Stationary points on the potential energy surfaces of (C2H2)2, (C2H2)3, and (C2H4)2

Ian L. Alberts, Timothy W. Rowlands, and Nicholas C. Handy

Stationary points on the potential energy surfaces of $(C_2H_2)_2$, $(C_2H_2)_3$, and $(C_2H_4)_2$

Ian L. Alberts, Timothy W. Rowlands, and Nicholas C. Handy
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

Minima on the potential energy surfaces of $(C_2H_2)_2$, $(C_2H_2)_3$, and $(C_2H_4)_2$ have been located by *ab initio* methods, using the Møller–Plesset second-order (MP2) procedure, with a DZP basis set. For $(C_2H_2)_2$, a T-shaped structure is predicted and for $(C_2H_2)_3$, a C_{3h} structure. For $(C_2H_4)_2$ there are two candidates, a T-shaped structure and a staggered-parallel structure, and it is difficult to distinguish between them. Other stationary points have been located on the surfaces, but they are all found to be transition states, by the method of analytic second derivatives. Existing experimental data is insufficient to decide unequivocally as to the geometry of the minima. These calculations appear to resolve these questions and there is no contradiction with the data.

I. INTRODUCTION

In recent years there has been much interest in the structure and properties of weakly bound complexes. Great advances in infrared and microwave spectroscopy have enabled both vibrational levels and rotational levels to be assigned. This has led to the experimental determination of fundamental frequencies of these complexes. Assignments of rotational lines enable moments of inertia to be determined. However, such information in many cases has not been sufficient to determine the geometry of the potential minima of these complexes and this is one area where the theoretician has a valuable role to play.

For example, our group has been studying over the past two years many hydrogen-bonded complexes, with binding energies of the order of 5 kcal/mol. (Examples include $H_2O\cdots HF$, ether$\cdots HCl$.[1]) We have found that the SCF method is insufficient for reliable quantitative calculations on these complexes though qualitatively the SCF results are often correct. To obtain accurate frequency shifts, geometries, and D_0, we find that second-order perturbation theory (MP2) with a DZP basis set (or better) is a great improvement. We have also studied $B_2H_6\cdots HF$[2] and ArH_3^+,[3] where there is a lack of definitive experimental information.

Here we shall look at much more weakly bound complexes with binding energies of less than 1 kcal/mol and where the latest quantum chemistry methodology must be used. The chosen complexes are $(C_2H_2)_2$, $(C_2H_2)_3$, and $(C_2H_4)_2$; these are all examples of hydrogen atoms interacting with a π-electron system. We do not believe that a definitive structure has been determined for any of these complexes. First, we summarize the experimental information for each of our chosen complexes.

Experimental observation of $(C_2H_2)_2$ has been limited with structural information being scarce. Miller *et al.*[4,5] have examined the predissociation lifetime of the complex, but with regard to structure have merely suggested that there may be more than one stable form. Pendley and Ewing[6] analyzed their spectrum based on the predictions of Sakai *et al.*[7] but were unable to definitely determine the structure of the

complex. Their frequency shifts agree with those found below, but they also agree with the results from the Sakai *et al.*[7] potential. Apart from the calculations of Sakai *et al.*[7] using electrostatic potentials which predict a staggered-parallel structure to be the minimum, the only other calculation has been by Aoyama *et al.*[8] who used a 6-31G basis and experimental monomer geometry and found that a T-shaped structure was lower in energy.

For $(C_2H_2)_3$, there has recently been published an experimental investigation by Prichard *et al.*[9] who gave some structural information including the apparent existence of a threefold axis of symmetry, but who were unable to choose between a true triangular shape and a distorted form. No previous theoretical work has been published on this species.

$(C_2H_4)_2$ has been trapped in argon matrices at low temperatures and its infrared and Raman spectra observed and studied.[10–12] However, the rotational structure has as yet not been resolved[5]; therefore no experimental structure of $(C_2H_4)_2$ has been definitely established. According to molecular beam experiments,[13] the ethylene dimer is nonpolar and this led to the assumption that a parallel-like structure with an inversion center was the most reasonable structure. This is similar to the packing arrangement in solid ethylene.[10]

Various theoretical calculations have been performed to try and solve the problems of the structure of $(C_2H_4)_2$. Malar and Chandra[14] used the exchange perturbation method, which treats the intermolecular potential energy as a perturbation correction to the energy of the molecules separated by a finite distance, and they separately calculated the π and σ electron contributions to the total energy. They found the equilibrium structure to be T shaped. Wormer and van der Avoird[15] performed *ab initio* valence bond and small basis set SCF calculations and also predicted the geometry of $(C_2H_4)_2$ to be T shaped. However, Iguchi and Suzuki,[16,17] using both a semiempirical exchange perturbation method employing the CNDO wave function and an *ab initio* exchange perturbation method employing the SCF wave function, predict the geometry of $(C_2H_4)_2$ to be parallel. Electrostatic calculations[18] also predict the lowest energy minimum

to be the parallel structure though the T-shaped structure was predicted to be a minimum as well.

So there is considerable uncertainty here. We shall see that our more sophisticated *ab initio* techniques help to resolve these problems.

II. COMPUTATIONAL DETAILS

For such weakly bound complexes, it is necessary to proceed beyond the SCF approximation and include dispersion corrections through the inclusion of electron correlation effects. Now that Amos, Handy, and Simandiras[19] have developed an efficient energy, gradient, and analytic second derivative code for the MP2 approximation, for use with large basis sets,[20] we are in a position to perform such calculations. These codes are part of the Cambridge Analytic Derivative Package CADPAC.[21]

In these calculations we used the standard Huzinaga–Dunning[22] DZ basis, with d functions ($\zeta = 0.8$) on C and p functions ($\zeta = 1.0$) on H, which yield 84, 126, and 104 basis functions for $(C_2H_2)_2$, $(C_2H_2)_3$, and $(C_2H_4)_2$, respectively. We optimized the geometries of all reasonable structures and characterized the nature of the stationary points through the analytic second derivatives package. Calculations were performed on the CRAY-1S and CRAY-XMP machines in the U.K.

III. RESULTS AND DISCUSSION

A. $(C_2H_2)_2$

Two structures for $(C_2H_2)_2$ were found at the SCF level to correspond to stationary points on the potential energy surface. The first was the staggered-parallel form shown in Fig. 1(a) and the second was the T-shaped form of Fig. 1(b). The staggered-parallel structure was found to correspond to a transition state with a single imaginary frequency of $i18$ cm^{-1} corresponding to a motion towards the T-shaped form. The T-shaped structure was found to have a ΔD_0 of 152 cm^{-1} at the SCF level. This resulted from a ΔD_e of 302 cm^{-1}, a zero-point vibrational energy correction of 121 cm^{-1}, and a basis set superposition error correction of 29 cm^{-1} calculated using the standard procedure of Boys and Bernardi.[23]

This T-shaped structure was then optimized at the MP2 level with a resultant ΔD_0 of 404 cm^{-1} composed of a ΔD_e of 606 cm^{-1}, a zero-point vibrational energy correction of 173 cm^{-1}, and a basis set superposition error correction taken to be 29 cm^{-1}, the SCF value. The calculated MP2 harmonic frequencies are listed in Table I. In going from the SCF to the MP2 level, it can be seen that the intermolecular distance has decreased by about 0.4 Å and the binding energy has increased by 252 cm^{-1} indicating the importance of dispersion effects in the bonding of such weakly bound complexes.

The intermolecular frequencies can be assigned as a bending rotation towards the staggered-parallel structure (22 cm^{-1}), an out-of-plane bend (67 cm^{-1}), a second in-plane bend (106 cm^{-1}), and the intermolecular stretch (81 cm^{-1}). The shifts of the monomer frequencies on complexation are small as are the intermolecular frequencies indicative of the small binding energy of the complex. The dipole moment was found to be 0.329 D and the rotational constants of the complex were 34 338, 1971.2, and 1864.2 MHz.

B. $(C_2H_2)_3$

In the case of $(C_2H_2)_3$, the size of the problem precluded a detailed investigation at the MP2 level, but the qualitative agreement between the SCF and MP2 results for $(C_2H_2)_2$ above provided grounds for confidence that an SCF calculation using a DZP basis on the trimer would be qualitatively useful.

Optimization of the structure within a C_{3v} symmetry framework produced the planar C_{3h} structure of Fig. 2. The threefold axis of symmetry was imposed in accordance with the experimental findings of Prichard *et al.*[9] The planar distorted triangular structure was found to be a minimum on the energy surface with a ΔD_0 of 486 cm^{-1} composed of a ΔD_e of 915 cm^{-1}, a zero-point vibrational energy correction of 330 cm^{-1}, and a basis set superposition error correction of 99 cm^{-1}. The harmonic vibrational frequencies are listed in Table II. The centers of mass of the monomers were found to be 2.668 Å from the center of mass of the complex compared with the experimental value of 2.514 Å. Consequently, the rotational constant B was found to be 1691.2 MHz compared with the experimental value of 1885.8 MHz.

The intermolecular frequencies of the complex can be

(a)   (b)

H —— C ≡≡ C —— H
        4.581
H —— C ═ C —— H
   1.061 1.191 1.060
   138.1

1.068   1.226 (1.191)
H —— C ≡≡ C —— H
(1.060)
        2.628 (3.008)
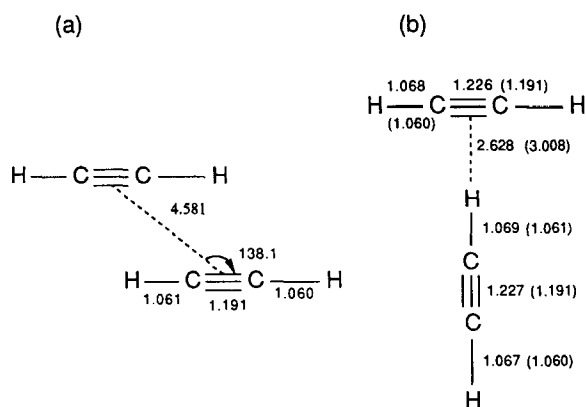H
1.069 (1.061)
C
1.227 (1.191)
C
1.067 (1.060)
H

FIG. 1. Structures for the acetylene dimer with distances in Å and angles in degrees. Values in (a) are at the SCF level. In (b), values are at the MP2 level with SCF values in parentheses.

TABLE I. Calculated harmonic frequencies ($\nu/$cm^{-1}) of the acetylene monomer and dimer at the DZP-MP2 level.

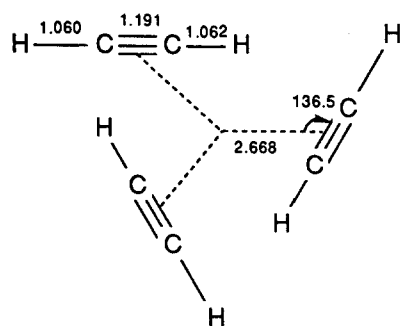| Mode	Monomer	Dimer
In-plane bend		22
Out-of-plane bend		67
Stretch		81
In-plane bend		106
CH stretch	3555	3547,3549
CC stretch	1956	1952,1954
CH stretch	3470	3458,3463
CH bend	560	561,568
		572,584
CH bend	732	730,743
		752,766

FIG. 2. Structure of the acetylene trimer with distances in Å and angles in degrees at the SCF level.

assigned as three stretches or shears (44, 44, and 61 cm^{-1}) with the mode at 61 cm^{-1} being the symmetric stretch or breathing mode, three in-plane bending modes (75, 75, and 133 cm^{-1}), and three out-of-plane bends (49, 49, and 61 cm^{-1}).

Finally we comment on the differences between the SCF and MP2 harmonic frequencies for the C_2H_2 monomers. The experimental harmonic frequencies are 3497, 2011, 3415, 624, and 747 cm^{-1}. We note that the CH stretch vibrations v_1, v_3 are reduced in error from 5.3%, 4.8% (SCF) to 1.6%, 1.6% (MP2) with respect to experimental values. The CC stretch changes from 9.7% (SCF) to −2.7% (MP2). The π_g bend (v_4) changes from 24.3% (SCF) to −10.2% (MP2) and the π_u (v_5) from 15.5% (SCF) to −2.0% (MP2). This rather extraordinary behavior for the bending vibrations is the subject of a manuscript in preparation.[24]

C. $(C_2H_4)_2$

In Fig. 3 we show the possible orientations of the ethylene dimer. Orientation (b) is a staggered-parallel structure with an inversion center, where the plane of each C_2H_4 unit is parallel. Orientation (c) consists of four possible T-shaped structures: (1) is a totally planar structure; (2) has one of the C_2H_4 units twisted by 90° out of the plane; (3) has the other C_2H_4 unit twisted by 90° out of the plane; and (4) has both units twisted by 90° out of the plane.

TABLE II. Calculated harmonic frequencies (v/cm^{-1}) of the acetylene monomer and trimer at the DZP-SCF level.

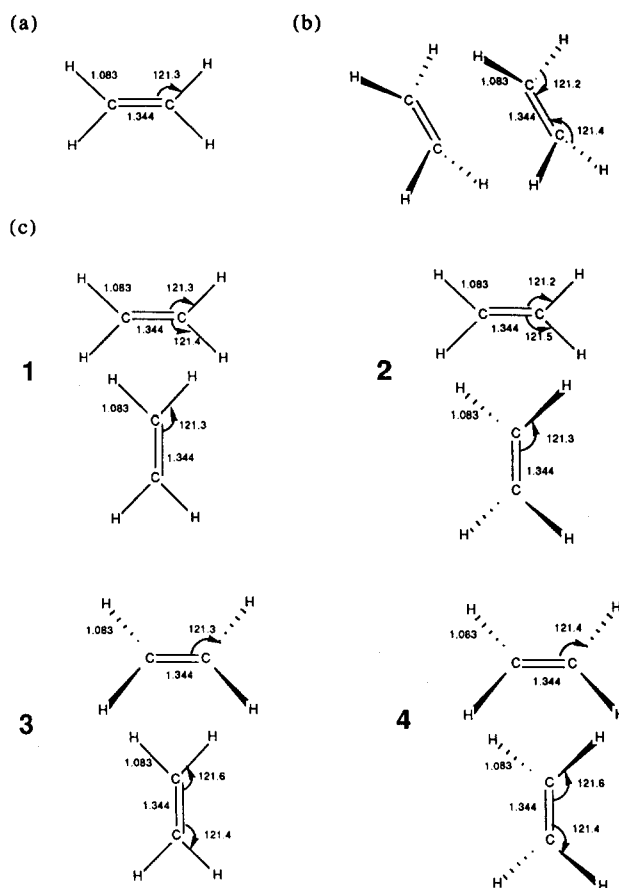| Mode	Monomer	Trimer
Shear		44,44
Out-of-plane bend		49,49
Stretch		61
Out-of-plane bend		61
In-plane bend		75,75
In-plane bend		133
CH stretch	3683	3673,3675,3675
CC stretch	2207	2201,2203,2203
CH stretch	3579	3566,3567,3567
CH bend	776	783,783,783
		787,787,795
CH bend	865	870,870,881
		881,883,891

FIG. 3. Structures for (a) the ethylene monomer, (b) the ethylene dimer in the parallel form, and (c) the ethylene dimer in the T-shaped forms 1–4. In (b), the angle between the intermolecular vector and the C–C of the ethylene molecule is 73.7° and the azimuthal angle of rotation of the monomers about the C–C bonds is 38.4°. All values are in Å or degrees and were calculated at the MP2 level.

We first studied the staggered-parallel structure and attempted a geometry optimization at the SCF level to obtain an initial guess of the geometrical parameters. It was not found possible to locate a stationary point, where the calculated "rotational frequencies" are all less than 0.1 cm^{-1} at this level of theory. Our view is that the surface is very flat in this region at the SCF level. We then moved to the MP2 level of theory and we were able to locate a stationary point. On calculating the harmonic frequencies, the stationary point was found to be a transition state with an imaginary frequency of $i16$ cm^{-1}. (As with all these calculations, rotational frequencies were less than 0.2 cm^{-1}.) The imaginary frequency appears to twist the C_2H_4 units into T-shaped structure (2), losing the inversion center.

The four T-shaped structures were optimized at the MP2 level and all of them are stationary points on this MP2 potential energy surface. We found the T-shaped (2) to be the only minimum on the surface and the other stationary points were found to be saddle points (higher order transition states).

The nature of the stationary point, energy lowering upon dimerization, intermolecular distance, and dipole moment of all the points are given in Table III. The T-shaped minimum has an equilibrium energy lowering with respect

TABLE III. Nature of the staionary point, distance between the center of C–C bonds (R_e/Å), energy lowering of the ethylene dimer with respect to isolated ethylene monomers (ΔD_e, ΔD_0/cm^{-1}), and dipole moment (D) of the various structures.

		Nature of stationary point	R_e/Å	ΔD_e/cm^{-1}	ΔD_0/cm^{-1}	Dipole moment/D
Parallel		Transition state	3.970	385	205	0
T-shaped	(1)	Transition state	4.690	180		0.002
	(2)	Minimum	4.312	420	220	0.007
	(3)	Transition state	4.463	270		0.054
	(4)	Transition state	4.493	240		0.051

to isolated monomers (ΔD_e) of 420 cm^{-1}. When this is corrected for zero-point energy, it gives a ΔD_0 value of 220 cm^{-1}. The parallel transition state has a ΔD_e of 385 cm^{-1} and a ΔD_0 of 205 cm^{-1}. The basis set superposition error was calculated at the SCF level using the standard procedure of Boys and Bernardi.[23] The correction for the T-shaped structure was 95 cm^{-1} and for the parallel structure was 51 cm^{-1}. The addition of the zero-point energy and the BSSE correction leads to the T-shaped structure being bound by 125 cm^{-1} and the parallel structure being bound by 154 cm^{-1}. Bearing in mind that the parallel structure has an imaginary frequency of only $i16$ cm^{-1} and the smallest real frequency of the T-shaped structure is 22 cm^{-1}, this means that these *ab initio* calculations indicate that it is not possible to say which is the minimum, but only that these two structures are both probable stable points on the surface. The fact that all of these transition states are so close in energy must mean that $(C_2H_4)_2$ has to be regarded as a highly dynamical system. The intermolecular distance between the center of the C–C bonds (R_e) is not directly comparable between the parallel and T-shaped structures. The parallel has a R_e of 3.970 Å. For the T-shaped structures, as expected, the minimum geometry has the lowest R_e of 4.312 Å.

There is a problem with the calculation of the BSSE at a correlated level. The evidence appears to be[25] that it is large for small basis sets (e.g., DZP). For $(C_2H_4)_2$ with MP2, it is indeed 340 cm^{-1} for the T-shaped minimum geometry. We investigated the BSSE for a larger basis set (TZ2P) and it is now 90 cm^{-1}, which is the same magnitude as the well depth. It is therefore not practical to use a basis set of a size which will reduce the BSSE to a value that is substantially smaller than the well depth. For this reason, in our calculations using a DZP basis, we have used the SCF value of the BSSE, and we recognize our MP2 values for ΔD_0 could be substantially in error, but it is the geometries that are the principal interest of this paper and we trust that these are not so affected by BSSE.

An interesting and enlightening feature of this study appears when one examines the dipole moment of the dimer in the various orientations. It was assumed[13] that the ethylene dimer had the parallel structure because the experimental measurements predicted a nonpolar system. However, the T-shaped minimum has a dipole moment of 0.007 D which is too low to be measured. So $(C_2H_4)_2$ having either an equilib-

rium geometry of T-shaped structure (2) or a staggered-parallel structure does not contradict the experimental result. T-shaped (1) also has a negligibly small dipole moment (0.002 D), however, T-shaped structures (3) and (4) have considerably larger dipole moments of 0.054 and 0.051 D, respectively, which are measurable. The dipole moment is along the C_2 axis with the positive end being the C_2H_4 unit containing the C–C bond that is bisected by the C_2 axis. If we define the dimer plane as the one containing the T-shaped structure (1), then twisting this C_2H_4 unit out of the dimer plane as in structures (3) and (4) causes the increase in the dipole. Contrast this with the low dipole of structures (1) and (2) which have the C_2H_4 unit in the dimer plane. Figure 3 shows the structural parameters of the ethylene dimer in all the orientations. It can be seen that the internal bond lengths and angles of each C_2H_4 unit are almost unchanged upon dimerization into any of the orientations. One of the small changes can be seen, e.g., in T-shaped structure (3), where one of the CCH bond angles has increased to 121.6° from the monomer value of 121.3°, to reduce slightly steric interactions.

Table IV shows the calculated intramolecular harmonic frequencies of $(C_2H_4)_2$ in T-shaped structure (2) and also the experimental frequencies of the ethylene dimer trapped in the argon matrix.[12] Each C_2H_4 molecule in the dimer must have a set of frequencies that are slightly different to each other due to coupling between the two molecules and that are shifted from the set of calculated isolated monomer frequencies. However, the shifts are small, with a calculated maximum magnitude of 6 cm^{-1}. This once again emphasizes the weakly bound nature of the complex. Experimentally, the coupled set of frequencies for each C_2H_4 molecule in the dimer could not be resolved, but as we calculated the splitting to be very small this must be expected, so only one peak was seen in each case (except for ν_5).[11] A direct comparison between the absolute calculated and experimental dimer frequencies is not applicable as the calculated values are harmonic frequencies, whereas the experimental values are fundamentals, however, we can look at the shifts. The experimental frequency shifts from ethylene monomer in the argon matrix to the dimer in the argon matrix are once again all small (less than 12 cm^{-1}), although there is a scatter between the calculated and experimental shifts, but it is also probable that part of the experimental shift originates from

TABLE IV. Calculated intramolecular harmonic frequencies (cm^{-1}) of $(C_2H_4)_2$ at equilibrium, experimental frequencies of $(C_2H_4)_2$ in the argon matrix, and monomer to dimer frequency shifts.

	Calculated			Experimental[a]		
	Dimer	Monomer	Shifts	Dimer	Monomer (in Ar matrix)	Shifts
ν_1	3247,3250	3249	$-2, +1$	3016	3028	-12
ν_2	1699,1704	1701	$-2, +3$	1623	1629	-6
ν_3	1390,1398	1394	$-4, +4$	1343	1345	-2
ν_4	1065,1072	1066	$-1, +6$	1027	$\cdots$	$\cdots$
ν_5	3334,3335	3334	$0, +1$	3078,3083	3094	$-16, -11$
ν_6	1259,1264	1262	$-3, +2$	1226	$\cdots$	$\cdots$
ν_7	958,959	959	$-1,0$	946	946	0
ν_8	799,800	802	$-3, -2$	$\cdots$	941	$\cdots$
ν_9	3360,3362	3362	$-2,0$	3097	3112	-5
ν_{10}	830,837	831	$-1, +6$	824	831	-7
ν_{11}	3222,3230	3224	$-2, +6$	2982	2995	-13
ν_{12}	1509,1510	1508	$+1, +2$	1437	1440	-3

[a] Experimental frequencies from Ref. 11.

the effect of the matrix rather than interaction between two ethylene molecules.

It should finally be added that the ν_8 monomer frequency appears not to be well calculated by this MP2-DZP approach. We are currently studying this problem and our conclusion appears to be that this "chair" vibration is not well described unless f functions are included in the basis set.[24]

The intermolecular frequencies of equilibrium $(C_2H_4)_2$ are all small and can be assigned as an in-plane bend (22 cm^{-1}), two out-of-plane bends (30 and 110 cm^{-1}), two out-of-plane shears (69 and 91 cm^{-1}), and the intermolecular stretch (72 cm^{-1}). In Table V, we list the full set of calculated harmonic frequencies for all the possible orientations. The splittings due to couplings between the C_2H_4 molecules are not large in any of the cases, always less than 10 cm^{-1}, and there are only small shifts in going from one orientation to the other. The T-shaped transition states all have more than one imaginary frequency because there is more than

TABLE V. Calculated harmonic frequencies (cm^{-1}) of $(C_2H_4)_2$ in all its orientations.

	Parallel	T shaped			
		(1)	(2)	(3)	(4)
ν_1	3248,3248	3249,3251	3247,3250	3247,3249	3248,3251
ν_2	1698,1700	1699,1702	1699,1704	1699,1700	1698,1700
ν_3	1393,1394	1390,1397	1390,1398	1390,1393	1390,1393
ν_4	1066,1069	1061,1065	1065,1072	1065,1067	1064,1067
ν_5	3333,3333	3334,3336	3334,3335	3331,3334	3332,3335
ν_6	1261,1262	1258,1262	1259,1264	1257,1262	1258,1262
ν_7	954,960	950,958	959,959	957,964	957,962
ν_8	792,800	790,795	799,800	794,805	794,805
ν_9	3360,3362	3363,3363	3360,3362	3360,3362	3360,3364
ν_{10}	830,831	828,832	830,837	826,832	826,831
ν_{11}	3224,3224	3225,3229	3222,3230	3223,3225	3223,3226
ν_{12}	1507,1508	1508,1508	1509,1510	1506,1507	1505,1508
Intermolecular	42	17	22	28	26
	48	53	30	35	33
	69	63	69	39	50
	76		72	54	
	121		91		
			110		
Imaginary	$i16$	$i42$		$i22$	$i23$
		$i61$		$i47$	$i24$
		$i74$			$i69$

one motion in each case that leads to the T-shaped minimum structure.

IV. CONCLUSION

In this paper MP2 studies have been performed for the minimum energy structures of $(C_2H_2)_2$ and $(C_2H_4)_2$. An SCF study has been performed to show that the minimum energy structure of $(C_2H_2)_3$ is C_{3h} rather than D_{3h}.

All three complexes have very shallow wells. For $(C_2H_2)_2$, $(C_2H_2)_3$, and $(C_2H_4)_2$, D_e is calculated as 606, 915, and 420 cm^{-1}, respectively. Zero-point vibrational energy correction for each is 173, 330, and 200 cm^{-1}, respectively. It is probably worth an observation that this correction is very much larger than might have been first thought, when one considers that the intermolecular stretch frequency for these complexes is 50, 61, and 72 cm^{-1}, respectively. However, the bend and shear intermolecular frequencies can be as large as 110 cm^{-1} and thus contribute very considerably to the zero-point vibrational energy correction. We must therefore recognize the possibility that the zero-point vibrational energy correction could be so large that certain weakly bound complexes may be unbound. For the complexes studied here, experimental evidence is that they do exist, but even so we observe that the zero-point vibrational energy correction is of the order of D_e. Of course, we must recognize that errors for such small *ab initio* values for D_e may be of the order of D_e.

Note added in proof: Professor R. O. Watts (University of Washington, Seattle) has communicated to us the probable existence of both the T-shaped and staggered-parallel structures for $(C_2H_2)_2$. We have optimized the staggered-parallel structure at the MP2-DZP level and find that it is a transition state with an imaginary frequency of 30 cm^{-1} level, and with a center-of-mass to center-of-mass distance of 4.310 Å, and weak-bond angle of 139.4°. Note that this dis-

tance is exactly the same as for the T-shaped structure. The T is lower in energy (D_e) by 76 cm^{-1}.

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