THE COMPUTATION OF VIBRATIONAL SPECTRA OF TRIPLET SPECIES

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

Computed IR spectra of triplet vinylidenecarbene, CH_2, CCO, and NCN are compared with experiment. Some triplets have much lower intensity spectra than the corresponding singlets, and for these care needs to be taken to get good computed spectra. Others are of higher intensity, and for these agreement is as good as in the usual singlet cases.

We have recently[1] computed the *ab initio* IR spectra of singlet and triplet vinylidene-carbene (*I*) in connection with Maier's photochemical synthesis of this new species (Scheme 1).
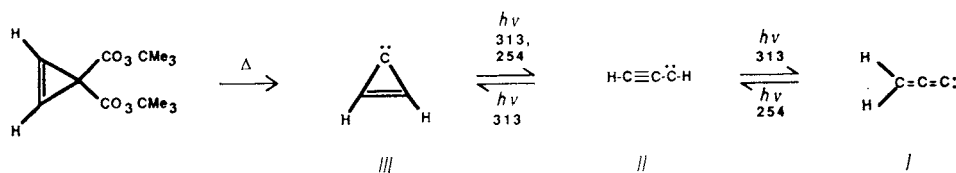
SCHEME 1

The two computed spectra are quite different, and comparison with Maier's experimental spectrum shows clearly (Fig. 1) that he has synthesized vinylidenecarbene in its singlet state.

On the other hand it appears that propargylene (*II*), the precursor of vinylidene-carbene, is a triplet; and to confirm its synthesis we set out to compute the spectrum of triplet propargylene. While there are now many examples of agreement between the *ab initio* computed IR spectra and those obtained experimentally[2], very few such examples exist for triplet species. One possible source of difficulty in the computation of triplet IR spectra is exemplified in Fig. 1 where relative, rather than absolute, intensities are plotted since absolute intensities are not easy to measure experimentally. That is, the strongest band in each of the three spectra in Fig. 1

is given unit intensity and others are shown in proportion. This disguises the fact that the strongest band in the theoretical spectrum of the triplet has an intensity of $2·4 \, \text{km mol}^{-1}$ which is only one seventh that of the strongest band in the singlet. It might then be expected that the per cent error in the computed triplet intensities would be greater than for the singlet. It is not obvious whether or not triplets will in general have low intensity IR spectra.

We therefore undertook the computation of several known triplets to determine whether *ab initio* spectra of triplets might be as reliable as has been found for singlet species. Unfortunately there are only a few experimental IR spectra for triplets of small enough size that reasonable theoretical calculations can be carried out. We shall examine three of these here.

CALCULATIONS

Methylene

It has now been well established that the ground state of methylene is a triplet, though the singlet has also been observed. Several basis sets were used to compute the vibrational spectra of singlet and triplet methylene with and without inclusion of correlation. Structures were first optimized for all basis sets (Table I) for both the singlet and triplet. Calculations of frequencies and intensities were then carried out using GAUSSIAN 86[3], and the results are given in Table II and Figs 2 and 3. In the case of singlet methylene the agreement between theory and experiment for the
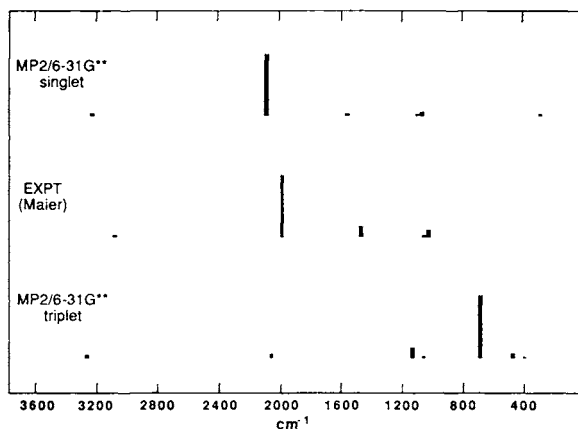

FIG. 1

Comparison of computed IR spectra of singlet and triplet vinylidenecarbene with experiment

frequencies is in line with what is expected based on our experience with other molecules[2]; and, except for the expected shift toward lower frequencies, Fig. 2 shows that the spectra change little as the calculation is improved from 6-31G*. While several groups have reported the IR spectrum of singlet methylene[4-7], unfortunately none has reported relative intensities.

For triplet methylene, the experimental situation is even worse since only v_2, the bending frequency, has been observed[8-10]. The computed spectra for triplet methylene shown in Fig. 3 change significantly as the calculations are improved. The antisymmetric C—H stretch is strongest in the UHF/6-31G* spectrum, but on going to MP2/6-311G* the absorption of the bending vibration becomes most intense, in agreement with the observation that only this frequency has been observed. Bunker and Langhoff[11] have also suggested that v_1 and v_3 should be of very low intensity based on *ab initio* calculations of the transition moments of triplet methylene. Table II shows that for triplet methylene, as for triplet vinylidenecarbene, the strongest band is much weaker than for the singlet. This may explain the unexpectedly poor quality of the UHF/6-31G* spectrum.

CCO *Triplet*

The free radical CCO is known to exist as a triplet $\left(^3\Sigma^-\right)^{12-13}$. Its geometry* was optimized in UHF/6-31G* (C—C: 1·3542, C—O: 1·139, $E/e_0 = -150.46216$) and

Computed geometries and energies of singlet and triplet methylene

Computation[a]	Singlet			Triplet		
	R_{C-H} 10^{-10} m	<HCH deg.	energy[b] E/e_0	R_{C-H} 10^{-10} m	<HCH deg.	energy[b] E/e_0
SCF/6-31G*	1·097	103·1	−38·87237	1·071	130·7	−38·92150
SCF/6-311G*	1·097	103·1	−38·88381	1·072	131·0	−38·92970
SCF/6-311G**	1·099	103·2	−38·88751	1·072	131·7	−38·93407
MP2/6-31G*	1·109	102·1	−38·97401	1·077	131·6	−39·00744
MP2/6-311G*	1·107	102·4	−39·00590	1·077	132·4	−39·03575
MP2/6-311G**	1·110	101·4	−39·02238	1·078	132·3	−39·05115
MP4/6-311G**	1·116	100·8	−39·04718	1·081	132·5	−39·07043

[a] Restricted SCF and MP2 calculations were done for the singlet and unrestricted for the triplet;
[b] e_0 is 1 *hartree*, i.e., $e_0 = 2·6255 . 10^6$ J/mol.

* Hereafter the bond lengths are in 10^{-10} m, and energies are treated as dimensionless quantities relative to 1 "*hartree*" ($e_0 = 2·6255 . 10^6$ J/mol).

TABLE II

Computed and experimental IR spectra of singlet and triplet methylene

Spectrum	Singlet[e]						Triplet[e]					
	$\nu_1(A_1)$ cm^{-1}	intensity km mol^{-1}	$\nu_2(A_1)$ cm^{-1}	intensity km mol^{-1}	$\nu_3(B_2)$ cm^{-1}	intensity km mol^{-1}	$\nu_1(A_1)$ cm^{-1}	intensity km mol^{-1}	$\nu_2(A_1)$ cm^{-1}	intensity km mol^{-1}	$\nu_3(B_2)$ cm^{-1}	intensity km mol^{-1}
SCF/6-31G*	3 130	61·98	1 564	0·02	3 193	125·38	3 325	0·50	1 239	2·36	3 525	3·84
SCF/6-311G*	3 116	76·46	1 545	1·92	3 176	113·11	3 281	0·00	1 216	3·92	3 486	3·41
SCF/6-311G**	3 092	69·12	1 502	1·27	3 154	98·21	3 265	0·06	1 201	5·11	3 476	0·99
MP2/6-31G*	3 002	69·10	1 499	0·29	3 086	110·17	3 251	1·44	1 192	5·91	3 472	0·44
MP2/6-311G*	2 995	75·38	1 480	1·20	3 077	93·31	3 206	0·59	1 153	9·23	3 437	0·01
MP2/6-311G**	2 992	76·85	1 426	0·00	3 064	94·65	3 208	0·54	1 156	6·98	3 440	0·00
MP4/6-311G**	2 934	—	1 426	—	2 997	—	3 175	—	1 144	—	3 401	—
Expt[a]	2 806	—	1 353	—	2 880	—	—	—	963	—	—	—
DZ + P[b]	3 127	—	1 495	—	3 204	—	3 297	—	1 304	—	3 505	—
CI/DZ + P[b]	2 992	—	1 441	—	3 076	—	3 218	—	1 175	—	3 435	—
CCD[c]	—	—	—	—	—	—	2 784	—	1 385	—	2 880	—
SOCI												
(anharmonic)[d]	—	—	—	—	—	—	2 985	—	967	—	3 205	—

[a] Refs[4-10], [b] ref.[16], [c] ref.[17], [d] ref.[11], [e] restricted SCF and MP2 calculations were done for the singlet and unrestricted for the triplet.

UMP2/6-31G* (C—C: 1·3760, C—O: 1·172, $E/e_0 = -150\cdot84152$) calculations. The vibrational spectrum of CCO in a matrix has been reported[12,13], and is compared with our computed spectra in Table III and Fig. 4. Although exact relative
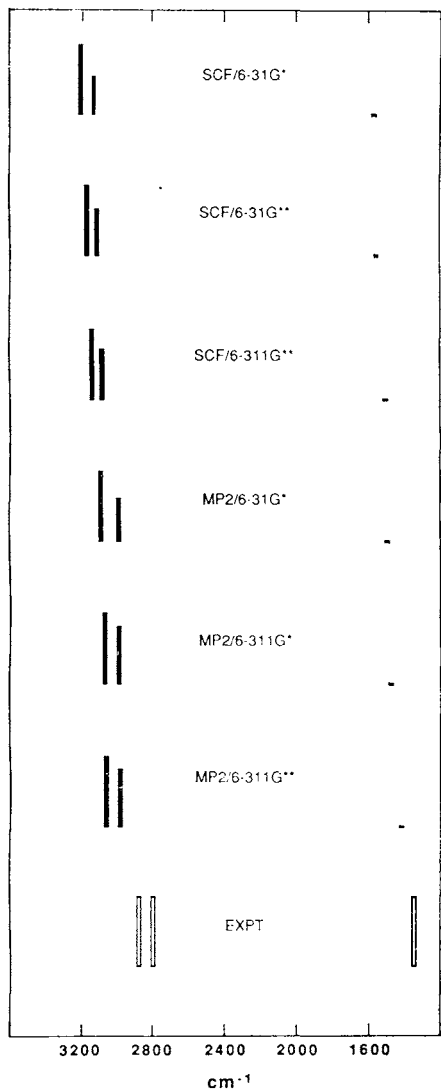

FIG. 2

Calculated and experimental IR spectra of singlet methylene. Intensities are not shown for the experimental spectrum
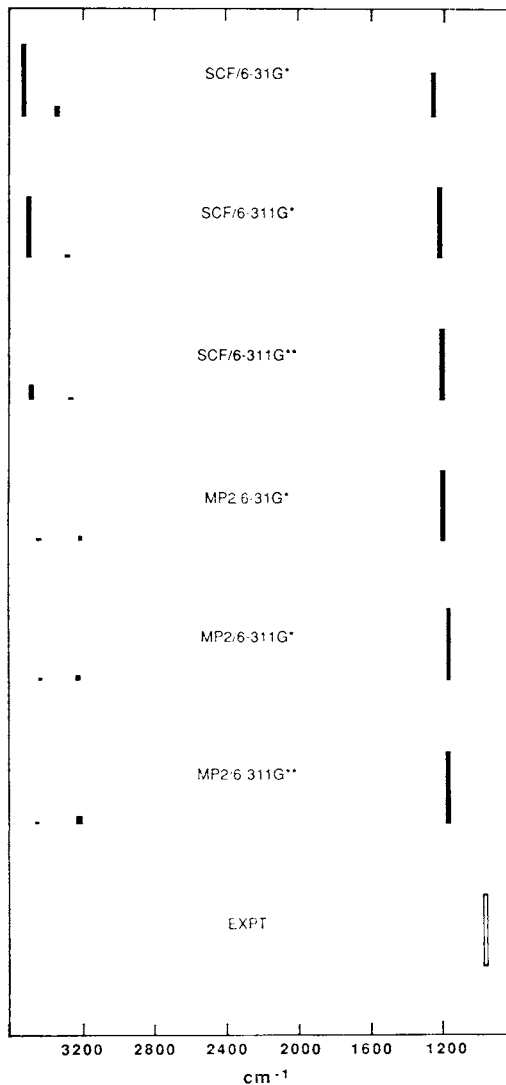
FIG. 3

Calculated and experimental IR spectra of triplet methylene. Intensities are not shown for the experimental spectrum

intensities were not reported, the intensities of the three bands were described qualitatively. Both methods of calculation predict a strong band, one of moderate intensity and one to be of very weak intensity. Calculated absolute intensities (Table III) are much greater than those of triplet methylene and give good agreement with experiment. Furthermore, the agreement between calculated and observed frequencies is like that we have come to expect for molecules with singlet ground states.

Cyanogen Azide

Unlike CCO, cyanogen azide (NCN) (UHF/6-31G*, C—N: 1·2332, $E/e_0 =$ $= -146·71547$ and UMP2/6-31G*, C—N: 1·2219, $E/e_0 = -147·06394$) has only two IR active bands while the third is Raman active only. The frequencies of the two IR active bands have been reported[14,15] along with a qualitative description of their intensities. The frequency of the third band (Σ_g) was deduced from a weak combination band with the Σ_u band[14]. Our computed vibrational spectra of NCN are compared with experiment in Fig. 5 and Table IV. Calculated absolute intensities are high for this triplet (Table IV), and the relative intensities in Fig. 5 are seen to

TABLE III
Comparison of computed vibrational spectra of triplet CCO with that of experiment

Spectrum	$\nu(\Sigma)$ cm^{-1}	Intensity km mol^{-1}	$\nu(\Pi)$ cm^{-1}	Intensity km mol^{-1}	$\nu(\Sigma)$ cm^{-1}	Intensity km mol^{-1}
UHF/6-31G*	2 221	368·20	455	74·19	1 171	0·00
UMP2/6-31G*	2 080	355·98	394	50·77	1 089	9·88
Experiment[a]	1 969	strong	381	medium	1 064	weak

[a] Ref.[12].

TABLE IV
Comparison of computed vibrational spectra of triplet NCN with that of experiment

Spectrum	$\nu(\Sigma_g)$ cm^{-1}	Intensity[a] km mol^{-1}	$\nu(\Pi)$ cm^{-1}	Intensity km mol^{-1}	$\nu(\Sigma_u)$ cm^{-1}	Intensity km mol^{-1}
UHF/6-31G*	1 242	—	423	13·67	1 470	329·30
UMP2/6-31G*	1 369	—	376	24·41	995	597·66
Experiment	1 197[b]	—	423	medium	1 475	v. strong

[a] This mode is not IR active; [b] see text.

agree reasonably well with experiment. The unusual feature is that while the UHF spectrum agrees well with experiment, in the UMP2 calculations the Σ_u band is shifted to 994 cm^{-1}, *below* the observed 1 475 cm^{-1}. Not only is this disagreement far greater than we have observed for any other comparison of computed with experimental spectra for singlets, but the dramatic shift from the UHF to UMP2 (1 470 to 995 cm^{-1}) is far greater than any we have seen in the past.

This is somewhat reminiscent of the problem that we encountered with propargylene when we computed its triplet spectrum at the UHF and UMP2 levels. The symmetric structure IV was found to be a minimum with the UHF/6-31G** basis set. On the other hand, on reoptimization at with UMP2/6-31G** IV becomes a transition structure which lies only about 1 kcal above the two equivalent unsymmetric structures Va and Vb (Scheme 2).

$$HC\equiv C-C\overset{H}{\diagup} \rightleftharpoons HC=C=CH \rightleftharpoons \overset{H}{\diagdown}C-C\equiv CH$$

$$Va \qquad\qquad IV \qquad\qquad Vb$$
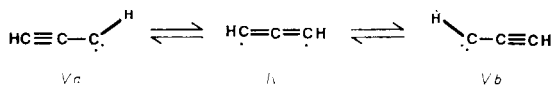
SCHEME 2

When one considers that NCN and HCCCH are isoelectronic, is it plausible that a similar problem might exist for NCN. However further studies are required here.
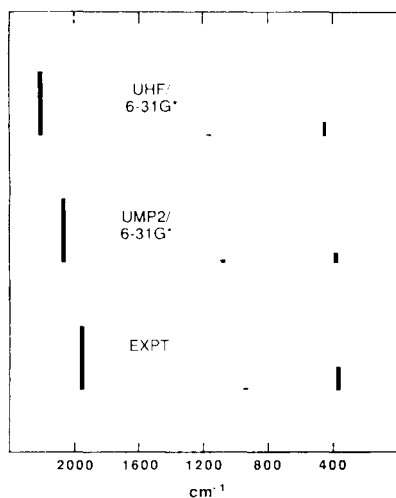

FIG. 4

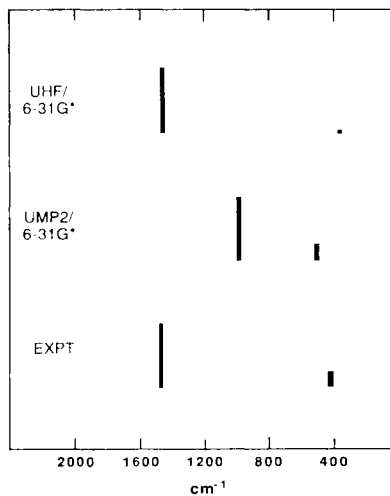Calculated and experimental IR spectra of triplet CCO

FIG. 5

Calculated and experimental IR spectra of triplet NCN

CONCLUSION

We conclude, based on these preliminary examples, that there is hope the good agreement found earlier between computed and experimental vibrational spectra of singlets will also be found for triplets, especially if one is careful to exclude cases of low absolute intensity. However, more examples need to be studied both experimentally and theoretically before a definite conclusion can be reached.

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