

***Ab initio* studies of internal rotation barriers and vibrational frequencies of $(C_2H_2)_2$, $(CO_2)_2$, and $C_2H_2-CO_2$**

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Abstract. We have performed large-scale *ab initio* calculations using second order Møller–Plesset perturbation theory (MP2) on the three van der Waals dimers formed from acetylene and carbon dioxide. Intermolecular geometrical parameters are reliably computed at this level of theory. Calculations of vibrational frequencies of the van der Waals modes, currently unobtainable by experimental means, give important information about the intermolecular potential and predict significant large-amplitude motion. Zero point energy contributions are shown to be vital in assessing the relative stability of conformations which are close in energy. Our studies suggest that the barrier to interconversion tunnelling in $(CO_2)_2$ is significantly smaller than previously inferred and is approximately the same as in $(C_2H_2)_2$. The reason for the rigidity of $(CO_2)_2$ is the difference in monomer centre-of-mass separation between ground state and transition state. We also show that, in addition to the previously observed C_{2v} form, the collinear form of $C_2H_2-CO_2$ is a local minimum on its potential energy surface.

Key words: Van der Waals dimers – Vibrational frequencies

1. Introduction

Ab initio methods have, to date, been successfully tailored to describe favourable conformations of a variety of small van der Waals dimers [1]. The most important consideration in the studies of these species is the nature of the binding forces between the constituent monomers. The dominant forces involved depend on monomer properties and dictate the most appropriate levels of calculation. The now well-established view of van der Waals systems [2–4] is that the conformations at stationary points on their potential energy surfaces are determined by electrostatic forces, where present, expressed, using the multipole expansion, as a power series of interactions between charge moments of increasing order. Induction and dispersion forces, which may be related to the electric polarizabilities of the monomers, have a secondary influence in structure determination, but contribute to the binding energy.

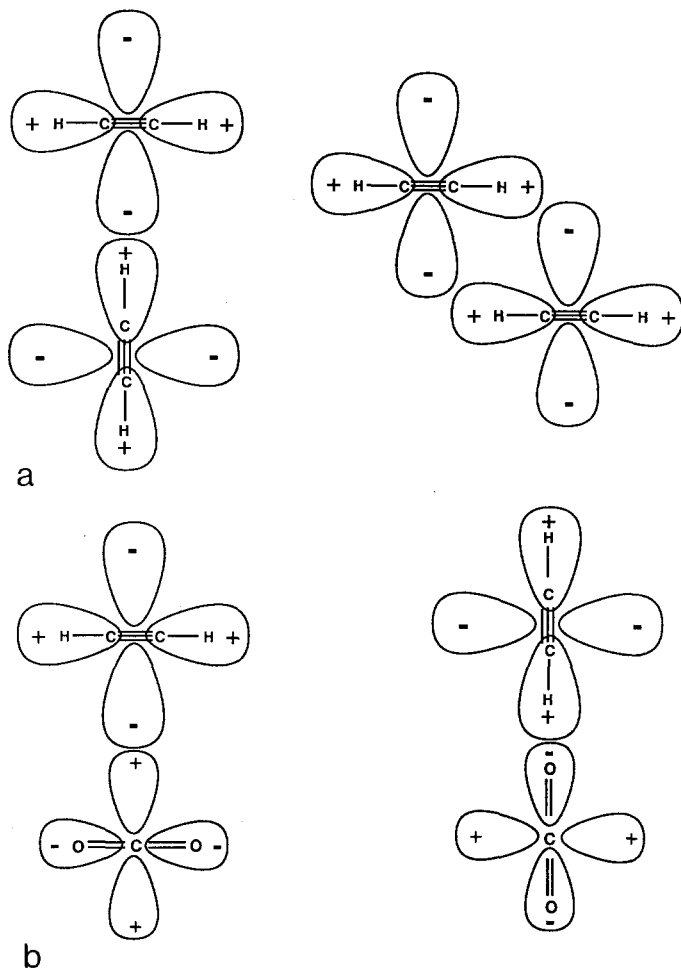


Fig. 1. Spherical harmonic representation of quadrupole-quadrupole interactions in **a** acetylene dimer; **b** acetylene-carbon dioxide dimer

In this study the van der Waals dimers of two non-dipolar monomers, acetylene and carbon dioxide, whose lowest order non-vanishing multipole moment is the quadrupole are examined. The most influential term in the electrostatic interaction energy between these molecules is quadrupole-quadrupole. Favourable planar configurations of two interacting identical quadrupoles [4, 5] are loosely described as "perpendicular" (C_{2v}) and "slipped parallel" (C_{2h}) (Fig. 1a). These conformations are pertinent to the discussions of the homodimers (C_2H_2)₂ and (CO_2)₂. If, however, the quadrupole moments are of opposite sign as is the case for the C_2H_2 - CO_2 dimer, the predicted stationary points on the potential energy surface are parallel or collinear (Fig. 1b). The influences of dispersion forces on the preference of one structure over another for each of these dimers and on their van der Waals vibrational modes are also assessed. These modes are important because they give a qualitative description of the curvature of the intermolecular potential energy surface. Induction forces and charge transfer are not important in the bonding of these species.

Important quantities to be obtained from similar calculations on van der Waals systems include the barrier height between conformations of similar energy but different geometry, shifts in monomer vibrational frequencies induced by complex formation, and the intermolecular frequencies which are difficult to determine experimentally. (Nesbitt and Namaan have pointed out [6] that rigid molecule parameters may fit a spectrum very well even though the observed species are undergoing high amplitude motion derived from their van der Waals vibrational modes.) It is also important to characterize stationary points as either true minima or transition states, which are not directly observable, but may mediate observable tunnelling between structures.

In earlier work on van der Waal clusters of acetylene and ethylene [7] and other clusters [8] it has been shown that the MP2 method (second order Møller–Plesset perturbation theory) of accounting for intermolecular electron correlation (dispersion forces) [9] resulted in substantial improvement over the Hartree–Fock method. In this paper we show that even in a simple weakly bound system such as the $(\text{CO}_2)_2$ the SCF method can be qualitatively wrong in its predictions of the minimum energy structure. Further, in order to obtain a meaningful SCF result very large basis sets are needed to overcome the basis set superposition error, and accurate zero point energy corrections are required for predicting the most stable form of such weakly bound species and computing energy barriers.

Our studies have been motivated by recent interest in interconversion tunnelling of many homomolecular van der Waals dimers [10–12], which complicates the interpretation of a spectrum. The energetic difference between the C_{2v} and C_{2h} forms of $(\text{C}_2\text{H}_2)_2$ and $(\text{CO}_2)_2$ is very small and both were thought to exist in either form although the minima are now firmly established to be C_{2v} for the acetylene dimer [13, 14] and C_{2h} for the carbon dioxide dimer [15, 16]. The acetylene dimer exhibits internal rotation using both conformations as stationary points [13, 14, 17] whereas $(\text{CO}_2)_2$ appears not to [16]. With the advent of high resolution spectroscopy of cooled species in molecular beams [18, 19] structural ambiguities may often be resolved by experiments. Thus the *ab initio* calculations are required to probe the details of quantitative uncertainty which will still haunt the spectroscopist.

We present a better estimate of the energy barrier for the interconversion tunnelling coordinate of the acetylene dimer and a discussion of the variation in its molecular frequencies at different levels of theory and on isotopic substitution. We show that $(\text{CO}_2)_2$ in fact has a small barrier to internal rotation suggesting that interconversion may in principle be possible. Finally we look at the recently observed dimer, acetylene-carbon dioxide [20–22], to obtain a fair estimate (including the effect of correlation) of the barrier to out-of-plane torsional rotation and to demonstrate that the collinear form may also be an observable conformation. These are the largest calculations yet performed on all these systems and are at the limit of current computational capabilities with this level of theory.

2. Computational details

Most *ab initio* “supermolecule” methods are plagued by a fortuitous cancellation of errors [1], though judicious choice of basis set and level of theory can minimize the inherent uncertainties due to this. We performed calculations at

both SCF and MP2 levels using the suite of programmes in CADPAC [23]. All orbitals were active in these calculations. The MP2 method [9] is the most convenient way to include electron correlation. Although we accept that, being an uncoupled method and involving a truncated Taylor expansion, MP2 overestimates the true dispersion energy, earlier large-scale calculations at this level on Ar-H_3^+ [8], where dispersion forces are even more important than in the systems studied here, demonstrate its validity by comparison with results obtained by CISD and CPF calculations on the same complex.

Of the undesirable features of an *ab initio* calculation, the most serious is the basis set superposition error (BSSE) [24]. This arises from deficiencies in the monomer basis set and argues for the use of the largest set possible. The standard Dunning and Huzinaga DZP basis set [25, 26] which has *d*-functions ($\zeta = 0.8$) on carbon and *p*-functions ($\zeta = 1.0$) on hydrogen were used (hence 42 basis functions for acetylene and 48 for carbon dioxide) for routine initial investigations and calculations of frequencies. The largest calculations of reliable energy barriers used the TZ2P basis set [26, 27], which has (*3s2p*) on hydrogen and (*5s4p2d*) on first row atoms (hence 76 basis functions for acetylene and 87 for carbon dioxide). (That this set is reasonable is discussed by Grev and Schaefer [28].) It is still necessary to include BSSE corrections. The full counterpoise method of Boys and Bernardi [29], which has been justified by the studies of Gutowski et al. [30], was used. The BSSEs found in this manner are very large, and for MP2 are often around half the binding energy even with basis sets as large as DZP. The additional computer time required by the counterpoise method is much smaller than the time required for either the geometry optimization stage or the second derivative calculation. In this work we present binding energies both before and after BSSE correction to demonstrate upper and lower limits on the well depth. Methods which involve optimizing BSSE-corrected energies are far too cumbersome to be worthwhile at present.

All geometries were fully optimized (in internal coordinates) at each level of calculation, the only constraint being that of symmetry. Our procedure included optimization of the intramolecular bond lengths and angles, since the "frozen monomer optimization" method, in which intramolecular parameters are kept constant at the isolated monomer values, made the determination of stationary points more difficult. In addition the non-zero rotational frequencies obtained in a second derivative calculation on a system optimized in this manner indicate that such constraints represent insufficient flexibility in the calculation. This is despite the fact that on complex formation, bond angles are typically changed by $<0.5^\circ$ and bond lengths by $\approx 0.001 \text{ \AA}$ relative to monomer equilibrium values at the same level of theory. Cartesian energy derivatives with respect to nuclear displacements of less than 10^{-4} hartrees/bohr at optimized geometries were deemed to be sufficient to define the location of a true stationary point.

Due to disc space requirements, DZP was the largest basis set for which it was possible to calculate MP2 harmonic frequencies by analytic derivative methods for these dimers. However, our assessment of changes in the intermolecular geometric parameters with increasing basis set size suggests that the greatest change in van der Waals frequencies occurs when correlation is included, so discussions of, say, zero point energy corrections calculated with a smaller basis set than used to obtain the final energy is reasonable.

Calculations were performed on the University of Cambridge Theoretical Chemistry Department Convex C-210 computer and on the CRAY-XMPs at the University of London and the Rutherford Laboratory.

3. Monomers

Although *ab initio* methods treat the system as a “supermolecule” and monomer properties are not explicitly handled, we can be sure that they have the most significant influence on the intermolecular potential. In large-scale calculations on small systems where subtle features are examined, it is necessary to use basis sets which describe the pertinent properties of the monomers well. An example of the importance of this is the MP2 description of N₂O–HF [31]. Here the minimum energy structure from correlated *ab initio* work is with N₂O bonding to HF in the opposite sense to that observed [32]. This is now understood to be because the MP2 calculated dipole moment of N₂O is of the wrong sign (the dipole moment is small anyway and the MP2 correction has an overcompensatory effect on the SCF description); yet it is the dipole moment which is most important in a consideration of the interaction potential of this complex.

For our systems we need to model the quadrupole moments, Θ , well. Some theoretical values of Θ_{zz} are shown in Table 1 for acetylene and carbon dioxide. Values quoted are at geometries optimized at each level of theory. (MP2 (TZ2P) intramolecular bond lengths are within 0.005 Å and 0.007 Å of the experimental values (R_e) for acetylene and carbon dioxide, respectively.) With the exception of STO3G and the SCF level, most of the values of Θ for acetylene fall within a close range, suggesting that, at least with regard to quadrupole moment, choice of basis set is not critical. Unfortunately experimental values are uncertain and very technique-dependent. They range from 4.2 to 8.4×10^{-26} esu [5], the former obtained from the pressure second virial coefficient, the latter from measurement of magnetizability anisotropy. The *ab initio* values all lie within this range. The most recent experimental value is 7.6×10^{-26} esu [33]. The best theoretical calculations (at the SCF level, close to the Hartree–Fock limit) give 7.3×10^{-26} esu [34]. We believe that the MP2 values for DZP and TZ2P basis sets, 6.9 and 6.5×10^{-26} esu (Table 1) respectively are sufficiently close to the experimental and best theoretical values to justify the level of theory used in this work. For carbon dioxide the agreement at MP2 (DZP and TZ2P) with

Table 1. Quadrupole moments $\Theta_{zz}/10^{-26}$ esu (electrostatic units^a) of the monomers at various levels of calculation. The quadrupole moment, Θ , is traceless ($\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$; $= \Theta$ for a linear molecule). By symmetry, for an axially symmetric molecule aligned along the z -axis, $\Theta_{xx} = \Theta_{yy} = -(1/2)\Theta_{zz}$. Tabulated are values of Θ_{zz}

Method	Basis set	Acetylene	Carbon dioxide
SCF	STO3G	4.1	-5.2
SCF	3-21G	6.6	-7.1
SCF	4-31G	6.3	-7.3
SCF	6-31G*	6.7	-5.5
SCF	DZP	7.4	-5.4
SCF	TZ2P	7.1	-5.2
MP2	6-31G*	6.3	-3.2
MP2	DZP	6.9	-4.3
MP2	TZ2P	6.5	-4.2

^a 1.345×10^{-26} esu = 4.48×10^{-40} cm²
= 1 au.

experimental values of -4.3 to -4.57×10^{-26} esu [5] is certainly good enough to give us confidence in our choice of basis. All the SCF values are overestimates, a further reason to justify the use of MP2.

A property of secondary importance for these monomers is the static polarizability, α , which influences structural parameters primarily through induction forces. The leading term in the perturbation theory expansion of the induction forces between two non-dipolar species is the quadrupole-induced-quadrupole term, which varies as α/R^8 [5] and so is less significant for determining the binding energy than the electrostatic or dispersion forces. The importance of inductive effects is readily assessed by consideration of the larger clusters of these monomers. Induction forces are known to introduce non-additive effects in the trimers of dipolar molecules $(\text{HF})_3$ and $(\text{HCl})_3$ [35], for example, where linear configurations have enhanced stability relative to cyclic configurations, however, $(\text{CO}_2)_3$ [36] and $(\text{C}_2\text{H}_2)_3$ [37, 38] are known to be cyclic. Our *ab initio* work has confirmed that all "open" configurations of acetylene trimer are much less stable than the cyclic form [39]. Further, $(\text{C}_2\text{H}_2)_4$ is a ring structure [40] and again *ab initio* studies [41] agree with this and show that the energies of the tetramer and larger clusters are, to all intents and purposes, additive, and that intermolecular geometric parameters are transferable between them. However it has been shown [42] that induction forces have a significant influence on the dipole moment of a complex. Values of α for both carbon dioxide and acetylene at all our levels of theory (Table 2) show consistently that α_{zz} is closer to the corresponding experimental value [43, 44] than α_{xx} ($=\alpha_{yy}$). (α_{xx} is in better agreement with experiment for carbon dioxide because it is a less extended molecule.) The inaccuracies are because there are insufficient diffuse functions in our basis set to describe α correctly. Addition of even a single shell of polarization functions on each atom at TZ2P level would make the basis sets too large to handle at the present time. (In fact we have found that the smallest basis set required to give MP2 polarizabilities in good agreement with experiment in both α_{zz} and α_{xx} is TZ2P with a *d*-shell on C and a *p*-shell on H which yields 94 basis functions in all for acetylene.) However, we believe that this omission is not of great significance for reasons discussed above. We believe that diffuse functions have a greater effect on the descriptions of hydrogen-bonded systems, see for example [43]. Therefore we expect our inadequate description of α to manifest itself in calculated dipole moments of structures in which the monomers are side on to one another.

Table 2. Static polarizabilities (a.u.) of the monomers at various levels of calculation

Method	Basis set	Acetylene		Carbon dioxide	
		α_{xx}	α_{zz}	α_{xx}	α_{zz}
SCF	DZP	8.8	29.3	7.5	21.1
MP2	DZP	8.7	28.2	8.2	25.9
MP2	TZ2P	12.6	29.5	10.6	27.2
Experimental ^a		19.4	32.0	13.0	27.1
Experimental ^b		18.8	30.6	13.3	26.4

^a From [43]

^b From [44]

The dispersion forces are related to the frequency-dependent polarizability [4]. Visser and Wormer [46] show that large basis sets with diffuse polarization functions are required to calculate these quantities accurately. We therefore expect them to be described as well or as poorly as the static polarizabilities, i.e. underestimated. However, in the limit of a complete basis, the MP2 method slightly overestimates the C_6 -term in the dispersion energy because it does not allow for relaxation of monomer wavefunctions in the presence of the other monomer. Therefore we expect there an approximate cancellation of errors. The alternative possibility that the omission of polarization functions might be cancelled out by the BSSE and that therefore the counterpoise correction need not be employed has been discussed [1]. However, since BSSE has an erratic dependence on monomer orientation and addition of polarization functions need not lead to greater estimation of the interaction energy [47], this is unreliable. Besides, in these studies, a more-or-less systematic error in the estimation of the isotropic C_6 -term is acceptable, since our concern is with relative energies.

4. Results

4.1. Acetylene dimer

Much experimental and theoretical work on the acetylene may be found in the literature. The most recent experiments (see below) indicate the need for more accurate calculations. Before discussing our calculations, the best experimental and theoretical data are presented.

The full infrared spectrum of a molecular beam of acetylene has six bands in the C–H stretching region, 3250–3300 cm^{-1} . These are attributable to clusters ranging from the monomer to the pentamer [38]. Early experimental work on four of the bands, which were identified as perturbed monomer stretches in the dimer, was able to definitively assign dimer rotational constants, though not establish whether the slipped parallel dimer (C_{2h} symmetry) or the T-shaped form (C_{2v} symmetry) [38, 48, 49] was adopted. Prichard et al. [50] measured both microwave and infrared spectra, thus indicating that the C_{2h} structure (which would have no dipole moment) was not adopted. These workers suggested the structure was “slipped T” conformation, in which the monomers were not quite perpendicular. The matter was finally successfully resolved in two independent publications: Ohshima et al. [13] studied the infrared band at 730 cm^{-1} and interpreted the rotational fine structure as belonging to a T-shaped dimer undergoing interconversion tunnelling between the four geometrically equivalent configurations; an effect which leads to splittings of the spectral lines. The more comprehensive infrared and microwave studies of Fraser et al. [14] enabled assignment of lines to rotation-inversion transitions involving the tunnelling states, in addition to pure rotational transitions. Fraser subsequently described vibrational exchange between the monomers at the transition state using this mechanism [17].

The earliest theoretical work on this system, by Sakai et al. [51], used a model intermolecular potential which assumed values for the intermolecular geometric parameters. This led to the prediction that the slipped-parallel form would be the minimum energy conformation. The first *ab initio* calculations, which require no parameters, by Aoyama et al. [52] were at the 6-31G level with no correlated treatment and no frequency analysis. They deduced that the

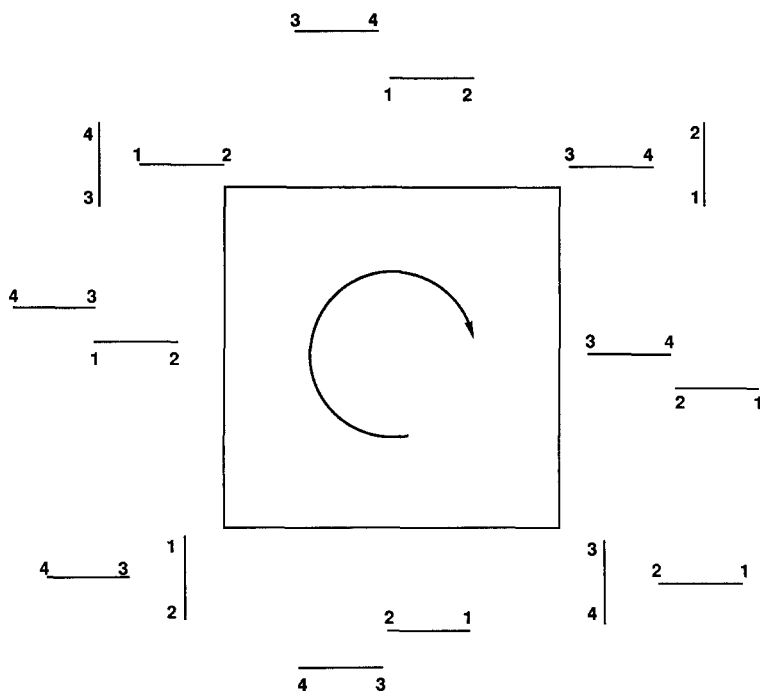


Fig. 2. Representation of interconversion tunnelling scheme in acetylene dimer. C_{2h} transition states on edges of square and C_{2v} minima at vertices

T-shaped form would be the lowest in energy. Alberts et al. [7] performed correlated calculations on the C_{2v} and C_{2h} structures (Fig. 2) using DZP basis set at both SCF and MP2 levels. Qualitative agreement between the two levels of theory was obtained. Both the C_{2h} and C_{2v} structures were identified as stationary points on the potential energy surface with the C_{2v} structure marginally the lower in energy, see Table 5a. More importantly the use of analytic second derivatives at both levels shows that the C_{2h} structure is the transition state on an intermolecular vibrational coordinate. However their estimate of the energy barrier [7] between these forms, 76 cm^{-1} , was seriously in error because of an incorrect choice of BSSE correction and an insufficient basis set. This in turn did not allow a valid assessment of zero point energy effects. Craw et al. [53] have performed calculations on both the important configurations of the acetylene dimer at the SCF level with STO/4-31G basis set. They obtain qualitative agreement in energetic ordering with those at the higher level but they omit dispersion effects.

In short, the acetylene dimer is now viewed as a “cat-and-mouse” type system in which the monomers rotate around each other accessing in a stepwise fashion all four permutations of the T-forms, as shown schematically in Fig. 2. This internal motion is the extension of the “geared” in-plane van der Waals mode (B_2), and correlates with motion along the B_u mode of the transition state (see Fig. 4). Each vibrational wavefunction can access two neighbouring wells by tunnelling through the equivalent barriers on either side of it.

The Longuet-Higgins group theoretical analysis of non-rigid molecules, which uses only "feasible" permutation and permutation-inversion operations, has been applied to the acetylene dimer [54, 55]. Thus the acetylene dimer is described by a molecular symmetry group G_{16} which is isomorphic to D_{4h} , the point group of a square, in accord with the representation of the interconversion in Fig. 2. Fraser et al. [14] estimated a barrier height, V , for the tunnelling process, of 33.2 cm^{-1} from the observed splittings of 0.07 cm^{-1} in microwave data. V is the energy difference between the C_{2v} and C_{2h} forms. Their procedure was to model the tunnelling coordinate by a single (internal rotation) angle, α . The hindering potential is then a simple function of this coordinate alone: $V(1 - \cos 4\alpha)/2$ with the T-shaped structures as minima at $\alpha = 0, \pi/2, \pi, 3\pi/2$, and the parallel forms as maxima at $\alpha = \pi/4, 3\pi/4, 5\pi/4, 7\pi/4$. They have shown that, according to this model, the resulting tunnelling splitting is very sensitively dependent on the value of V .

In the light of these experimental studies [14, 17] we feel it important to get a better estimate of the barrier between the two structures, and to study the basis set dependence of the result. At all levels of calculation the C_{2v} structure lies lower in energy than the C_{2h} . The energy barriers are not a reliable parameter for comparison and analysis of basis sets because of the different factors contributing to them. Instead we use the centre-of-mass to centre-of-mass distance, R , and the intermolecular vibrational frequencies. (R varies with basis set or level of theory to a far greater extent than any intramolecular bond lengths.)

The first important observation is that R gets shorter at the MP2 level, where dispersion forces are included, relative to the SCF level for each basis set, so the dispersion forces have deepened and contracted the potential well along the intermolecular stretching coordinate. From the quadrupole-quadrupole formula expressed as $3\Theta^2 f(\theta_a, \theta_b, \phi)/4R^5$ [5], where Θ is the quadrupole moment for each monomer and $f(\theta_a, \theta_b, \phi)$ is the angular dependence, the energy is $-3\Theta^2/R^5$ for perpendicular and $-39\Theta^2/16R^5$ for slipped-parallel conformations, showing that for constant R and when electrostatics dominate, the perpendicular structure is always favoured. The dispersion forces will only tip the balance between these two forms if the centre-of-mass to centre-of-mass distance, R , can be significantly different in the two structures. This distance is largely determined by the repulsive wall at each atom, i.e. the short-range repulsion. However, for acetylene, the van der Waals radii and intramolecular bond lengths ensure more-or-less constant R for both at any given level of theory. Dispersion forces typically vary at least as R^{-6} (cf. R^{-5} for quadrupole-quadrupole interactions) and their dominant term is isotropic and this since R is much the same for C_{2h} and C_{2v} , do not alter this picture significantly. This is why SCF is a fair starting point for qualitative information such as the relative energy of configurations of any acetylenic van der Waals cluster [39, 41].

In a true hydrogen-bonding situation, we would expect the C_{2v} intermolecular distance to be noticeably shorter than that in the C_{2h} one because the bonding hydrogen would be attracted by the high electron density region of the $C\equiv C$ bonds. As noted by Fraser et al. [14], the distance of the hydrogen- π -bond separation in this system ($\approx 2.7\text{ \AA}$) is much longer than that found in true hydrogen-bonding systems involving acetylene, either acting as a proton acceptor or a proton donor. Therefore, although the acetylene dimer conforms to Millen and Legon's hydrogen-bonding rules [56], the energetic favouring of the C_{2v} over the C_{2h} form may be explained purely by the electrostatic quadrupole-quadrupole interaction formula without need to invoke the short-range attractive forces

commonly used to explain the stability of hydrogen-bonded configurations [57].

We note also that the variation in R with increasing basis size is more gradual at the MP2 than at the SCF level. At either level the progression from 6-31G* to DZP in the C_{2h} form contains the sharpest jump. This is attributed to the lack of polarization functions on hydrogen in the 6-31G* basis, which means that the effective radius of the hydrogen is reduced. The 6-31G* is the least well-balanced of the three basis sets under consideration. At the MP2 level, the trend in R for the T-shaped geometry follows the trend in size of Θ so that the largest Θ gives the smallest R .

Frisch et al. in their studies of hydrogen-bonded dimers of first row hydrides [47] observed a lengthening of internal bond parameters with increasing numbers of polarization functions. We observe this consistently at the SCF level for both the C_{2v} and C_{2h} forms, where the divergence from the experimental quantity gets greater with a larger basis set. It is interesting that this effect is occurring for non-dipolar species too. However, in the absence of diffuse polarization functions, these results suggest that, at the MP2 level, R is fairly stable for this system. The MP2 (TZ2P) is the best description currently available. The full set of optimized geometric parameters at this level are presented in Fig. 3. The intermolecular hydrogen-bond length in the C_{2v} form is 2.677 Å at this level, agreeing well with the experimental value, which includes contributions from zero point amplitudes, of 2.743 Å [14]. So it is to be expected that our R value is slightly shorter than the experimental one. The rotational constants are 35226, 1945 and 1843 MHz to be compared with experimental values [14] of 35188, 1914 and 1799 MHz. The dipole moment is 0.300 D, which is similarly in close agreement with the experimental 0.280 D [50].

We turn now to a discussion of the four intermolecular frequencies at different levels of calculation (Table 4). These were all calculated at the ge-

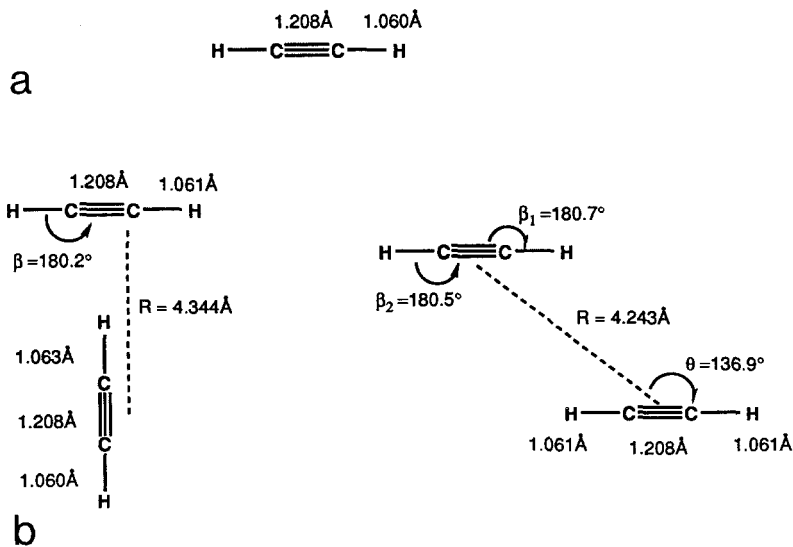


Fig. 3. Geometric parameters and optimized geometries of **a** isolated acetylene monomer; **b** acetylene dimer at the MP2 (TZ2P) level

Table 3. Geometrical parameters (see Fig. 3) of the global minimum (C_{2v}) and transition state (C_{2h}) of acetylene dimer at SCF and MP2 levels with a range of basis sets

Parameter	SCF			MP2		
	6-31G*	DZP	TZ2P	6-31G*	DZP	TZ2P
C _{2v}						
R/Å	4.616	4.664	4.727	4.216	4.309	4.344
β/°	180.4	180.3	180.3	180.1	180.2	180.2
C _{2h}						
R/Å	4.403	4.582	4.650	4.204	4.318	4.243
θ/°	136.2	138.1	136.5	137.1	139.6	136.9
β ₁ /°	180.6	180.0	180.2	181.4	179.7	180.7
β ₂ /°	180.4	180.2	180.2	181.1	180.0	180.5

Table 4. (a) Intermolecular frequencies (cm⁻¹) of global minimum (C_{2v}) of the acetylene dimer at SCF and MP2 levels with a range of basis sets. (Symmetry labels assume that the molecule is the yz-plane.) Descriptions of normal modes refer to motions depicted in Fig. 4a

Mode	SCF			MP2	
	6-31G*	DZP ^a	TZ2P	6-31G*	DZP
“Geared” (B ₂)	31	18	22	49	22
Stretch (A ₁)	57	50	45	87	81
Out of plane (B ₁)	58	54	50	83	66
“Anti-geared” (B ₂)	105	96	92	107	106

(b) Intermolecular frequencies (cm⁻¹) of global minimum (C_{2h}) of the acetylene dimer at SCF and MP2 levels with a range of basis sets. See Fig. 4b for a representation of the normal modes

Mode	SCF			MP2	
	6-31G*	DZP ^a	TZ2P	6-31G*	DZP
“Geared” (B _u)	30i	18i	20i	36i	29i
Out of plane (A _u)	47	45	40	49	46
Stretch (A _g)	49	43	36	54	51
“Anti-geared” (A _g)	112	98	86	130	122

^a See [7]

ometries optimized at the appropriate level of theory; rotational frequencies at the MP2 (DZP) level were less than 1 cm⁻¹ before application of a projection operator to the force constant matrix. The vibrations associated with each frequency are shown in Fig. 4.

For the C_{2v} structure, a comparison of the DZP values at MP2 and SCF level shows that the inclusion of correlation affects different modes to different extents. The surface curvature along the “geared” and out-of-plane normal

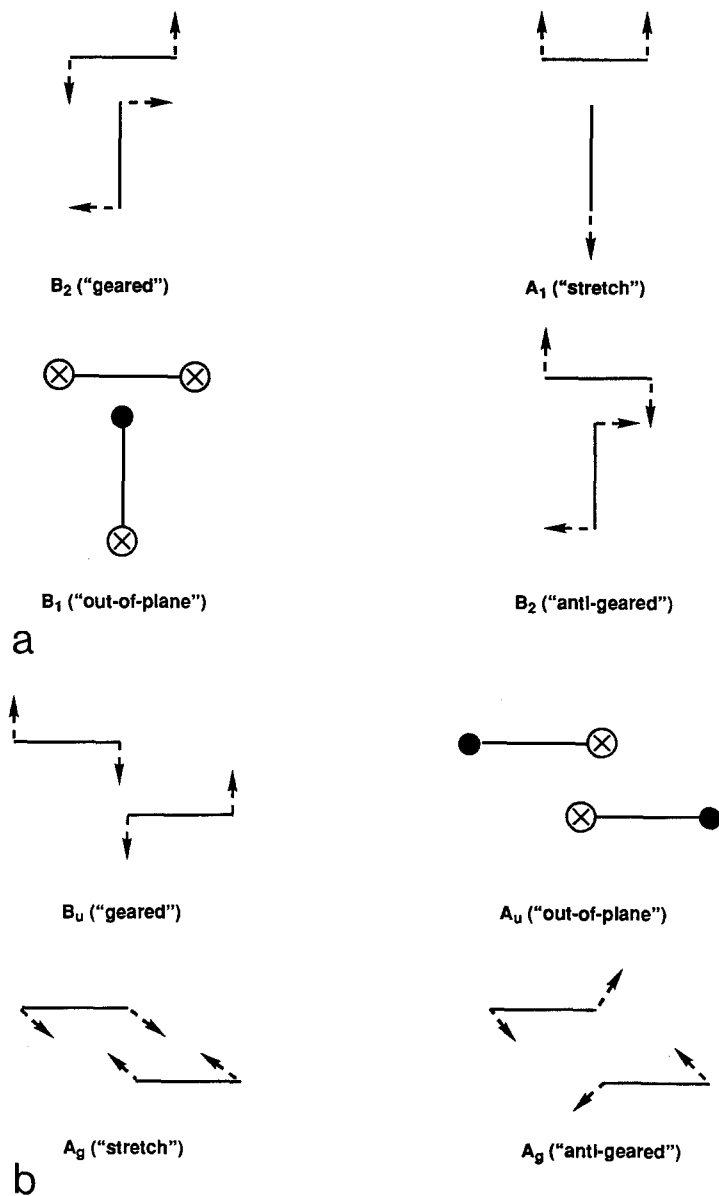


Fig. 4. Normal modes of (CO_2) and $(\text{C}_2\text{H}_2)_2$ in **a** C_{2v} , and **b** C_{2h} geometries. \rightarrow , motion in the plane of the paper; ●, motion upwards out of page; ⊗, downwards motion into page

coordinates is changed by $\sim 20\%$ in progressing from SCF to MP2, and that of the "anti-g geared" by $\sim 10\%$. However the stretching frequency is changed by over 60%. This last observation is not surprising, because inclusion of correlation has made the complex more tightly bound along that very stretching (dissociating) coordinate. The other data are telling us that angular potentials are not very sensitive to dispersion forces, at least for small displacements from equilibrium. Overall, though, all surface curvature is increased at the MP2 level;

no frequencies are reduced in magnitude. The effect of the basis set at MP2, where we can compute 6-31G* and DZP, is almost as large but only in some coordinates, noticeably the geared and out-of-plane modes. However we do not trust the 6-31G* values because they do not model the geometries well and because they give the poorest value of Θ_{zz} at the MP2 level. At SCF, the frequencies diminish in size as basis set size increases and the complex becomes more open.

In the C_{2h} structure, we observe again that, for a given basis set, MP2 increases the value of all frequencies relative to the SCF but at the SCF level changes of basis set produce the greatest percentage change in the imaginary frequency. This ties in directly with the observed geometry variations discussed above. The 6.31G* geometries are tighter than others. For molecules in this orientation, we do not expect correlation to have a major effect on any of the directions, and this is seen to be the case for the other coordinates, even the stretch. This suggests that correlation has, overall, a less significant contribution to the C_{2h} form and therefore that it has an important effect on the barrier height between the C_{2v} and C_{2h} forms.

There are currently no experimental values for the intermolecular frequencies for this system. What is certain is that for these potentials the harmonic approximation is wildly inaccurate so our computed values (harmonics) will be subject to large higher order anharmonic corrections to bring them in line with any future measurements of fundamentals. But one significant observation is that at most levels of theory, the magnitude of the B_2 -“geared” frequency of the T-shaped geometry is close to that of the imaginary B_u -frequency in the transition state, supporting Fraser’s use of a simple sinusoidal potential to describe this motion [14]. Our overall conclusions from this are that the MP2 harmonic frequencies are the most meaningful, and that those at the DZP level are as good as any that are likely to be computed at this level of theory simply because the intermolecular parameters are good and do not change significantly with basis set at this level. Trends with basis set are hard to predict at any level.

The energy barrier, V , determined by the experimentalists includes the zero point energy contribution. There is an imprecision in calculation of V by *ab initio* methods because it involves differences of three uncertain quantities: the calculated energy of the dimer relative to separated monomers, the BSSE correction and the zero point energy. In this work we make the best possible assessment of each of these. We start from the calculated difference between two large numbers, the absolute energies of the dimer and the separated monomers, which is usually only $\approx 0.01\%$ of their magnitude. (These complexes are especially weakly bound: $D_e \approx 5 \text{ kJ mol}^{-1}$, MP2.) However, our choice of basis set and level of theory to optimize monomer properties and the observation that monomer bond lengths are very little changed on complexation ensures that our estimate of the interaction energy is not unreasonable. The BSSE correction cannot be ignored at correlated levels. Even using the largest practical basis set to minimize its contribution, it amounts to a quarter of D_e . Its value is usually unpredictable but as Table 5 demonstrates, it is of different magnitude for different structures and therefore plays a vital part when assessing energy differences. The computed frequencies allow us to correct the binding energies for zero point effects. Table 5 shows all the relevant data. The zero point energy represents a further half of the D_e and is also a difference in two large numbers since its calculation involves the difference ($\sim 100 \text{ cm}^{-1}$) between the sum of all monomer frequencies and the sum of all the dimer frequencies both of which are

Table 5. (a) Energies (cm^{-1}) of two conformations of the acetylene dimer at the SCF level. ΔD_0 : ZPE correlated binding energies; ΔD_e : well depth of intermolecular potential, BSSE corrected

Structure/basis set	SCF energy ^a	BSSE ^b	ZPE	ΔD_0	ΔD_e	$\Delta D_0 (3N - 5)^c$
'T'-shaped (C_{2v})/DZP	302	29	121	152	273	161
'Parallel' (C_{2h})/DZP	270	46	102	122	224	122
Energy barrier, V						39

(b) As above, at the MP2 level

Structure basis set	SCF energy ^a	BSSE ^b	ZPE	ΔD_0	ΔD_e	$\Delta D_0 (3N - 5)^c$
'T'-shaped (C_{2v})/DZP	606	267	174	165	339	176
'Parallel' (C_{2h})/DZP	531	228	124	179	303	179
Energy barrier, V						-3
'T'-shaped (C_{2v})/TZ2P	551	111	—	266 ^d	440	277
'Parallel' (C_{2h})/TZ2P	454	73	—	257 ^d	381	257
Energy barrier, V						20

^a Energy of the dimer relative to two isolated monomers^b BSSE correction for each monomer using ghost orbitals of the other; non-symmetry equivalent monomers were calculated separately^c Zero-point corrected binding energies calculated by omitting tunnelling coordinate vibrational frequency^d Calculated using the DZP values of the zero point energy, ZPE

$\sim 10^5 \text{ cm}^{-1}$. For the reasons discussed above and comparing the trend in the magnitude of each frequency with basis set at the SCF level (for which a wider range of data is available) we believe that it is reasonable to use MP2 (DZP) zero point energy corrections in the TZ2P (MP2) D_e calculations to obtain D_0 values, at least for the C_{2h} form. We do the same for the C_{2v} form for consistency even though there appears to be less stability in the frequency changes with basis set for this structure.

In an assessment of V for acetylene dimer, we note that the zero point energy of the transition state is less than that of the ground state. The reason is trivial: the definition of zero point energy for a transition state (which is characterized by a single imaginary frequency) involves summing over real frequencies only.

Further, a breakdown of the contributions to the zero point energy of each structure (Table 6) shows also that the monomer bending vibrations differ greatly between C_{2h} and C_{2v} . The implication of this is that the monomers do not remain rigidly linear and distorted by the same amount throughout the interconversion process. Their bending vibrations are changed most. This leads us to expect that a better description of the monomer frequencies would also be useful. It is known from recent work that for acetylene f -functions are required to get accurate MP2 bending frequencies [58]. It would therefore be desirable to repeat this work with such a basis but unfortunately this is beyond present computing power.

The path along the tunnelling coordinate between the T-form and the transition state represents a "cut" through the $(3N - 6)$ -dimensional potential energy surface in normal coordinate space. In calculating the energy barrier we must factor out the frequency of the mode we follow and consider only the

Table 6. Intramolecular frequencies (cm^{-1}) of global minimum and transition state of acetylene dimer at SCF and MP2 levels with DZP Basis set

(a) SCF			
Monomer		Ground state ^a (C_{2v})	Transition state (C_{2h})
v_4	776(π_g)	777,780 782,787	779,780 780,784
v_5	865(π_u)	863,870 876,880	864,866 872,877
v_2	2207(σ_g^+)	2203 2206	2205 2207
v_3	3580(σ_u^+)	3572 3576	3575 3576
v_1	3683(σ_g^+)	3678 3680	3680 3680
(b) MP2			
Monomer		Ground state ^a (C_{2v})	Transition state (C_{2h})
v_4	560(π_g)	561,570 573,584	558,565 568,571
v_5	732(π_u)	730,743 753,766	730,732 741,746
v_2	1956(σ_g^+)	1952 1954	1954 1955
v_3	3470(σ_u^+)	3457 3462	3464 3464
v_1	3555(σ_g^+)	3547 3549	3551 3552

^a See [7]

($3N - 5$) modes (corresponding to the intramolecular bends and stretches and the remaining van der Waals modes) as components of the zero point contribution to the barrier. This is consistent with the fact that we do not add in the imaginary frequency at the transition state when computing its zero point energy and that the internal motion may be thought of as taking place on the “bath” of the ($3N - 5$) modes. Barriers calculated in this manner are shown in Table 5.

There is a substantial variation in the barrier height at the different levels of theory but we must also bear in mind the probable uncertainties in the experimental value, derived as it is, not by direct measurement but by model-fitting. What we can say is that all our values are consistent with the barrier height being small enough ($\sim 20 cm^{-1}$) to allow the observed significant tunnelling. The SCF barrier ignores the dispersion contribution to the intermolecular potential so is not expected to be accurate. However, even a DZP basis is not large enough to reduce BSSE to a sensible level, so our MP2 (DZP) value for the barrier is also wrong (the transition state in fact lies lower in energy than the ground form). Such a result would imply that $(C_2H_2)_2$ was a “potential-defying” species [59], i.e. the (periodically varying) potential that it is subject to is so shallow that there is no true entity resident in the bottom of the wells. We therefore believe our

MP2 (TZ2P) value of 20 cm^{-1} , using the DZP zero point corrections, to be the best *ab initio* estimate of the true barrier in the potential.

Fraser et al. [14] have noted the effect of isotopic substitution on the tunnelling splittings. These are calculated on the basis of changes in moments of inertia of monomers. However from our data, it is necessary to include zero point energy effects and these may be of greater significance when considering such a small barrier. We have computed MP2 (DZP) intermolecular frequencies and barriers for the species $(\text{C}_2\text{HD})_2$ (both T-shaped and all three slipped-parallel isotopomers) and $(\text{C}_2\text{D}_2)_2$ (Tables 7, 8).

Table 7. (a) Vibrational frequencies (cm^{-1}) of each conformation of isotopically substituted acetylene dimer, $(\text{C}_2\text{HD})_2$ at MP2 level with DZP basis set

Monomer (C_2HD) ^a	Ground state (C_{2v})		Transition state (C_{2h})		
	"D-bonded"	"H-bonded"	HCCD-DCCH	HCCD-HCCD	DCCH-DCCH
	20	20	28i	27i	27i
	61	62	43	43	43
	80	80	50	49	49
	98	99	112	115	119
482(ν_4)	483,490	483,483	481,489	482,484	482,483
	501,511	484,492	493,493	487,491	483,484
482(ν_5)	665,671	666,678	665,667	666,668	664,671
	672,680	701,721	668,669	679,680	684,692
1847(ν_2)	1841	1844	1845	1845	1846
	1845	1845	1846	1846	1846
2678(ν_3)	2665	2674	2672	2673	2677
	2674	2678	2673	2678	2678
3516(ν_1)	3510	3495	3516	3508	3508
	3518	3510	3516	3516	3508

^a Modes labelled by comparison with C_2H_2 : ν_3 is mainly C-D stretch; ν_1 is mainly C-H stretch

(b) Vibrational frequencies (cm^{-1}) of each conformation of isotopically substituted acetylene dimer, $(\text{C}_2\text{D}_2)_2$ at MP2 level with DZP basis set

Monomer (C_2D_2)	Ground state (C_{2v})		Transition state (C_{2h})	
		18		25i
	57		40	
	78		48	
	93		109	
466(ν_4)	467,473		465,470	
	473,478		471,471	
537(ν_5)	536,547		536,538	
	553,562		545,547	
1761(ν_2)	1756		1759	
	1759		1760	
2547(ν_3)	2539		2544	
	2542		2544	
2793(ν_1)	2788		2791	
	2789		2791	

Table 8. Energies (cm⁻¹) of two conformations of isotopically substituted acetylene dimer at the MP2 (TZ2P) level. ΔD_e : MP2 (TZ2P) well depth of intermolecular potential, BSSE corrected; ΔD_0 : ZPE corrected binding energies using MP2 (DZP) frequencies

(i) (C ₂ D ₂) ₂				
Structure/basis set	ΔD_e	ZPE	ΔD_0	$\Delta D_0 (3N - 5)^a$
'T'-shaped (C _{2v})	440	146	294	303
'Parallel' (C _{2h})	381	105	276	276
Energy barrier, V				27
(ii) (C ₂ HD) ₂				
Structure/basis set	ΔD_e	ZPE	ΔD_0	$\Delta D_0 (3N - 5)^a$
'T'-shaped (C _{2v})				
(a) "H-bonded"	440	167	273	283
(b) "D-bonded"	440	152	288	288
'Parallel' (C _{2h})				
(c) HCCD-DCCCH	381	109	272	272
(d) HCCD-HCCD	381	113	268	268
(e) DCCCH-HCCD	381	118	263	263
Energy barriers, V				
(a)-(e)				20
(a)-(d)				15
(b)-(d)				20
(c)-(c)				16

^a Zero-point corrected binding energies calculated by omitting tunnelling coordinate vibrational frequency

The changes in each of the intermolecular frequencies on isotopic substitution proved to be quite small, but the monomer bending frequencies changed significantly relative to the isolated monomers. In comparing barrier heights between the various isotopically substituted forms, both effects contribute significantly however. In (C₂HD)₂ there are four barriers to compute: two from each of the two T-shaped isotopomers loosely described as "H-bonded" and "D-bonded". The potential has now lost its four-fold periodicity, but on the basis of these results, it is anticipated that any of the large-amplitude motions will be quenched. The observation of tunnelling will require penetrations of wavefunctions through two barriers, because adjacent minima in the potential represent different isotopomers. The exchange symmetry arises only from the two distinct labellings of either the "H-bonded" or "D-bonded" forms.

In the accepted interconversion mechanism of (C₂H₂)₂ [13, 14, 17], however, there is no possibility of direct tunnelling between minima separated by 180° on the cyclic potential, that is between configurations at opposite ends of diagonals of the square (Fig. 2). We can rule out such tunnelling via other conceivable mechanisms: An in-plane mechanism derived from the B₂-"anti-gear" vibration would proceed via a D_{2h} transition state in which the monomers were parallel but not staggered. This is not a favourable orientation of two quadrupoles of the same sign, would not be a stationary point on the intermolecular

potential energy surface and in fact would be unbound relative to two isolated monomers at these proximities and therefore does not represent the zenith of a feasible pathway. An out-of-plane mechanism must proceed via a transition state or intermediate of the same level of symmetry of lower than that of the C_{2v} form [60]. However, in this case the only likely structure is of D_{2d} symmetry (with the monomers "crossed" relative to one another) from an inspection of the B_1 normal mode. Not only is this of higher symmetry than C_{2v} but is another electrostatically unfavourable conformation and is also necessarily degenerate in the interconversion coordinate (which would transform as an E -vibration of this structure) and therefore it cannot represent the lowest energy route between two C_{2v} configurations.

4.2. Carbon dioxide dimer

The carbon dioxide dimer has received much interest from theoreticians and experimentalists alike. Again, early attention focused on resolving the debate about the equilibrium configuration: C_{2h} or C_{2v} ? Early experimental work in the gas phase by Mannick et al. [61] and Novick et al. [62] suggested a T-shaped dimer, and studies of CO_2 trapped in rare gas matrices [63] seemed to confirm this. However, later molecular beam deflection experiments by Barton et al. [64] concluded that $(\text{CO}_2)_2$ need not have a dipole moment and therefore favoured the C_{2h} slipped parallel configuration. More recent studies by Walsh et al. [65] of the ν_3 CO_2 monomer stretch are consistent with a C_{2h} structure with geometric parameters (Fig. 5) $R = 3.602 \text{ \AA}$ and $\theta = 57.9^\circ$. Pubanz et al. [66] applied CARS methods to show that $(\text{CO}_2)_2$ had to have a centre of symmetry and therefore could not be T-shaped. Jucks et al. [15, 16] have studied the Fermi diad arising from $\nu_1 + \nu_3/2\nu_2^0 + \nu_3$ CO_2 bands in which the nuclear spin statistics lead unam-

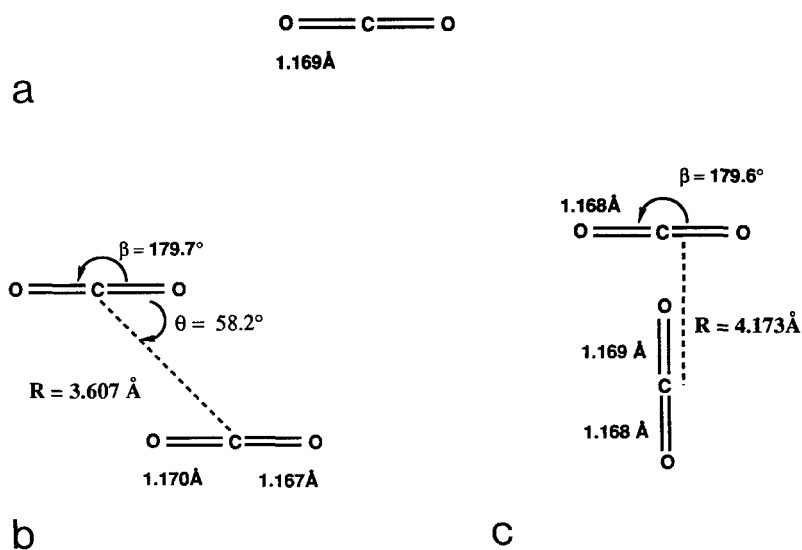


Fig. 5. Geometries of **a** CO_2 monomer; **b** dimer global minimum; **c** dimer T-shaped stationary point optimized at the MP2 (TZ2P) level

biguously to the centrosymmetric slipped parallel form, shown to have $R = 3.599 \text{ \AA}$ and $\theta = 58.2^\circ$ (Fig. 5). Their fitting of the $\nu_1 + \nu_3$ component [15] was imperfect, however, and led them to suggest that interconversion tunnelling might be important in carbon dioxide dimer too. In their later analysis [16] they dismissed this.

Any reliable theoretical work should identify both T-shaped and C_{2h} structures as stationary points. Sakai et al. [51] used model potentials and Brigot et al. [67] used a mixture of empirical (CNDO/2) and *ab initio* calculations with an unspecified basis set to show that the C_{2h} form was lower in energy. Hiraoka et al. [68] used 4-31G basis set CISD and 6-31G* optimization and concluded that the dimer has a bent equilibrium structure between T-shaped and slipped parallel, a most unusual result. The most recent and extensive work has been by Illies et al. [69]. They too conclude that the C_{2h} form is lower in energy; however, close inspection of their results shows that the absolute energies of the C_{2h} are not always lowest, and its stability is due only to the zero point energy correction which has been calculated at a much lower level of theory (SCF3-21G). Further, their highest level calculations [69], 6-31G/MP4(SDQ), were performed at 3-21G geometries and are therefore subject to unpredictable errors, and no BSSE correction has been employed at any level. Our work on acetylene dimer has shown that zero point corrections need to be calculated at the correlated level and that they should be employed with caution when correcting energy calculations at other levels.

We have performed calculations with DZP basis set at SCF and MP2 levels and with TZ2P basis at the MP2 level. Our results are presented in Tables 9, 10 and 11. The difference that correlation makes is even more striking than for acetylene. That the SCF results are wrong is apparent: the energy ordering (Table 11) of the two forms before BSSE correction suggests the T-shape is more stable, and the frequency analysis based on this predicts the C_{2h} form to be the transition state. BSSE makes the energy ordering correct but results in a transition state lower in energy than the ground form related to it. At the MP2 level, the C_{2h} form is the lowest in energy even when BSSE and zero point energy corrections are employed. The difference in the behaviour of $(CO_2)_2$ and $(C_2H_2)_2$ arises because as noted above, for $(C_2H_2)_2$ R is the same in both configurations, whereas for the shorter CO_2 , the monomers are capable of getting closer to one

Table 9. Geometrical parameters of (C_{2v}) and (C_{2h}) forms of the CO_2 dimer at SCF and MP2 levels (see Fig. 5)

Parameter	SCF	MP2	
	DZP	DZP	TZ2P
C_{2v}			
$R/\text{\AA}$	4.275	4.137	4.173
$\beta/^\circ$	178.2	179.7	179.8
C_{2h}			
$R/\text{\AA}$	3.898	3.578	3.607
$\theta/^\circ$	55.1	58.2	58.2
$\beta/^\circ$	179.8	179.6	179.6

Table 10. (a) Intermolecular frequencies (cm^{-1}) of C_{2h} form of the CO_2 dimer at SCF and MP2 levels with (DZP) basis sets. See Fig. 4b for forms of normal modes

Mode	SCF DZP	MP2 DZP
"Geared" (B_u)	12i	22
Out of plane (A_u)	27	26
Stretch (A_g)	34	46
"Anti-geared" (A_g)	89	99

(b) Intermolecular frequencies (cm^{-1}) of C_{2v} form of the CO_2 dimer at SCF and MP2 levels with (DZP) basis sets. (Symmetry labels assume that the molecule is in the yz -plane.) See Fig. 4a for forms of normal modes

Mode	SCF DZP	MP2 DZP
"Geared" (B_2)	4	8
Stretch (A_1)	49	66
Out of plane (B_1)	24	25
"Anti-geared" (B_2)	67	61

Table 11. (a) Energies (cm^{-1}) of two conformations of the CO_2 dimer at the SCF (DZP) level. ΔD_0 : ZPE corrected binding energies; ΔD_e : well depth of intermolecular potential, BSSE corrected

Structure	SCF energy ^a	BSSE ^b	ZPE	ΔD_0	ΔD_e	$\Delta D_0 (3N-5)^c$
'T'-shaped	316	126	74	116	190	118
'Parallel'	301	90	72	139	211	139
Energy barrier, V						21

(b) As above, at the MP2 level

Structure	MP2 energy ^a	BSSE ^b	ZPE	ΔD_0	ΔD_e	$\Delta D_0 (3N-5)^c$
(DZP)						
'T'-shaped	529	348	84	97	181	101
'Parallel'	550	355	95	100	195	111
Energy barrier, V						10
(TZ2P)						
'T'-shaped	392	74	—	234 ^d	318	238
'Parallel'	445	98	—	252 ^d	347	263
Energy barrier, V						25

^a Energy of the dimer relative to two isolated monomers

^b BSSE correction for each monomer using ghost orbitals of the other, non-symmetry equivalent monomers were calculated separately

^c Zero-point corrected binding energies calculated by omitting tunnelling coordinate vibrational frequency

^d Calculated using the DZP values of the zero point energy, ZPE

another in a slipped-parallel than in a perpendicular orientation so R is not constant. Although this is probably not enough to counterbalance the order of favoured structures electrostatically it reduces their energy difference substantially. Inclusion of correlation (favouring the tighter parallel form over the perpendicular form) is enough to tip the balance and produces a picture in agreement with experiment. Our best geometric parameters of $R = 3.697 \text{ \AA}$ and $\theta = 58.2^\circ$ (MP2/TZ2P) are in excellent agreement with the experimental values [15, 16, 64]. The rotational constants, 8809, 1595, 1351 MHz, compared well with the measured $A'' = 9003$, $B'' = 1606$, $C'' = 1359$ MHz [64].

We now have a qualitative explanation of another feature of Table 11: the energy barrier separating the C_{2h} and C_{2v} forms is very small, 25 cm^{-1} (MP2/TZ2P), which is about the same as in $(C_2H_2)_2$. Tunnelling is therefore possible in this system. (The nuclear spin statistics of the boson ^{16}O nuclei mean that spectral lines will not be split but be shifted [16]. This was in part invoked as an explanation of anomalies in the $\nu_1 + \nu_3$ band [15].) The most popular tunnelling coordinate considered to date [15, 16, 64] involves the monomers sliding past one another maintaining a constant perpendicular separation of their intramolecular axes. However, such a motion does not derive from a ground state normal mode (a criterion for any interconversion path [70]) and passes through a repulsive maximum in the quadrupole-quadrupole interaction potential at the proposed D_{2h} "transition state". Another possibility is the intermolecular normal coordinate of the "geared" form, which must be present by symmetry for any homo-dimer with C_{2v} and C_{2h} stationary points. In this case the higher energy of the structures would be the transition state on the "geared" coordinate. It would not be unreasonable to suppose on the basis of symmetry and our energetic data that a tunnelling coordinate, analogous to that in acetylene dimer, but in which the four C_{2h} configurations are at minima and the C_{2v} forms at transition states, is operative. (Then, as is discussed elsewhere [60], the MS group for this process at the transition state would be isomorphic to D_{4h} , and the schematic representation would be as in Fig. 2, but with the square rotated about its midpoint by 45° .) This motion would allow the positions of the two symmetry equivalent monomers in the C_{2h} form to interchange through a transition state in which they had become inequivalent. Although this is entirely plausible, we note that the C_{2v} form is not in fact identified as a true transition state but as a local minimum. However, the "geared" frequency, the lowest, is very small and may possibly change sign at higher levels of theory. It is best thought of as indicative of the flatness of the potential energy surface in that region. That it is substantially different in magnitude from the corresponding "geared" frequency in the C_{2h} form confirms our supposition that an internal rotation coordinate could not be expressed as a simple sinusoidal function. This is due to the difference in centre-of-mass to centre-of-mass separation between transition state and ground state, so that it would not be reasonable to model this cyclic potential by a single internal rotation parameter. Furthermore, this large anisotropy in the potential may in fact be the reason for inconclusive observation of tunnelling. The simultaneous increase in R and rotation may be unfavourable, arising from the coupling of two normal modes of different symmetries. Also, such a motion may be quenched by excitation of certain monomer vibrations. Certainly Fraser [17] has observed a strong dependence on monomer vibrational frequency of the tunnelling barrier. Alternatively, it may be an effect of monomer moment of inertia (at zero-point bond lengths), $I^{(0)}$: compare acetylene, $23.8 \times 10^{-47} \text{ kg m}^2$, and carbon dioxide $71.9 \times 10^{-47} \text{ kg m}^2$ [71]. Unfortunately since the C_{2h} form

does not possess a permanent dipole moment microwave studies are unable to measure tunnelling frequencies in the absence of vibrational excitation in order to elucidate this problem fully.

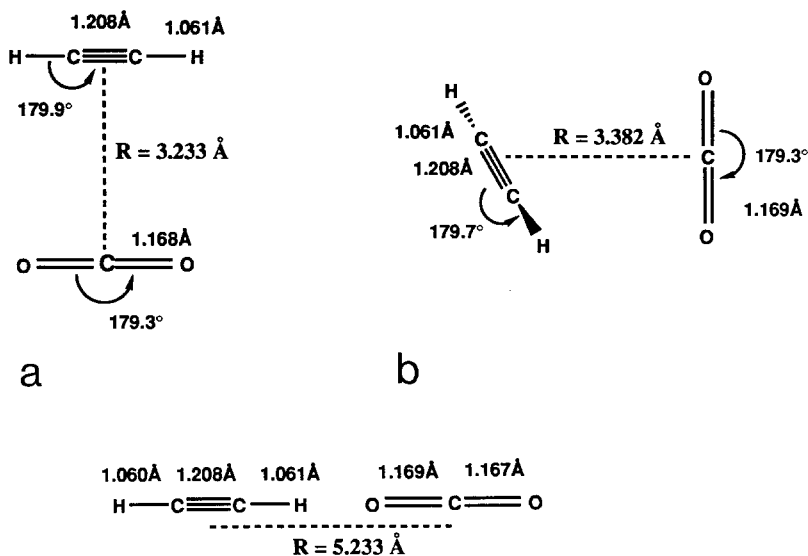
Finally we discuss the $(\text{CO}_2)_2$ intermolecular frequencies (Table 10). (In the C_{2v} structure the largest rotational frequency at the MP2 (DZP) level is 0.5 cm^{-1} (before projection) but in the C_{2h} form it is 6 cm^{-1} , both of which are substantially smaller than the respective smallest vibrational frequency.) The low (B_2) frequency of the C_{2v} form is still consistent however with the failure to observe it as yet [15, 16], since it is likely that any C_{2v} dimer formed in the molecular beam expansion would drop into the C_{2h} potential well due to subsequent large amplitude vibrations along the geared normal coordinate, arising either thermally or induced by collisions. Alternatively excitation of the monomer stretching mode along the upright of the "T" may induce dissociation.

Brigot et al. have calculated the intermolecular frequencies of $(\text{CO}_2)_2$ [72] using empirical potentials and their earlier uncorrelated *ab initio* data [67]. They calculate 32, 22, 42 and 85 cm^{-1} for the B_u , A_u , A_g and A_g modes, respectively, which are listed in Table 10a. These are in fairly good agreement with our values. Only two of the modes have been characterized from experimental data: the harmonic frequencies of the A_g modes [16], estimated to be 32 and 90 cm^{-1} compared with our 46 and 99 cm^{-1} , respectively. The stretch is in poorer agreement and this is hard to account for. The key feature though is that $(\text{CO}_2)_2$ has two low-valued van der Waals frequencies and this could account for difficulties in fitting spectral data whether tunnelling occurs or not. In particular the out-of-plane motion could give rise to the large inertial defect observed by Jucks et al. [16]. However it would not lead to tunnelling because it leads inevitably to a high energy conformation in which the monomers are parallel. Finally, Jucks et al. [16] observe only small shifts in complex A_g monomer frequencies relative to isolated monomers (0 , 0.4 and 4.9 cm^{-1} for ν_1 , ν_3 and ν_2 , respectively). The comparisons with our values of 1.0 , 1.0 , 3.8 cm^{-1} , respectively, though not quantitative, are fair in that they establish the weakness of the interaction and the different effect on monomer modes.

4.3. Acetylene-carbon dioxide dimer

The van der Waals dimer of carbon dioxide and acetylene has a well-defined unique equilibrium structure determined unambiguously from both infrared and microwave spectra and should be a routine investigation for *ab initio* calculations. It was felt important to obtain values of intermolecular frequencies or binding energies for comparison with those derived experimentally and also to investigate the predictions of the electrostatic model that there would be other stationary points on the potential energy surface. In the absence of any previous theoretical studies, as high-quality a characterization as possible is presented.

The experimental studies of this complex include the vibration-rotation spectrum of Prichard et al. [20], the microwave analysis of Muentner [21] and the near-infrared study of Huang and Miller [22]. They all indicate that the equilibrium configuration is of C_{2v} symmetry with both monomers parallel to one another and perpendicular to the line joining their centres. This is a structure predicted by the electrostatic model, and would therefore confound the hydrogen-bonding models [56]. From a consideration of electrostatic interactions, we predict the three structures to be stationary points: the observed structure with



C

Fig. 6. Geometries of acetylene- CO_2 dimer optimized at the MP2 (TZ2P) level. **a** global minimum; **b** torsional transition state; **c** local minimum

interaction energy $(-9\theta_a\theta_b/4R^5)$, a linear ($C_{\infty v}$ one (corresponding to the hydrogen-bonding picture) with energy $(-6\theta_a\theta_b/R^5)$, and a “crossed” structure where the monomers are perpendicular to one another but in orthogonal planes with energy $(-3\theta_a\theta_b/4R^5)$ (Fig. 6). The last structure is the expected “torsional” transition state obtained by following the out-of-plane (B_2) normal mode of the experimentally observed form in which the monomers rotate in opposite directions relative to one another. On this basis we expect the linear structure to be greatly favoured at constant R . However, we must realize that the lengths of the molecules (determined by the van der Waals radii) are such that the centre-of-masses will be much further apart in the linear case than in the parallel case and that the R^{-5} dependence will then be the determining feature. We do not expect R to vary as significantly between the parallel form and the torsional transition state. All of these forms are indeed found to be stationary points and Tables 12–15 present SCF results at DZP and MP2 results at DZP and TZ2P basis sets for the three forms. The largest rotational frequencies at the MP2 (DZP) level (before projection) for the C_{2v} ground state, torsional transition state and linear local minimum are 0.2, 1.8 and 6.3 cm^{-1} respectively, in each case considerably smaller in magnitude than the smallest intermolecular frequency. The intermolecular normal modes of all three structures are depicted in Fig. 7.

Our best set of data for the C_{2v} ground form (MP2/TZ2P), Table 12, gives an equilibrium monomer-monomer distance, R_e , of 3.233 Å which corresponds favourably with the experimental R_0 from microwave spectra of 3.292 Å [21] and from infrared spectra of 3.285 Å [22]. (The rotational constants at MP2 (TZ2P) are 8711, 2949 and 2203 MHz whereas those of experiment are [22] $A = 8871$,

Table 12. Geometrical parameters of global minimum, local minimum and torsional transition state of the acetylene-CO₂ dimer at SCF and MP2 levels. Refers to Fig. 6

Parameter	Ground state		Local minimum ($C_{\infty v}$)		Torsional transition state (C_{2v})	
	SCF	MP2	SCF	MP2	SCF	MP2
$R/\text{\AA}$						
DZP	3.596	3.251	5.217	5.110	3.974	3.377
TZ2P		3.233		5.233		3.382
$\angle \text{OCO}/^\circ$						
DZP	179.2	179.3	—	—	179.4	179.2
TZ2P		179.3				179.3
$\angle \text{HCC}/^\circ$						
DZP	180.0	180.0	—	—	179.7	179.7
TZ2P		179.9				179.7

Table 13. (a) Relative energies (cm^{-1}) of stationary points of the acetylene-CO₂ dimer at the SCF (DZP) level

Structure/symmetry	SCF energy	BSSE	ZPE	ΔD_0	ΔD_e
Ground state (C_{2v})	370	67	105	198	303
Local minimum ($C_{\infty v}$)	422	149	161	112	273
Torsional T.S. (C_{2v})	102	28	55	19	74

(b) As above, at the MP2(DZP) level

Structure/symmetry	MP2 energy	BSSE	ZPE	ΔD_0	ΔD_e
Ground state (C_{2v})	794	402	153	239	392
Local minimum ($C_{\infty v}$)	672	390	207	75	282
Torsional T.S. (C_{2v})	395	291	78	26	104

(c) As above, at the MP2 (TZ2P) level

Structure/symmetry	MP2 energy	BSSE	ZPE	ΔD_0^a	ΔD_e
Ground state (C_{2v})	704	136	—	415	568
Local minimum ($C_{\infty v}$)	416	58	—	151	358
Torsional T.S. (C_{2v})	398	126	—	194	272

^a Calculated using DZP zero point values

$B = 2862$ and $C = 2156$ MHz showing a similarly close agreement, though obviously subject to inaccuracies in calculated monomer bond lengths.) The dipole moment shows reasonable agreement (0.119 D (MP2/TZ2P) vs experimental 0.1611 D [21] and 0.167 D [22]). As discussed in Sect. 3 above, this is probably due to our poor description of the perpendicular component of the monomer polarizabilities.

A brief consideration of the data in Table 12 for the other two structures (which have not been experimentally characterized) demonstrates that, as anti-

Table 14. Intermolecular frequencies (cm⁻¹) of global minimum, local minimum and torsional transition state of the acetylene-carbon dioxide dimer at SCF and MP2 levels with DZP basis set. Refer to Fig. 7

Ground state			Local minimum (C _{∞v})			Torsional transition state (C _{2v})		
Mode	SCF	MP2	Mode	SCF	MP2	Mode	SCF	MP2
"Geared" (B ₁)	82	93	Bend "in-phase"	82,82	88,88	"Torsion"	37i	47i
Stretch (A ₁)	51	85	Stretch	67	89	"Yaw" (C ₂ H ₂)	45	48
"Torsion" (B ₂)	46	52	Bend	17,17	25,25	"Yaw" (CO ₂)	39	58
			"out-of-phase"					
"Anti-geared" (B ₁)	33	66				Stretch	28	63

Table 15. Intermolecular frequencies (cm⁻¹) of global minimum, local minimum and torsional transition state of the acetylene-CO₂ dimer at SCF and MP2 levels with DZP basis set

(a) SCF			
Monomers	Ground state	Local minimum (C _{∞v})	Torsional transition state (C _{2v})
Acetylene			
776(π _g)	780,780	785,785	775,781
865(π _u)	867,868	884,884	863,869
2207(σ _g ⁺)	2206	2205	2207
3580(σ _g ⁺)	3576	3578	3578
3683(σ _g ⁺)	3681	3683	3682
CO ₂			
768(π _u)	764,768	768,768	765,768
1517(σ _g ⁺)	1516	1520	1517
2594(σ _u ⁺)	2599	2598	2594
(b) MP2			
Monomers	Ground state	Local minimum (C _{∞v})	Torsional transition state (C _{2v})
Acetylene			
560(π _g)	566,570	573,573	557,563
732(π _u)	736,740	755,755	728,737
1956(σ _g ⁺)	1953	1956	1955
3470(σ _u ⁺)	3464	3475	3466
3555(σ _g ⁺)	3551	3560	3551
CO ₂			
658(π _u)	650,658	659,659	650,659
1330(σ _g ⁺)	1332	1338	1331
2462(σ _u ⁺)	2462	2470	2463

pated, the unfavourability of the linear form is due to the greater centre-of-mass separation. One feature of note is that the difference in the separation of the monomers between the torsional transition state and the ground form is much larger at SCF than at MP2. This is attributable to the non-angular dependence of the leading term in the dispersion correction, so that intermolecular correlation contributes to the binding of the transition state in a broadly comparable

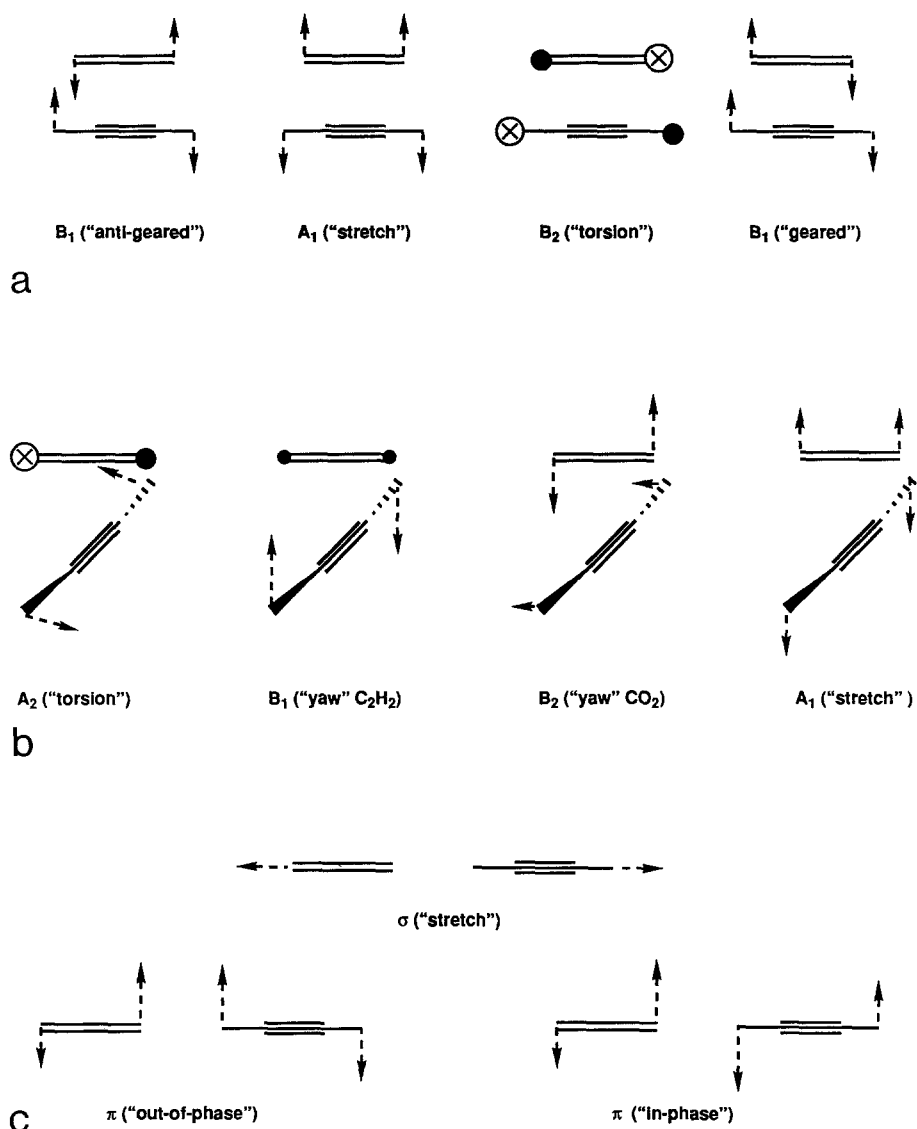


Fig. 7. Normal modes of $C_2H_2-CO_2$ in **a** ground state (C_{2v}); **b** torsional transition state (C_{2v}); **c** linear local minimum ($C_{\infty v}$). \rightarrow , motion in the plane of the paper; \bullet , motion upwards out of page; \otimes , downwards motion into page. Size of symbol indicates amplitude of motion. \equiv , the CO_2 monomer; \equiv , C_2H_2 monomer

manner for all geometries. The SCF picture, relying almost totally on the electrostatics for interaction, would show the transition state to be far more weakly bound than the ground state and thus with a wider optimized monomer separation. Therefore using MP2 it is reasonable to describe torsional motion by a single parameter, an internal angle with a fixed centre-of-mass to centre-of-mass distance, R .

As for energies (Table 13), the experimental [20, 21] estimates of the binding energy of the observed complex were determined using the point quadrupole and distributed multipole analysis (DMA) models [73]. The former gave 965 cm^{-1} and the latter 650 cm^{-1} . These models of course do not account for dispersion and are therefore more fairly compared with our SCF results which, BSSE corrected, gave 303 cm^{-1} . This large discrepancy between the three sets of data is partly because the DMA studies were performed at the experimental distance, which is tighter than the SCF distance. This accounts for perhaps 50% of this discrepancy. Our best correlated results give 568 cm^{-1} . This is greater than for either $(CO_2)_2$ or $(C_2H_2)_2$ as is predicted by the electrostatic model alone.

Muenter [21] estimated the torsional potential barrier to be $\approx 400\text{ cm}^{-1}$ by DMA. There is once again a severe disagreement with the SCF calculation (229 cm^{-1}), but more serious is the discrepancy between the DMA estimated binding energy of the transition state (250 cm^{-1}) and the SCF value (74 cm^{-1}). A possible factor could be once again the intermolecular separation, which was underestimated by Muenter for the type of model employed and also assumed to be constant for the model torsional potential.

From our calculations we can make the following conclusions. BSSE calculations are important. At the SCF level, the linear structure is predicted to be the lowest in energy before the counterpoise corrections, although zero point energy effects would show it to be 5 cm^{-1} above the parallel form without BSSE. The indication from the SCF is that the linear form is of some importance as a low-lying species. At the MP2 level, our DZP results are once again slightly confused by BSSE effects, but the linear structure is consistently the higher in energy (both at TZ2P and DZP). The barrier on the torsional potential using DZP ΔD_0 ($3N - 5$) values is now 218 cm^{-1} (TZ2P), little different from the SCF value (202 cm^{-1}), indicating a balancing of intermolecular separation and correlation effects. The most striking result is the effect of zero point energy (see Table 13); not only do the transition states have smaller zero point energy corrections than ground forms, but also that the zero point energy of the linear structure is markedly different, this time much larger. This is because for the linear species there is an extra vibrational mode ($3N - 5$ vs $3N - 6$) to consider. In fact at the MP2 (TZ2P) level the linear form is now higher in energy than the torsional transition state. The binding energy of the torsional transition state is almost entirely due to dispersion forces. Its small zero point energy correction is easily rationalized because in this orientation the monomers are not perturbing each other much (through distortions created by their respective electric fields) and so the monomer frequencies are not shifted much from the isolated monomer values. In addition, there are only three intermolecular frequencies to be added, each of which is small because the surface is flatter in that region. The intermolecular frequencies at any level of theory show that the curvature in the torsional coordinate is similar for the transition state and the ground state. The MP2 results suggest that the torsional coordinate could be effectively modelled by a sinusoidal function like the acetylene dimer. Also as with the acetylene dimer the torsional normal coordinate is that with the shallowest curvature at the minimum. But although the torsional structure is the true transition state for interconverting the only two distinctly labelled forms of this complex, its energy is so high that tunnelling splittings will probably be unobservable (cf. the analysis of Fraser [14] for the acetylene dimer, where the tunnelling splittings are very sensitive to barrier height).

Only two of the intermolecular frequencies (Table 14) have been estimated directly from experiment; Prichard et al. [20] used centrifugal distortion data from their vibration-rotation spectrum to put a lower bound on the value of the harmonic for the A_1 stretching mode of 120 cm^{-1} . However the later work of Muentner [21] used the same method to suggest a value of 75 cm^{-1} whilst Huang and Miller estimate $84 \pm 15\text{ cm}^{-1}$. This indicates the high level of uncertainty in present experimental methods of obtaining this data. The out-of-plane torsional mode (B_2) was also investigated by Muentner; from nuclear hyperfine data he arrived at 45 cm^{-1} for the harmonic frequency (his DMA calculations gave 49 cm^{-1}), though he considers that these values are likely to be on the low side.

Our calculated stretching frequency at MP2 (DZP) is 85 cm^{-1} , very close to the latest experimental value [22] and our torsional frequency is 52 cm^{-1} , within 15% of experiment. These results are very encouraging and suggest that for this simple system, the MP2 surface may be a rather good approximation. The inclusion of dispersion forces once again has a dramatic effect on the stretching frequency. It is increased by $\approx 70\%$ in the ground form, $\approx 33\%$ in the linear form and $\approx 125\%$ in the transition state. More unusually (cf. the acetylene dimer), in the ground form dispersion forces are seen to affect angular potentials too, particularly the "anti-gearred" mode (B_1). Alternatively this might be an effect of a contracted complex with monomers closer to their respective repulsive walls. The experimentalists also suggest that the most significant zero point motions of the complex are in-plane ones [20, 21]. Our data are not in complete agreement with that conclusion as we would perhaps expect lower B_1 -frequencies to be consistent with this. In the linear structure, the out-of-phase bend that moves the complex from linear to V-shaped (Fig. 7c) is the lowest frequency mode. A hydrogen-bonding model would predict the surface to be very flat in the direction of this motion, i.e. the hydrogen bond would be very floppy, allowing the system to undergo large-amplitude angular fluctuations.

The shifts in the monomer frequencies are also worthy of comment. Although calculated absolute frequency magnitudes are in poor agreement with measured values, their shifts are significant: for example acetylene ν_3 is calculated to be red-shifted by 6 cm^{-1} in the ground state, and the experimentally observed red-shift is 6 cm^{-1} [22] or 7 cm^{-1} [20]. The collinear structure isomer of $\text{C}_2\text{H}_2\text{-CO}_2$, which has not been reported, has frequency shifts that are entirely different from the observed C_{2v} ground state shifts (Table 15). The much larger frequency shifts in acetylene monomer bending modes in the collinear form could be due to a deficiency in the basis functions on acetylene [58], however, as the bending modes are not usually those studied this effect is not important. More significantly is the fact that the shifts in the C-H stretches of the linear form are in the opposite direction from those in the C_{2v} form. In addition the shifts in the CO_2 stretches are greater in the linear form than in the ground state.

One criterion for the occurrence of structural isomers under the experimental conditions usually employed to observe van der Waals complexes is that there is a sufficiently high interconversion barrier between the two minima so that species of the higher energy form do not collisionally relax to the lower energy one. In order for the linear form to distort to the ground state, it must vibrate along a bending coordinate; the "out-of-phase" mode is most appropriate on account of its shallow curvature (25 cm^{-1} , MP2/DZP). However, the

amplitude of vibration must be enormous to swing the monomers into the parallel C_{2v} form and there must clearly be some barrier to the process because of the positive curvature in the potential. The tighter curvature in the direction of the “in-phase” bending mode coordinate suggests that high-amplitude motion along it would be less favourable. It would lead to a slipped-parallel type orientation from which the monomers would have to slide past one another to access the C_{2v} form. The studies of Prichard et al. [20] have demonstrated that this distortion is energetically unfavourable on purely electrostatic grounds, a reasonable conclusion. We therefore speculate that the collinear form of the acetylene-carbon dioxide dimer may persist for long enough to allow observation, even though it lies at some 250 cm^{-1} above the ground state. Of course in these calculations we are unable to account for an aspect of the dynamics of cluster formation in molecular beam conditions which somehow precludes formation of this higher energy form. That other van der Waals dimers have been observed in linear or near-linear “end-to-end” conformations, however, (see for example [32]), is encouraging for these studies.

5. Conclusions

We have demonstrated that non-dipolar van der Waals dimers in a variety of conformations can be reliably described by currently available *ab initio* methods and that a frequency analysis is of great importance. Quantitative estimates of binding energies are still very hard and unreliable for these systems. However these studies show that provided the pertinent monomer properties are modelled accurately, relative energies between different conformations are described successfully using second order Møller–Plesset perturbation theory. As with all *ab initio* methods, this method suffers from certain inherent cancelling of errors. However, it does ensure correct intersystem antisymmetry (a necessary requirement to model short-range interactions) and is at present the most computationally efficient correlated method. It is also the only correlated method for which analytic second derivatives are widely available. In the limit of a complete basis set, it is known to overestimate dispersion coefficients, and at smaller bases it, like all correlated methods, has a large BSSE.

Recent advances in far-infrared work which enable van der Waals modes to be directly observed enable the measurement of the fundamental and several vibrational levels of one mode. This will lead to the determination of the true form of the surface curvature in at least some coordinates, as well as an estimate of the binding energy, and thus overcome the problem of only the harmonic frequencies being available for highly anharmonic systems.

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