Unveiling the non-covalent interactions of molecular homodimers by dispersion-corrected DFT calculations and collision-induced broadening of ro-vibrational transitions: application to $(CH_2F_2)_2$ and $(SO_2)_2$

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Abstract

Thermodynamic and spectroscopic properties of molecular complexes featuring non-covalent interactions, such as van der Waals forces and hydrogen bonds, are of fundamental interest in many fields, ranging from chemistry and biology up to nanotechnology. In the present work the homodimers of difluoromethane (CH_2F_2) and sulfur dioxide (SO_2) are investigated theoretically by dispersion-corrected density functional theory (DFT-D3) and experimentally by tunable diode laser (TDL) infrared (IR) spectroscopy. The dissociation energies of $(CH_2F_2)_2$ and $(SO_2)_2$ are determined experimentally from the broadening of the ro-vibrational transitions of the corresponding monomers collisionally perturbed by a range of damping gasses. The resulting dissociation energies are $2.7_9 \pm 0.3_2$ and $2.6_2 \pm 0.1_6$ kcal mol^{-1} for the CH_2F_2 and SO_2 dimers, respectively. Six to nine different stationary points on the PES of the two complexes are investigated theoretically at the DFT-D3 level, retrieving the corresponding dissociation energies, structures and rotational constants. Computations are carried out by employing six different density functionals (BLYP, TPSS, B3LYP, PBE0, TPSSh, PW6B95) in conjunction with the def2-TZVP and in a few cases def2-QZVP basis sets. DFT-D3 dissociation energies are benchmarked against reference values from CCSD(T)/CBS computations, and furthermore compared to experimental ones. A very good agreement between theory and experiment is attained, showing that DFT-D3 provides a significant improvement over standard DFT. This work shows that dissociation energies of homodimers can be consistently derived from collisional broadening cross sections and that interaction energies at various DFT-D3 levels (nearly) reach the accuracy of highly correlated wavefunction methods.

Keywords. DFT-D3; high resolution IR spectroscopy; molecular complexes; non-covalent interactions; collisional broadening.

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1. Introduction

Non-covalent interactions involved in hydrogen bonded- and van der Waals- complexes, are of paramount importance in many multidisciplinary fields, ranging from chemistry and biology up to condensed matter physics. Nevertheless, for many reasons measuring the thermochemical and spectroscopic properties of molecular complexes is an expensive, non-trivial and time-consuming task.[1] On the other hand, thanks to the huge progresses made in computer hardware resources and the development of efficient theoretical approximations and numerical algorithms, quantum chemistry has become a powerful tool to access thermodynamic and spectroscopic information.

Non-covalent interactions are ubiquitous in chemistry and play a key role in biochemistry, hence it is of fundamental importance to incorporate them in a physically sound manner into Kohn-Sham density functional theory (DFT). This need is even more exacerbated by the fact that methods rooted in DFT represent, at present, the working option for the investigation of large systems composed of hundreds to thousands atoms. Although standard DFT can handle such large systems and has proven itself to provide accurate results for numerous molecular properties, many standard DF approximations fail to correctly describe the long range London dispersion interactions (in particular the correct $-R^{-6}$ dependence of the interaction energy on the intermolecular separation R). Therefore, it is not surprising that over the last years, many research efforts have been profuse for the development of dispersion corrected density functionals. Various approaches to tackle the problem have been proposed in the literature (for an overview see Ref. 2-4 and references therein), such as the DFT-D method,[5] nonlocal van der Waals functionals,[6,7] dispersion-corrected atom-centered potentials [8] and highly parameterized density functionals.[9] Among these, the DFT-D3 scheme represents a general and widely used tool for the computation of dispersion energy in molecules and solids, that joins a low numerical complexity to the profitable computational costs typical of DFT.[10] Up to now, it has been extensively tested and successfully applied to thousand of different systems including dimers, large supramolecular complexes and reaction energies and barriers, featuring high accuracy and robustness.[10-17]

In this paper, the dimers of difluoromethane (CH_2F_2, HFC-32) and sulfur dioxide (SO_2) are investigated by tunable diode laser (TDL) infrared (IR) spectroscopy and quantum chemical calculations. Both monomers are of atmospheric relevance as trace gas pollutants, and therefore they have been widely investigated by spectroscopic methods (for an overview of the relevant literature see Refs. 18-21 and references therein). HFC-32 is widely used in refrigerant mixtures and its concentration in the atmosphere has been estimated around 3 ppt with a growing trend. Sulfur dioxide is naturally emitted by volcanic eruptions and biomass burning, although its main sources arise from anthropogenic activities, in particular combustion of fuels, metallurgy and food preserving.

As far as the dimers are concerned, difluoromethane forms a complex in which the two monomers are bound through a triple (weak) hydrogen bond, in which one CH_2F_2 molecule acts as a double proton donor, and the second one plays as double proton acceptor. The structure of the $(CH_2F_2)_2$ was first determined by Caminati and co-workers [22] and later refined by Blanco et al.[23] by molecular-beam Fourier transform microwave spectroscopy. Further, it was also studied theoretically at HF, MP2 and B3LYP levels of theory.[24] Hydrogen bonds involved within $(CH_2F_2)_2$ can be classified as weak-hydrogen bonds, which are of great interest as they determine many molecular structures and their functions in biological systems. Hence, theoretical investigations of weak hydrogen bonds are of particular relevance, though they require reliable computational tools able to properly model the molecular structures and the corresponding potential energy surfaces.[25] Besides, it has also been suggested that the $(CH_2F_2)_2$ complex provides an example of the insurgence of an anti-hydrogen bond.[26]

Within the sulfur dioxide dimer, SO_2 can act as either a Lewis base or Lewis acid, respectively by donating the electron from the oxygen lone pair or by accepting charge into the π anti-bonding orbitals of the sulfur atom. Over the years the $(SO_2)_2$ complex has been widely studied both experimentally and theoretically.[27,28] Microwave investigations have led to the determination of its structure, in which the two non-symmetric SO_2 units behave as one electron donor and one electron acceptor, respectively, leading to a complex belonging to the C_s point group.[29] Although a number theoretical investigations have appeared in the literature, mainly carried out at HF and MP2 levels of theory, it has been emphasized that this complex is a difficult problem for quantum chemistry.[30]

In the present work, the dissociation energies of $(CH_2F_2)_2$ and $(SO_2)_2$ dimers are determined experimentally from the collision-induced broadening of the ro-vibrational transitions of the corresponding monomers. The energies and structures of the stationary points on the potential energy surfaces of the two dimers are then investigated theoretically by adopting the DFT-D3 scheme in order to account for long-range dispersion correlation effects. From the obtained results, it will be demonstrated that (i) collisional broadening cross sections can be used for determining the dissociation energies of homo-dimers; (ii) DFT including dispersion corrections, and the DFT-D3 approach in particular, can reach the accuracy of highly correlated wavefunction methods for the prediction of thermochemical data; (iii) the interplay between experimental spectroscopic techniques and state-of-the-art theoretical approaches leads to a deep insight into the characterization of the potential energy surfaces of hydrogen-bonded- and van der Waals-complexes.

The paper is structured as follows: the theoretical framework is briefly summarized in Section 2, and the experimental and computational methods are described in Sections 3 and 4, respectively. Results are presented and discussed in Section 5, and finally conclusions are addressed in Section 6.

2. Theory

Besides giving the basic information for the interpretation of observational data retrieved by means of remote sensing spectroscopic techniques,[31,32] pressure broadening coefficients (γ), being related to the real part of the collisional cross section σ, can provide important information about intermolecular interactions driving the scattering event in the gas phase (e.g. Refs. 33-40 and references therein).

The determination of the dissociation energy of a homodimer from the foreign broadening coefficients of the corresponding monomer molecule is based on the approximate relationship derived by Lin et al.[41] and denoted as Parmenter-Seaver (PS) equation in the following of the paper. They developed a model that, relying on the formation of a complex between the colliding species A and M, correlates the collisional cross section for A - M collisions to the well depth, $\varepsilon_{\mathrm{AM}}$, of the corresponding complex. By approximating this well depth with the geometric mean of the well depths of the two dimers (A_2 and M_2), the following expression is obtained for the cross section of a given collision process involving the radiator A (i.e. the species that absorbs the radiation) and a colliding partner M (i.e. the buffer gas):

$$\sigma_{\mathrm{AM}} = Ce^{\beta\left(\frac{\varepsilon_{MM}}{K_B T}\right)^{1/2}} \qquad (1)$$

with

$$\beta = \frac{1}{T}\left(\frac{\varepsilon_{AA}}{K_B}\right)^{1/2} \qquad (2)$$

where C is a constant, K_B is the Boltzmann constant, T is the absolute temperature, ε_{AA} and $\varepsilon_{\mathrm{MM}}$ are the well depths of dimers A_2 and M_2, respectively. The PS relation has been demonstrated to hold for a variety of energy transfer processes, provided that attractive forces dominate the interaction. [41-43]

The theoretical modeling of molecular complexes adopting Kohn-Sham DFT requires the inclusion of London dispersion (long-range electron correlation) effects. The simplest way of incorporating them and providing an asymptotically correct $-R^{-6}$ dependence of the interaction energy on the intermolecular distance R is the DFT-D approach. The method supplies an atom pair-wise additive treatment of non-covalent interactions and the dispersion energy is added to the result of standard DFT calculations without any significant additional computational cost:

$$E_{\mathrm{DFT-D3}} = E_{\mathrm{DFT}} + E_{\mathrm{disp}} \tag{3}$$

According to the DFT-D3 scheme adopting the so-called Becke's and Johnson's (BJ) rational damping,[44] the general form of the dispersion energy is given by

$$E_{\mathrm{disp}}^{\mathrm{DFT-D3(BJ)}} = -\frac{1}{2}\sum_{\mathrm{A}\neq\mathrm{B}} \frac{C_6^{\mathrm{AB}}}{R_{\mathrm{AB}}^6 + \left[f\left(R_{\mathrm{AB}}^0\right)\right]^6} + s_8 \frac{C_8^{\mathrm{AB}}}{R_{\mathrm{AB}}^8 + \left[f\left(R_{\mathrm{AB}}^0\right)\right]^8} \tag{4}$$

with

$$f\left(R_{\mathrm{AB}}^0\right) = a_1 R_{\mathrm{AB}}^0 + a_2 \tag{5}$$

and

$$R_{\mathrm{AB}}^{0} = \left(\frac{C_{8}^{\mathrm{AB}}}{C_{6}^{\mathrm{AB}}} \right) \tag{6}$$

where a_1 and a_2 are free fit parameters introduced by BJ. The summation runs over all atom pairs in the system and C_n^{AB} represent the pair-specific nth-order dispersion coefficients for atom pair AB, whose internuclear distance is R_{AB}; s_8 is used to adapt the correction to the repulsive character of the short/medium-range behavior of the exchange correlation. As a result, DFT-D3(BJ) requires for each short-range functional three fit parameters (a_1, a_2 and s_8) which have been determined for more than 45 different density functionals.[45]

3. Experimental details and data inversion procedure

The measurements for the determination of foreign broadening coefficients of SO_2 and CH_2F_2 perturbed by noble gases He, Ne and Ar, as well as of SO_2 perturbed by O_2 and N_2 collisional partners, were carried out on a tunable diode laser (TDL) spectrometer operating in a three beam configuration. The experimental setup has been described previously [46-48] and here it will be just summarized. The source was a commercial lead salt diode laser cryogenically cooled at liquid nitrogen temperature: two different lasers, one centered at 9.1 μm and one at 8.7 μm, were used for the SO_2 and CH_2F_2 measurements, respectively. The laser radiation was split into three beams: one passed through the sample cell, while the other two were sent to a germanium etalon and to a cell containing a low-pressure SO_2 reference sample, respectively, both used for frequency calibration. The three beams were then collected by three different HgCdTe detectors and the resulting spectral microwindows, about 0.3 cm^{-1} wide, were recorded by the digitization system. According to the intensities of the observed spectral lines, the radiator pressure was maintained around 100 Pa, and for each spectral micro-window, increasing quantities of damping gas were added in the range 300

Pa – 6000 Pa. All the spectra were recorded at room temperature (294 ± 1 K). A more detailed description of the experimental work will be given in dedicated paper in which a larger number of spectral lines is considered and analyzed.[49]

The recorded spectra were first wavenumber calibrated by using the frequency of the SO_2 lines obtained from the high resolution FT-IR spectrum and then the transmittance spectra were obtained from the incident and transmitted radiation intensities, according to Beer-Lambert's law. For each transition, line parameters were retrieved by fitting all the experimental features in a microwindow to the Voigt profile employing the VLSFP program [50] in the multi-line mode following the procedure described in Ref. 20 and 48 for SO_2 and CH_2F_2, respectively. An example of the fitting procedure based on the Voigt profile is given in Figure 1: as it can be seen from the small residuals, the Voigt model not only is computationally favourable, but it also well reproduces the experimental line shapes, in agreement to the results obtained in the case of SO_2 and CH_2F_2 ro-vibrational transitions collisionally perturbed by N_2 and O_2.[20,48] For each transition and for each damping gas, foreign broadening coefficients, γ_{M}^{0} (where M = He, Ne, Ar, O_2 or N_2), were retrieved according to a weighted linear fit of the collisional half widths, obtained from the line profile analysis, against the pressure of the perturbing species, P_{M} :

$$\Gamma_L = \Gamma_0 + \gamma_{\mathrm{M}}^{0} \times P_{\mathrm{M}} \tag{7}$$

where Γ_0 takes into account both instrumental and self broadening contributions. The collisional half widths obtained for the $25_{10,15} \leftarrow 24_{9,15}$ transition of the ν_7 band of CH_2F_2 employing different pressures of the noble gases, together with the corresponding linear interpolations, are reported in Figure S.1 of the Supplementary Information. The obtained foreign-broadening coefficients are listed in Table 1 for both CH_2F_2 and SO_2 ro-vibrational transitions.

4. Computational details

All DFT computations were carried out employing the Turbomole 6.5 quantum chemistry package [51,52] by using six different density functionals (DFs) in conjunction with the def2-TZVP basis set.[53] The extended def2-QZVP basis set which provides results quite close to the Kohn-Sham-limit was used in selected cases for monitoring the corresponding convergence behavior of the interaction energy. In particular, BLYP [54,55] and TPSS [56] were employed as GGA- and meta-GGA functionals respectively, while among hybrid-GGA the popular B3LYP [55,57] and the parameter-free PBE0 [58] were used. Finally two meta-hybrid GAA, TPSSh [56] and PW6B95,[59] were considered as well. For each complex structure, as well as for CH_2F_2 and SO_2 monomers, geometry optimizations were carried out at first, followed by the computation of the harmonic force field (except for PW6B95 for which analytical second energy derivatives were not implemented) in order to obtain harmonic vibrational frequencies and zero-point vibrational corrections to the electronic energy. Dissociation energies (ΔE) were computed as the difference between dimer's and monomer's energies, and are indicated as ΔE^{0} if ZPVE is taken into account. In all calculations the BLYP and TPSS functionals were treated within the framework of the resolution of identity (RI-J) approximation,[60] with the auxiliary basis sets taken from the Turbomole basis set library.[61] In order to account for the basis set superposition error (BSSE), counterpoise corrections were applied.[62,63] In general, the Turbomole grid m5 was used, except for some difficult cases in which the larger m7 grid was required for the geometry optimization to converge.

In addition, reference values for electronic energies were obtained from wavefunction calculations at the estimated CCSD(T)/CBS level. These calculations, performed by using the MOLPRO software,[64] were carried out on the geometry obtained from B3LYP-D3(BJ)/def2-TZVP computations. Following Hobza and co-workers the energy at the CCSD(T)/CBS level was estimated according to a 3/4 extrapolation scheme, in which the electronic energy is given by the following equation [65,66]

$$E^{\mathrm{CCSD(T)/CBS}} = E_{\mathrm{SCF}}^{\mathrm{HF/aVQZ}} + E_{\mathrm{corr}}^{\mathrm{MP2/CBS}} + E_{\mathrm{corr}}^{\mathrm{CCSD(T)/aVTZ}} - E_{\mathrm{corr}}^{\mathrm{MP2/aVTZ}} \quad (8)$$

where $E_{\mathrm{SCF}}^{\mathrm{HF/aVQZ}}$ is the electronic energy computed at HF/aug-cc-pVQZ level; $E_{\mathrm{corr}}^{\mathrm{CCSD(T)/aVTZ}}$ and $E_{\mathrm{corr}}^{\mathrm{MP2/aVTZ}}$ are CCSD(T) and MP2 correlation energies, respectively, computed in conjunction with the aug-cc-pVTZ basis set. The MP2 correlation energy was extrapolated to the CBS limit ($E_{\mathrm{corr}}^{\mathrm{MP2/CBS}}$) by using Halkier's formula [67] from the aug-cc-pVTZ and aug-cc-pVQZ basis sets).

5. Results and discussion

5.1. Experimental ($(CH_2F_2)_2$) and ($(SO_2)_2$) well depths from foreign-broadening coefficients

The foreign-broadening coefficients obtained from the line-shape analysis of the recorded ro-vibrational lines (Table 1) were first converted to the corresponding collisional cross sections according to the following equation

$$\sigma_{\mathrm{AM}} = \frac{2\pi K_B T \gamma_{\mathrm{M}}^{0}}{v_{\mathrm{rel}}} \quad (9)$$

where v_{rel} is the relative speed of the colliding partners and all quantities are expressed in S.I. units. These were in turn employed to derive the experimental dissociation energies of the $(CH_2F_2)_2$ and $(SO_2)_2$ dimers according to Equation 1 expressed in a logarithmic form in order to obtain a linear relation between log(σ_{M}) and $\left(\varepsilon_{\mathrm{AA}}\right)^{1/2}$: for each spectral transition, He-, Ne-, Ar-, N_2- and O_2-collisional cross sections were fitted to straight lines against the well depth of the damping gas dimers (i.e. $\varepsilon_{\mathrm{MM}}^{1/2}$) which are tabulated in the work by Lin et al.[41] The slope of the interpolating line correlates to the well depth of the dimer of the radiation species. An example of such procedure is illustrated in Figure 2, in the case of $25_{14,12} \leftarrow 25_{15,11}$ transition of the ν_1 band of SO_2.

By taking the average of the interaction energies obtained from the different ro-vibrational transitions analyzed, the dissociation energies of $(CH_2F_2)_2$ and $(SO_2)_2$ resulted $2.7_9 \pm 0.3_2$ and $2.6_2 \pm 0.1_6$ kcal mol^{-1}, respectively.

5.2. Stationary points on the PES of $(CH_2F_2)_2$ and $(SO_2)_2$ complexes: DFT-D3 vs. CCSD(T)/CBS

DFT-D3 computations with all density functionals led to the identification of six and nine stationary points on the PES of difluoromethane and sulfur dioxide dimers, respectively, which are presented in Figure 3. The dissociation energies obtained in correspondence of these stationary points, at DFT/def2-TZVP, DFT-D3/def2-TZVP and CCSD(T)/CBS levels, are presented in Table 2, while the relative energies of the different conformers are given in Table S.1 of the Supplementary Information. Referring to the estimated CCSD(T)/CBS values, the interaction energies for the $(CH_2F_2)_2$ complex are in the range between -1.39 kcal mol^{-1} (Structure 1) and -3.07 kcal mol^{-1} (Structure 5), while for the $(SO_2)_2$ dimer they take values between the -0.99 and -2.85 kcal mol^{-1} for Structures 9 and 1, respectively. Concerning the relative energies, the different conformers are, in general, very close in energy. For $(CH_2F_2)_2$, structures 3, 4 and 6 are within 0.6 kcal mol^{-1} from the most stable conformer (Structure 5), and structures 2 and 6 are higher in energy by 1.1 and 1.7 kcal mol^{-1}, respectively. In the case of $(SO_2)_2$, there are 5 conformers within 0.8 kcal mol^{-1} from structure 1 which represents the minimum on the PES, and only structures 3, 4 and 9 much higher with relative energies in the range 1.4 - 2 kcal mol^{-1}.

First of all it is worth comparing DFT-D3 and uncorrected DFT interaction energies against the reference values from CCSD(T)/CBS correlated wavefunction calculations. For the purpose, Figures 4 (a) and (b) illustrates the mean absolute deviations (MADs) of DFT and DFT-D3 from CCSD(T)/CBS obtained over the six and nine different stationary points found for $(CH_2F_2)_2$ and $(SO_2)_2$, respectively, while Figure 4 (c) shows mean deviations (MDs) and MADs computed by considering jointly the 15 different complexes. Concerning the $(CH_2F_2)_2$ dimer, DFT-D3 slightly underbinds interaction energies, by about 0.4 kcal mol^{-1}, with B3LYP-D3 and PW6B95-D3 providing the best agreement to reference data (MAD around 0.3 kcal mol^{-1}). In the case of $(SO_2)_2$, TPSS, PBE0, TPSSh and PW6B95 slightly overbinds the interaction energy, by 0.3 kcal mol^{-1} at most, whereas the functional employing Lee-Yang-Parr correlation, deviate most, showing too strong binding by about 0.7 kcal mol^{-1}. By summarizing together the results obtained for the two complexes (see Figure 4c), the best performing functionals are PW6B95-D3 and PBE0-D3 with MADs of 0.30 and 0.39 kcal mol^{-1}, respectively, and an MD very close to zero, although sensible results are provided even by BLYP, that presents a larger MAD (0.57 kcal mol^{-1}). The relative deviations range, on average, from 2 to 40 % for PBE0-D3 and B3LYP-D3, although the latter value stems from the small interaction energy for Structure 9 of $(SO_2)_2$ leading to a large relative error. In passing it is noted that most of the uncorrected DFs yield no bonding for this conformer. Therefore, it is evident that DFT-D3 yields results in very good accordance with highly correlated wavefunction predictions. The Figure 4 clearly illustrates the poorer performances of uncorrected DFT, which underbinds by more than 1 kcal mol^{-1} on average, as a consequence of the missing dispersion interactions, and they clearly demonstrate the improvement provided by D3 corrections. It is worth noticing that only dispersion-uncorrected PW6B95 is able to provide satisfactory results (MAD $\approx$ 0.6 kcal mol^{-1}), but it also improves further when D3 dispersion correlations are introduced.

Furthermore, it is interesting that for the sulfur dioxide dimer, DFT and DFT-D3 respectively underbinds and overbinds, yielding similar MADs (~ 1 kcal mol^{-1}) if the BSSE is not corrected for. This apparent similar performance is the consequence of error compensation between the neglect of dispersion interactions and the additional stabilization energy arising from the BSSE, the two effects acting in opposite directions. When the CP corrections are introduced, DFT-D3 is closer to the CCSD(T)/CBS reference energies, while standard DFT experience a further worsening, thus highlighting again the physical grounds of the D3 scheme. In order to check the residual basis set effects, for TPSS and PW6B95 functionals as typical examples, CP-uncorrected single point calculations were carried out by using the huge def2-QZVP basis set. The differences with respect to CP-corrected dissociation energies obtained employing the def2-TZVP basis set are only around 0.14 kcal mol^{-1}, (6% of the interaction energy), and -0.25 kcal mol^{-1} in the worst case.

5.3 (CH_2F_2)$_2$ and (SO_2)$_2$ dissociation energies: experiment vs. theory

In the previous section, dissociation energies of $(CH_2F_2)_2$ and $(SO_2)_2$ computed at the DFT-D3 level were compared to CCSD(T)/CBS reference values, showing that DFT-D3 can reach an accuracy similar to that of highly correlated wavefunction methods, with MADs as low as 0.3 kcal mol^{-1}.

In comparing theoretical dissociation energies to the experiment, it should be considered that laboratory measurements are carried out at 294 K, and hence experimental determinations actually provide the Boltzmann average over the different structures available to the two dimers. Therefore, Table 3 compares experimental results against the Boltzmann average of theoretical energies computed at CCSD(T), DFT-D3 and DFT levels for the considered conformers, and the corresponding errors are illustrated in Figure 5 for both $(CH_2F_2)_2$ and $(SO_2)_2$ complexes. In computing the Boltzmann average of theoretical values, the weights being reported in Table S.2 for transition states are not considered. Furthermore because the PESs are very flat and the corresponding conformational motions are not relevant to the interpretation of the experimental data, the rather approximate transition states are only given for completeness and not discussed further.

Referring to Table 3 and Figure 5, it is observed that the CCSD(T)/CBS results are in perfect agreement with the experimental data, with negligible deviations for both dimers. Concerning the difluoromethane dimer, the TPSS-D3 functional and its hybrid form provide the worst predictions, with errors around 0.7 kcal mol^{-1}. With BLYP-D3 and PBE0-D3 the average error is reduced to 0.6 kcal mol^{-1}, and the best results are provided by B3LYP-D3 and PW6B95-D3 with deviations of only 0.4 and 0.3 kcal mol^{-1}, respectively. For the sulfur dioxide dimer, DFT-D3 energies agree even better to experiment, the largest deviations of -0.6 kcal mol^{-1} and -0.5 kcal mol^{-1} being given by B3LYP-D3 and BLYP-D3, respectively. The TPSSh-D3, PBE0-D3 and PW6B95-D3 functionals provide very good accuracy, reaching errors better than -0.2 kcal mol^{-1}. If not dispersion corrected, all the considered DFs yield poorer results, with errors up to 2.2 kcal mol^{-1} in the case of BLYP/def2-TZVP. The huge improvement brought by D3 corrections is clearly demonstrated in Figure 5.

At this point one may wonder whether the PS equation actually provides well depths, or it considers zero point contributions. For the purpose, zero-point vibrational energies (ZPVE) have been computed, within the harmonic approximation, at DFT-D3/def2-TZVP level. It is worthwhile to note that harmonic ZPVE actually provides an upper bound to the “true” energy at zero-point. The comparison of dissociation energies obtained experimentally against those computed by considering either the electronic energy (ΔE) only or, the energy at zero-point (ΔE^0) is given in Figure 6. With the exception of the $(SO_2)_2$ interaction energies computed by the BLYP and B3LYP functionals, in the remaining cases the inclusion of ZPVE worsens the agreement between theory and experiment (in particular for the difluoromethane dimer), thus indicating that the PS equation seemingly provides the well depth of an homodimer A_2.

5.4 ($(CH_2F_2)_2$) and ($(SO_2)_2$) geometries and rotational constants

Finally, for the most stable structures (i.e. structures 5 and 1 of difluoromethane and sulfur dioxide dimers, respectively) it is possible to compare geometries and rotational constants from DFT-D3 computations against the experimental counterparts obtained from MW experiments and available in the literature.[23,29] MADs and MDs from experimental values are illustrated in Figure 7 for bond lengths and angles, while the full list of geometrical parameters is reported in Tables S.3 and S.4 of the Supplementary Information. By considering jointly both complexes, statistics have been evaluated over 17 bond lengths (five inter-fragment distances) and 10 bond angles (four inter-fragment). Overall the best geometries are provided by PBE0-D3 and B3LYP-D3 and, to a lesser extent, PW6B95-D3, that show MADs <~ 2 pm and 2° for lengths and angles, respectively. For bond lengths, the worst predictions, but still in reasonable agreement to experimental values, are given by the TPSS-D3 and TPSSh-D3 functionals: the former predicts too large interfragment distances for $(CH_2F_2)_2$, by about 12 pm, the latter overestimates the center of mass separation between the SO_2 units by 23 pm. Concerning bond angles, it is worth noticing that BLYP-D3 and TPSSh-D3 present errors of about 10° in the angles describing the relative orientation of the SO_2 monomers within the dimer.

Statistics for rotational constants have been computed over *A*, *B* and *C* as MPE (Mean Percentage Errors) and MAPE (Mean Absolute Percentage Errors), and are reported in Figure 8 for the $(CH_2F_2)_2$ and $(SO_2)_2$ dimers, as well as by considering jointly both complexes. In general, the results for rotational constants mirror the findings obtained for geometry. For $(CH_2F_2)_2$, B3LYP-D3 and PBE0-D3 lead to MAPE around 1%, and in general all dispersion-corrected DFs yield deviations within 6%. Concerning the $(SO_2)_2$ dimer there is a poorer agreement, but B3LYP-D3, PBE0-D3 and PW6B95-D3 still provide the best rotational constants. This is well illustrated in Figure 7(c), reporting the overall results and showing that B3LYP-D3, PBE0-D3 and PW6B95-D3 provide MAPE <~ 4%, while the worst rotational constants result from TPSS-D3 and TPSSh-D3 as a consequence of their relatively high errors in the prediction of interfragment distances. Anyway, although it should be recalled that the computed rotational constants refer to equilibrium values, whereas the experimental results yielded ground state rotational constants, the agreement between experiment and theory can be considered very satisfactory. For a recent in depth discussion of the influence of dispersion corrections on molecular structures of medium-sized organic molecules in comparison to those obtained from rotational spectroscopy in the gas phase see Refs. 68,69.

6. Conclusions

This work dealt with a combined experimental and theoretical investigation of the difluoromethane and sulfur dioxide dimers by combining IR spectroscopy and density functional theory including atom pair-wise dispersion corrections (DFT-D3). In particular, the dissociation energies of the two homo-dimers have been determined from the foreign-broadening coefficients of the corresponding monomers perturbed by a range of atomic (He, Ne, Ar) and molecular (O_2, N_2) collision partners, by adopting the Parmenter-Seaver equation. The stationary points on the PES of $(CH_2F_2)_2$ and $(SO_2)_2$ have been investigated by DFT-D3, thus determining dissociation energies, equilibrium geometries and rotational constants. For the computations the BLYP, TPSS, B3LYP, PBE0, TPSSh and PW6B95 functionals have been employed in conjunction with the def2-TZVP basis set. According to a basis set study for two functionals, this basis set provides results to within about 5 % of the basis set limit interaction energy for the two investigated complexes. DFT-D3 dissociation energies have been benchmarked against accurate reference values, computed at the estimated CCSD(T)/CBS level. It has been shown that DFT-D3 nearly reaches the accuracy of highly correlated wavefunction methods (MAD ~ 0.4 kcal mol^{-1}). In agreement with previous experience it is found that the D3 corrections provide significantly improved interaction energies over standard DFT computations, that show MADs up to 1.9 kcal mol^{-1}.

Concerning the comparison between experiment and theory, theoretical dissociation energies at the CCSD(T)/CBS level have resulted a perfect agreement with those determined experimentally through the PS equation, with insignificant deviations. A very remarkable accord has also been obtained between experiment and DFT-D3 results, in particular by using the PW6B95 functional which yields deviations of only 0.3 kcal mol^{-1} and -0.2 kcal mol^{-1} for $(CH_2F_2)_2$ and $(SO_2)_2$, respectively, for thermally averaged dissociation energies. Conversely, standard (not dispersion corrected) DFT provide errors as large as 2.2 kcal mol^{-1}in the case of the BLYP functional.

In addition, theoretical geometries and rotational constants computed for the most stable structures of the two dimers have also resulted in good accord to the experimental counterparts determined through MW spectroscopy and available in the literature. In particular the dispersion-corrected hybrid functionals B3LYP and PBE0, as well as the meta-hybrid PW6B95, compute geometries with an accuracy better than 2 pm and 2° for distances and angles, and they have provide rotational constants with an MAPE lower than 3%.

Summarizing, it has been demonstrated that (i) pressure broadening parameters can be conveniently employed for determining the dissociation energies of homo-dimers with a relatively simple, non-expensive instrumental setup, and that (ii) the DFT-D3 approach can almost reach the accuracy of highly correlated wavefunction methods at the modest computational costs of DFT. All in all the outcomes of the work have shown that the interplay between experiment and theory can lead to important insights into the physical-chemistry of such molecular complexes.

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Figure Captions

Figure 1. CH_2F_2 ro-vibrational transitions between 1221.35 and 1221.70 cm^{-1} perturbed by noble gases and analyzed by means of the Voigt profile (grey circles: experimental spectrum; red line: calculated spectrum). The residuals (observed - calculated differences) reported in panels (a) - (c) refer to the broadening of about 157 Pa of CH_2F_2 perturbed by He (P_{He} = 1076 Pa), Ne (P_{Ne} = 1065 Pa) and Ar (P_{Ar} = 1532 Pa), respectively.

Figure 2. Collisional cross sections obtained for the $25_{14,12} \leftarrow 25_{15,11}$ transition of the ν_1 band of SO_2 perturbed by different buffer gases and their dependence on the dissociation energy of the damping gas dimer. The fitting procedure employed for retrieving the dissociation energy of $(SO_2)_2$ is also illustrated. The slope of the interpolating straight line is $T^{-1}(\varepsilon_{AA} / K_B)^{1/2}$.

Figure 3. Stationary points on the PES of (a) difluoromethane dimer and (b) sulfur dioxide dimer.

Figure 4. MADs of DFT-D3 and standard DFT from CCSD(T)/CBS reference dissociation energies for (a) $(CH_2F_2)_2$ and (b) $(SO_2)_2$ stationary points. (c) Overall MADs and MDs evaluated by considering the dissociation energies of the15 different structures obtained for $(CH_2F_2)_2$ and $(SO_2)_2$.

Figure 5. Deviation of theoretical dissociation energies (ΔE) at CCSD(T)/CBS, DFT-D3/def2-TZVP and DFT/def2-TZVP levels from experimental values for (a) difluoromethane dimer and (b) sulfur dioxide dimer.

Figure 6. Effect of ZPVE on the computed dissociation energies: deviation of theoretical ΔE^0 at CCSD(T)/CBS, DFT-D3/def2-TZVP and DFT/def2-TZVP level from experimental values for (a) difluoromethane dimer and (b) sulfur dioxide dimer.

Figure 7. Deviations from experimental values of theoretical bond distances (a) and angles (b) of $(CH_2F_2)_2$ and $(SO_2)_2$ dimers.

Figure 8. Deviations from experimental values of theoretical rotational constants of (a) difluoromethane dimer and (b) sulfur dioxide dimer, and (c) overall MPEs and MAPEs evaluated by considering the rotational constants of both $(CH_2F_2)_2$ and $(SO_2)_2$.

Table 1. Resonant frequencies (ν_0 / cm^{-1}) and foreign-broadening coefficients (γ^0 / cm^{-1}atm^{-1}) obtained for the ro-vibrational transitions of the CH_2F_2 ν_7 band and SO_2 ν_1 band.[a]

CH_2F_2 transition	ν_0	γ^0_{He}	γ^0_{Ne}	γ^0_{Ar}	$\gamma^0_{O_2}$ [c]	$\gamma^0_{N_2}$ [c]
$30_{9,21} \leftarrow 29_{8,21}$	$1221.3891_0(1_8)$	$0.0683_0(9_9)$	$0.0559_6(1_4)$	$0.0748_4(8_8)$	$0.072_3(4_2)$	$0.090_9(8_3)$
$25_{10,15} \leftarrow 24_{9,15}$	$1221.53120_6(8_6)$	$0.0762_5(5_5)$	$0.0511_1(5_0)$	$0.0724_4(9_9)$	$0.073_3(2_1)$	$0.090_8(7_2)$
$20_{11,9} \leftarrow 19_{10,9}$	$1221.64426_4(6_4)$	$0.0625_1(9_3)$	$0.0506_8(7_1)$	$0.0631_2(6_0)$	$0.071_4(2_5)$	$0.094_4(2_1)$

SO_2 transition	ν_0	γ^0_{He}	γ^0_{Ne}	γ^0_{Ar}	$\gamma^0_{O_2}$	$\gamma^0_{N_2}$
$26_{14,12} \leftarrow 26_{15,11}$	$1102.7893_2(1_3)$	$0.063_8(1_9)$	$0.053_7(1_4)$	$0.064_0(3_1)$	$0.070_2(1_2)$	$0.093_4(3_2)$
$29_{8,22} \leftarrow 30_{9,21}$	$1102.56123_6(3_5)$	$0.0733(1_0)$	$0.0553_8(3_8)$	$0.0657_9(4_9)$	$0.072_2(1_1)$	$0.096_5(2_0)$
$25_{14,12} \leftarrow 25_{15,11}$	$1102.57417_4(6_8)$	$0.067_1(1_9)$	$0.059_3(1_7)$	$0.065_7(1_3)$	$0.0802_6(9_8)$	$0.092_7(2_4)$
$15_{11,5} \leftarrow 16_{12,4}$	$1102.61642_6(6_3)$	$0.0701_7(7_0)$	$0.0619_6(3_2)$	$0.073_8(1_2)$	$0.078_3(1_1)$	$0.102_6(1_9)$
$24_{14,10} \leftarrow 24_{15,9}$	$1102.65607_8(8_6)$	$0.071_8(1_6)$	$0.059_4(1_9)$	$0.072_2(1_1)$	$0.0839_6(2_8)$	$0.111_7(1_7)$
$23_{14,10} \leftarrow 23_{15,9}$	$1102.73502_4(9_9)$	$0.062_4(1_6)$	$0.050_3(1_3)$	$0.068_7(1_0)$	$0.075_7(1_4)$	$0.091_5(4_6)$

[a] Figures in parentheses are uncertainties in the units of the last significant digits.

[c] From Ref. [48].

Table 2. Dissociation energies (kcal mol^{-1}) at the stationary points on the PES of $(CH_2F_2)_2$ and $(SO_2)_2$ at CCSD(T)/CBS, DFT-D3/def2-TZVP and DFT/def2-TZVP levels of theory.

$(CH_2F_2)_2$	CCSD(T)/CBS	BLYP-D3	TPSS-D3	B3LYP-D3	PBE0-D3	TPSSh-D3	PW6B95-D3	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95
Struct1	-1.39	-1.08	-1.13	-1.18	-1.17	-1.10	-1.19	-0.59	-0.79	-0.75	-0.88	-0.78	-1.00
Struct2	-1.98	-1.68	-1.73	-1.78	-1.74	-1.65	-1.78	-0.69	-1.06	-0.91	-1.19	-1.04	-1.43
Struct3	-2.71	-2.09	-2.01	-2.28	-2.13	-1.99	-2.41	-0.65	-1.08	-1.04	-1.38	-1.05	-1.95
Struct4	-2.57	-2.18	-2.04	-2.28	-2.12	-1.99	-2.20	-0.98	-1.25	-1.20	-1.46	-1.19	-1.79
Struct5	-3.07	-2.39	-2.28	-2.57	-2.40	-2.24	-2.77	-0.75	-1.23	-1.15	-1.56	-1.19	-2.26
Struct6	-2.48	-2.10	-1.97	-2.19	-2.04	-1.90	-2.15	-0.87	-1.17	-1.14	-1.40	-1.12	-1.75

$(SO_2)_2$	CCSD(T)/CBS	BLYP-D3	TPSS-D3	B3LYP-D3	PBE0-D3	TPSSh-D3	PW6B95-D3	BLYP	TPSS	B3LYP	PBE0	TPSSh	PW6B95
Struct1	-2.85	-3.40	-2.75	-3.55	-3.05	-3.10	-3.17	-0.52	-1.01	-1.13	-1.74	-0.70	-2.24
Struct2	-2.44	-2.97	-2.38	-3.10	-2.59	-2.57	-2.59	0.05	-0.53	-0.54	-1.14	-0.28	-1.59
Struct3	-1.16	-1.89	-1.64	-1.83	-1.63	-1.52	-1.61	-0.03	-0.50	-0.27	-0.72	-0.38	-0.94
Struct4	-1.45	-2.36	-2.02	-2.33	-2.07	-1.94	-2.06	-0.43	-0.83	-0.71	-1.13	-0.73	-1.38
Struct5	-2.19	-2.46	-2.00	-2.58	-2.23	-2.11	-2.33	-0.34	-0.71	-0.78	-1.23	-0.58	-1.62
Struct6	-2.71	-3.09	-2.48	-3.27	-2.78	-2.71	-2.73	-0.34	-0.81	-0.94	-1.50	-0.63	-1.85
Struct7	-2.26	-3.04	-2.52	-3.10	-2.68	-2.67	-2.49	-0.17	-0.72	-0.69	-1.35	-0.56	-1.55
Struct8	-2.08	-2.97	-2.49	-2.96	-2.61	-2.60	-2.40	-0.53	-0.95	-0.93	-1.47	-0.78	-1.59
Struct9	-0.99	-1.81	-1.48	-1.83	-1.50	-1.34	-1.69	0.96	0.20	0.54	-0.18	0.35	-0.77
MD [a]	-	-0.23	0.09	-0.30	-0.03	0.06	-0.08	1.76	1.33	1.38	0.93	1.44	0.57
MAD [b]	-	0.58	0.39	0.55	0.37	0.39	0.31	1.76	1.33	1.38	0.93	1.44	0.57

[a] Mean deviation computed from CCSD(T)/CBS reference data computed over the 15 structures obtained for the two dimers.

[b] Mean absolute deviation from CCSD(T)/CBS reference data computed over the 15 structures obtained for the two dimers.

Table 3. Comparison of experimental and theoretical dissociation energies (kcal mol^{-1}) obtained for $(CH_2F_2)_2$ and $(SO_2)_2$ dimers.[a]

	ΔE $(CH_2F_2)_2$	ΔE $(SO_2)_2$
Experiment	2.79	2.62
CCSD(T)/CBS	2.80	2.60
BLYP-D3	2.18	3.14
TPSS-D3	2.08	2.55
B3LYP-D3	2.34	3.27
PBE0-D3	2.18	2.80
TPSSh-D3	2.04	2.80
PW6B95-D3	2.49	2.62
BLYP	0.80	0.39
TPSS	1.17	0.85
B3LYP	1.09	0.92
PBE0	1.43	1.50
TPSSh	1.13	0.63
PW6B95	2.00	1.90

[a] DFT computations carried out by using the def2-TZVP basis set.