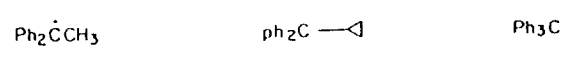

10 **11** **12**

more, the vibrational structure of **8** similar to that reported for radicls **10#12**.[10] The first observable vibrational line in the spectrum of **8** is 1041 cm^{-1}. Similar values were reported for **10**−**12** (1049 cm^{-1}, 1060 cm^{-1} and 1020 cm^{-1},[5] respectively) which the authors attributed to a C-C stretching mode. Finally, the intermediate **8** has been demonstrated to be photolabile, producing diphenylcarbene upon photolysis. We find it difficult to envision another plausible structure for **8** which could be consistent with all of the facts presented above.

In summary, 254 nm photolysis of **7** at 77K yields monoradical **8**, which was detected by its fluorescence spectrum. Monoradical **8** can be further photolyzed to **9** either by continued 254 nm irradiation, or more efficiently by laser irradiation. This represents the first case to our knowledge where a dihalide has been photolyzed to the corresponding carbene. This is possible due to the interesting photochemical properties of the intermediate radical **8**, which is able to undergo photodissociation to a carbene. This procedure readily lends itself to extension into various other systems where one wishes to achieve similar goals of selective excitation.

Acknowledgement. This work was supported by the Korea Science and Engineering Foundation Program.

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The ab Initio Calculation of the Spectroscopic Properties of FO and FO^+

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The spectroscopic properties of FO† and FO were investigated by ab initio calculation. Several different levels of theory, MP3/6-31G*, MP4/6-311G* and CISD/6-31G*, were tried and compared with experimental results of FO. In the overall performance the CISD showed the best agreement. Based on these results the spectroscopic constants of FO† are predicted.

Introduction

In the past few years the vibrational-rotational transitions of molecular ions were investigated by more improved experimental techniques[1]. The astrophysical work has shown that those molecular ions are widely distributed in the interstellar medium and has provided a great deal of information on their chemistry and dynamical conditions.

The molecular ions studied so far include CO^+,[2] HCO^+,[3,4] HN_2^+,[3] NO^+,[6] NH_4^+,[7] H_2F^+,[8]…*etc.*

The search for the spectra of such species may be considerably facilitated by predictions from very accurate *ab initio* calculations[9]. An important use of accurate *ab initio* geometries is corroborating evidence for the discovery of new molecular species in the interstellar medium and in the laboratory. Theoretical geometry predictions for candidate molecules, particularly those terrestrially evanescent species not amenable to ordinary laboratory analysis, can be used to define frequency regions for spectroscopic searches in the laboratory and in space. And it is the purpose of this work to provide spectroscopic information about position of rotational and vibrational transitions of FO^+.

The fluorine monoxide radical, FO, has been observed in the gas phase by recent laser magnetic resonance[10](LMR) and photoelectron spectroscopy[11]. The existence of the oxygen monofluoride radical has been a matter of interest for over 30 years. The conclusive evidence for the existence of this molecule was derived by matrix isolation[12,13] and the molecular beam mass spectrometry[14]. The theoretical calculations on this molecule are also available[15,16]. But for FO^+ no experimental search has been tried and the theoretical calculations[15] are also scarce.

In this paper the Moller Plesset(MP) perturbation method[17] and the configuration interaction(CI) method are tried with the different basis sets. The same methods of calculations are also tried on FO to estimate possible error and to get some idea for the empirical corrections.

Since FO radical have been studied in both experiment and theory it will give good criteria for the estimation of the data of FO^+ molecule.

For the simple molecules with first row atoms the *ab initio* calculation data with GAUSSIAN-82 program have been analyzed for the error[18]. Starting from the Hartree-Fock(HF) wave function, either Moller-Plesset perturbation theory to third order(MP3) or configuration interation with all double substitution(CID), in the 6-31G* basis, reduces the mean bond length error to $\pm 1\%$.

The configuration interaction including all single and double substitutions(CISD) in 6-311G* basis gave rotational frequencies to an accuracy of ± 0.4GHz when an empirical correction is applied. For FO^+ and FO molecules all these level of molecular orbital theory are applied.

Calculation and Results

FO^+. Throughout this calculation the GAUSSIAN-82 program by J.A. Pople has been used. The bond length of FO^+ can be obtained by optimization routine of the program, but this optimized bond length is not always same as the one obtained from potential function curve, which can be used for the other spectroscopic properties. Several different levels of single point calculations were performed for this potential energy curve. First thirdorder Moller-Plesset (MP3) perturbation method[19] with 6-31G* basis set[20] (single-zeta core, double-zeta valence, polarization functions on nonhydrogen atoms) are tried and the results are shown in Table 1.

The complete fourth-order Moller-Plesset calculations including single, double, triple and quadruple substitutions (MP4SDTQ)[19] are also carried out with 6-311G* basis set[21] (single-zeta core, triple-zeta valence, polarization functions on all atoms) and the results are listed in Table 2. In the process of this MP4SDTQ calculations the MP3 and the MP4DQ (fourth-order Moller-Plesset method including double and quadruple substitutions) energies were also calculated and those results are shown in Table 1 and 2.

Table 1. The Results of MP3/6-31G* and MP3/6-311G* Calculations of FO^+

R(a.u.)	Energy (a.u.)	
	6-31G*	6-311G*
1.800	-173.770829	-173.909700
1.900	-173.864198	-173.990045
2.000	-173.923304	-174.038894
2.100	-173.958215	-174.065757
2.200	-173.976095	-174.077421
2.300	-173.982085	-174.078743
2.350	-173.981780	
2.400	-173.979651	-174.072923
2.450	-173.975742	
2.500	-173.969911	-174.060690
2.550	-173.962294	
2.600	-173.953817	-174.043260
2.700	-173.938492	-174.028036
2.800	-173.927738	-174.018093
2.900	-173.920984	

Table 2. The Results of MP4SDTQ/6-311G* and MP4DQ/6-311G* Calculations of FO^+

R(a.u.)	Energy (a.u.)	
	MP4SDTQ/6-311G*	MP4DQ/6-311G*
1.800	-173.922531	-173.911147
1.900	-174.005652	-173.991887
2.000	-174.057847	-174.041203
2.100	-174.088459	-174.068571
2.200	-174.103786	-174.080706
2.300	-174.107806	-174.082343
2.400	-174.102799	-174.076597
2.500	-174.089365	-174.064338
2.600	-174.069397	-174.047046
2.700	-174.050750	-174.031879
2.800	-174.037323	-174.021792

For the potential curve these energy points are fitted to the following polynomial.

$$V - V_0 = \sum_{n=2}^{6} f^n \Delta R^n / n! \qquad \Delta R = R - R_e \tag{1}$$

This polynomial of sixth degree was used in Botschwina's work[22] of fitting the potential energy points and it gave good results of spectroscopic data. Therefore the energy points from MP3 and MP4 calculation were fitted to 7 parameters including R_e and V_o values with 5 coefficients. The results are in Table 3. The potential curves obtained from the fits are shown in Figure 1. The higher order of polynomial functions were tested to find out whether they gave better fit, but the fit wasn't improved by more terms in polynomial function.

The experimental transition frequency of the molecular

Table 3. The Results of Fit with the Data of MP3 and MP4 Calculations of FO^+

	MP3/6-31G*	MP4SDTQ/6-311G*	MP4DQ/6-311G*
R_e(Å)	1.2274	1.2117	1.2006
V_0(a.u.)	-173.98207	-174.10806	-174.08262
f^2	0.82338	0.96055	0.79826
f^3	-1.63967	-1.50870	-2.01285
f^4	25.97861	2.64638	7.05473
f^5	-156.39607	-119.07110	-101.48916
f^6	-2260.02941	53.13074	-93.34966

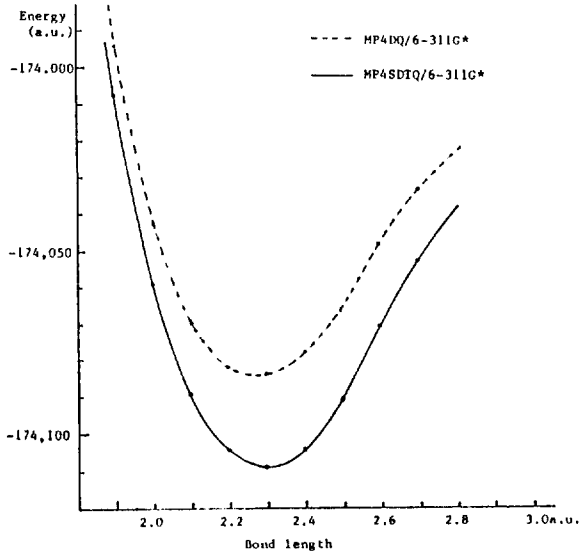

Figure 1. The potential curve of FO^+ with 6th degree of polynomial function.

rotation can be obtained from B_v, rotational constants at specific vibrational state. The B_v is related to the equilibrium rotational constant, B_e by the following equation

$$B_v = B_e - \alpha_e (V + \frac{1}{2}) + \quad (2)$$

The B_e can be calculated with R_e value obtained from above fitting results. The α_e must be known to get B_v, and it can be derived, if the potential function is known[23].

$$\alpha_e = \frac{24 B_e^3 r_e^3 g}{\omega_e^3} - 6\frac{B_e^2}{\omega_e} (cm^{-1}) \quad (3)$$

The g is the coefficient of cubic term in the potential function. The term determines the asymmetry of the potential curve. Therefore the g value from the fit gave α_e value, and with α_e and B_e the B_v was calculated. Then the transition frequencies were obtained from B_v. These final spectroscopic constants. ω_e, α_e, B_0 and B_e values are given in Table 4.

Table 5. The Results of CISD/6-31G* Calculation of FO^+

R(a.u.)	Energy(a.u.)
1.800	-173.764475
2.000	-173.917687
2.100	-173.953540
2.200	-173.972765
2.300	-173.980439
2.400	-173.980119
2.500	-173.974011
2.700	-173.952608
2.900	-173.934438
3.100	-173.923034
3.400	-173.914783
3.900	-173.910732

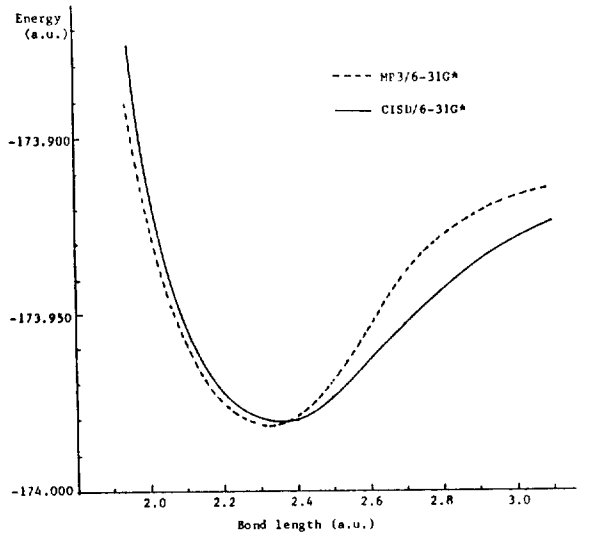

Figure 2. The potential curve of FO^+.

The bond length in MP4 calculation is shorter than MP3 results. From the photoelectron spectroscopy of FO[11] the lowest ionic state of FO^+, $X^3\Sigma^-$ was analyzed to obtain R_e and ω_e. The estimated R_e value was 1.23 ± 0.01Å and ω_e was 1300cm^{-1}. The R_e from MP3 results agrees with that value reasonably well but the ω_e values are too large compared to the experimental value.

To check the possibility of lowering the vibrational constant we next tried CI calculation. The single point CI calculation takes much longer time and gives higher energy than

Table 4. The Spectroscopic Properties of FO^+

Method	V_0(a.u.)	R_e(Å)	ω_e(cm^{-1})	α_e(cm^{-1})	B_e(cm^{-1})	D_e(MHz)
MP3/6-31G*	-173.98207	1.2274	1582.9	0.0034	1.28853	0.1024
MP4DQ/6-311G*	-174.08262	1.2006	1558.5	0.0063	1.34682	0.1206
MP4SDTQ/6-311G*	-174.10806	1.2117	1709.6	0.0012	1.32227	0.0949
CISD/6-31G*	-173.98098	1.2327	1426.6	0.0187	1.27760	0.1228
Exp.[a]		1.23	1300			

[a] Photoelectron spectroscopy ref. (11).

Table 6. The Results of MP3/6-31G*and MP4/6-311G* Calculations of FO

R(a.u.)	Energy(a.u.)		
	MP3/6-31G*	MP4DQ/6-311G*	MP4SDTQ/6-311G*
1.950	-174.268427	-174.394583	-174.404815
2.050	-174.337711	-174.455778	-174.467255
2.150	-174.383972	-174.495883	-174.508694
2.250	-174.413714	-174.520969	-174.535128
2.350	-174.431637	-174.535378	-174.550832
2.400	-174.437258		
2.450	-174.441087	-174.542170	-174.558818
2.500	-174.443349		
2.550	-174.444115	-174.543147	-174.560822
2.600	-174.443029		
2.650	-174.438841	-174.535710	-174.553944
2.750	-174.422977	-174.519533	-174.536796
2.850	-174.409130	-174.506704	-174.521818
2.950	-174.400017	-174.498724	-174.511578
3.050	-174.394469	-174.494280	-174.505173
3.150		-174.492123	-174.501425
3.500	-174.388507	-174.492015	-174.497986
4.000	-174.389411	-174.494453	-174.498669

Table 7. The Results of Fit with data of MP3 and MP4 Calculations of FO

	MP3/6-31G*	MP4SDTQ/6-311G*	MP4DQ/6-311G*
R_e(Å)	1.3214	1.3046	1.2981
V_0(a.u.)	-174.44282	-174.55729	-174.53966
f^2	0.71549	0.56908	0.49895
f^3	-2.23339	-2.61719	-2.74853
f^4	0.95977	0.99133	2.01951
f^5	0.04491	20.75254	27.27834
f^6	18.72672	-45.27458	-60.99118

MP calculation, but the potential curve usually differ from the previous ones. The results of CISD with 6-31G* basis set are shown in Table 5 and the spectroscopic constants are listed in Table 4. In Figure 2 the potential curve obtained from CISD/6-31G* calculation is illustrated with MP3/6-31G* curve. Indeed the shape of potential curve is different for CISD calculation. The minimum point has shifted to the longer distance and the curve broaden out. The bond length get longer and ω_e value decrease, and these values seem closer to the above investigated results.

Table 8. The Total Energies from CISD/6-31G* Calculations of FO

R(a.u.)	Energy(a.u.)
2.050	-174.327324
2.200	-174.390212
2.300	-174.413542
2.400	-174.426809
2.500	-174.432822
2.550	-174.433701
2.600	-174.433231
2.700	-174.427173
2.900	-174.409163
3.100	-174.396380
3.400	-174.387031
3.900	-174.383811

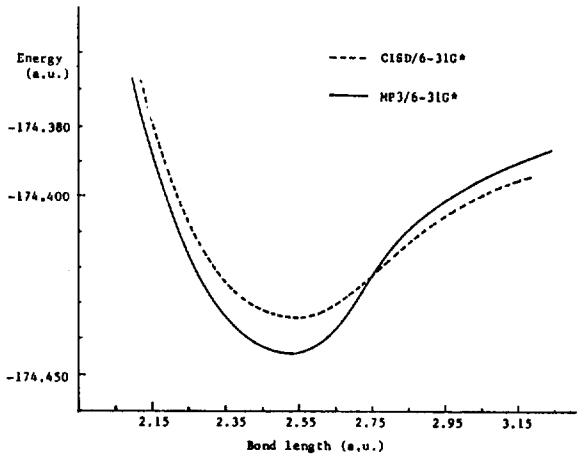

Figure 3. The potential curve of FO.

Therefore the CISD calculation seems to give most reasonable results, even though it takes much longer time for whole potential curve.

FO. The FO radical was studied to estimate the error in the calculation of FO^+ molecule. For FO radical both the experimental[10-14] and also theoretical data[15,16,24] are available. The MP3 calculation with 6-31G* basis set and MP4 calculation with 6-311G* basis set are performed and the results are in Table 6. The fit to the sixth order polynomial gave the results listed in Table 7. All the energy points were included in these fittings. Specially the last two points at 3.50 and 4.0 a.u. made a marked difference in fit. As in FO^+ case the CISD calculations with 6-31G* basis set were tried and the results are listed in Table 8. For comparison purpose the

Table 9. The Spectroscopic Properties of FO

Method	V_0(a.u.)	R_e(Å)	ω_e(cm^{-1})	α_e(cm^{-1})	B_e(cm^{-1})	D_e(MHz)
MP3/6-31G*	-174.44282	1.3214	1475.5	0.0080	1.11183	0.0757
MP4DQ/6-311G*	-174.53966	1.2981	1232.2	0.0226	1.15204	0.1208
MP4SDTQ/6-311G*	-174.55729	1.3046	1315.9	0.0165	1.14061	0.1028
CISD/6-31G*	-174.43331	1.3387	1267.6	0.0128	1.08318	0.0948
SCF[a]	-174.19502	1.321	1211	0.0097	1.104	
Exp.[b]		1.35789	1033.4	0.0135	1.05955	0.12

[a] Reference (15) [b] Laser magnetic resonance ref. (10).

potential curve with MP3 and CISD energies are shown in Figure 3. After fitting with CISD data the spectroscopic constants were calculated. In Table 9 the spectroscopic properties from all calculations are given along with experimental and theoretical literature values.

Discussion

From the spectroscopic data of FO, it can be noted that the best performance is achieved by the configuration interaction technique, CISD. With the 6–31G* basis set the energies are rather higher in CISD calculations, but the spectroscopic constants from the potential function show a good agreement. The bond length of FO is about 0.02Å shorter than the experimental value, but accounting the experimental error estimated as about ±0.01Å, the 1.3387Å is close to that value. The most of theoretical values are shorter than these values. Besides above SCF value, 1.321Å, Lathan *et al.*[24] gave 1.337Å.

The ω_e values are the ones which show the most discrepancies from the experimental value. Most of the calculations, regardless of the basis set and method, showed higher value of ω_e. For MP4DQ/6–311G* the ω_e value seems to be lower, but the bond length gets too short. The relation between bond length and ω_e exists in all MP calculations. Therefore the most reasonable values were obtained from CISD/6–31G*. The reason of the high ω_e value was not found, but the basis set improvement in CI calculation, for example CISD/6–311G* or CISD with input basis set, might give better results.

For the other α_e and D_e values also CISD gave good agreement with experimental values. In our previous paper[25], the spectroscopic properties of SiO were found to be close to the results of MP4DQ calculations. But the work of DeFrees *et al.*[18] has proved that the CI level of theory gave the best agreement. In this study also the CISD calculations show the best overall performance. Therefore the spectroscopic transitions of FO^+ can be calculated from the results of CISD, and the value is expected to be reasonably close to real transition frequencies.

Acknowledgement. This work was supported by 1987 research program of Asan Foundation.

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