $CO\cdot OCS$, (d) $CO\cdot CS_2$.

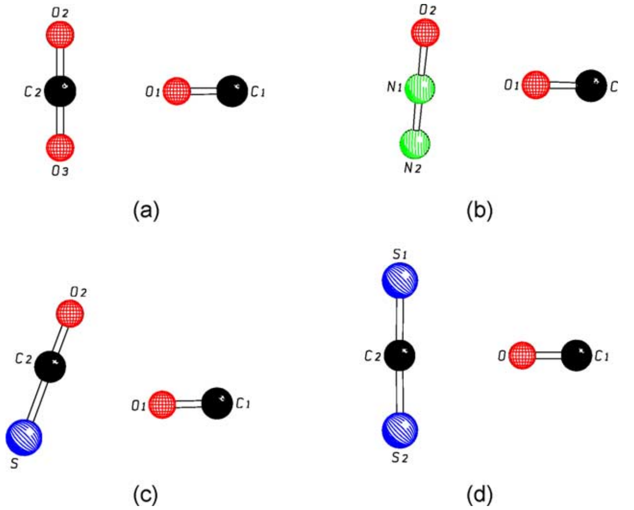

Fig. 2. Optimized structures of the O-bound complexes: (a) $CO\cdot CO_2$, (b) $CO\cdot N_2O$, (c) $CO\cdot OCS$, (d) $CO\cdot CS_2$.

The optimized structural parameters of the CO species studied in this work are shown in Table 1. The intermonomer separations are consistently greater by from 17 to 26 pm for the C-bound species relative to the O-bound; this is partly accommodated by the larger van der Waals radius (170 compared with 152 pm [21]) of C compared with that of O. The perturbations of the monomer bond lengths are all within ±0.05 pm; in general the bond lengths of the CO fragments decrease in the C-bound complexes and increase in the O-bound species, but these differences are probably not significant. The behaviour of the bond lengths of the electron acceptors on complexation is variable. The bond angles of the triatomic molecules deviate from linearity by no more than ±0.60° on formation of the complex;