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DENSITY FUNCTIONAL THEORY ANALYSIS OF GROUND STATE AND EVALUATION OF TRANSITION PROBABILITY PARAMETERS FOR CARBON MONO-FLUORIDE MOLECULE[**]

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In view of astrophysical application, the ground state molecular parameters such as bond length, dipole moment, rotational constant, harmonic frequency, IR intensity, vibrational temperature of the astrophysically significant diatomic molecule of carbon mono-fluoride (CF) were derived using B3LYP hybrid density functional theory with three basis sets of 3-21G, 6-31G, and 6-311G. The computed data were collectively compared with the values reported in the literature. It was found that the vibrational temperature obtained using the density functional theory approach resembles the favorable temperature for the formation of the CF molecule in an interstellar medium. The transition probability parameters, namely Franck–Condon factors and r-centroids were evaluated for A–X, B–X, and D–X band systems of the CF molecule, using a more reliable numerical integration procedure. The molecular parameters of ground state obtained in the present study was compared with the reported values for better justification. The results of Franck–Condon factors and r-centroids were also discussed in view of astrophysical application.

Keywords: *carbon mono-fluoride molecule, density functional theory, Franck–Condon factor, r-centroid, astrophysical significance.*

АНАЛИЗ ОСНОВНОГО СОСТОЯНИЯ И ВЕРОЯТНОСТЕЙ ПЕРЕХОДОВ В МОЛЕКУЛЕ МОНОФТОРИДА УГЛЕРОДА МЕТОДОМ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

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Для астрофизически значимой двухатомной молекулы монофторида углерода (CF) получены параметры молекулы в основном состоянии (длина связи, дипольный момент, постоянная вращения, частота гармоники, интенсивность ИК-излучения и колебательная температура) с использованием теории функционала плотности с тремя базовыми наборами 3-21G, 6-31G и 6-311G и сопоставлены

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с литературными данными. Установлено, что колебательная температура, найденная с помощью теории функционала плотности, схожа с температурой, благоприятной для образования молекулы CF в межзвездной среде. Параметры вероятности перехода, а именно факторы Франка–Кондона и r-центроиды, оценены для систем полос A–X, B–X и D–X молекулы CF с использованием более надежной процедуры численного интегрирования. Факторы Франка–Кондона и r-центроиды рассмотрены с точки зрения применения в астрофизике.

Ключевые слова: *молекула монофторида углерода, теория функционала плотности, фактор Франка–Кондона, r-центроид, астрофизическое значение.*

Introduction. Molecules play a fundamental role in deciding the dynamics and evolution of each and everything in the universe. The most interesting astronomical phenomena, such as the arrangement of galaxies, galactic collisions, configuration of stars and planets, and the injection of material into the interstellar medium (ISM) through stellar winds and explosions are particularly revealed only through the matter, which is assumed to be the atoms and molecules packed at a higher-than-average density. The study of the spectra of diatomic molecules has longstanding importance in various applications such as laser cooling [1–3], machine learning [4], astrophysics [5], physical chemistry, and nuclear physics [6], etc. The numerous diatomic species that are produced from gaseous (or) solid precursors are frequently probed via astronomical observations. The analysis of such species is very much significant for i) the understanding of celestial objects and ii) the estimation of physical conditions of the astrophysical sources emitting radiation. In view of astronomical applications, it was found that the study on diatomic molecules is very prominent for both theoretical and experimental investigations [7–10]. Among the astrophysically significant diatomic molecules, the light diatomic fluorides, particularly the alkaline earth metal fluorides are of great importance for the understanding of a chemical bond and for the estimation of physical conditions of the astrophysical sources emitting the radiation.

The fluorine-bearing diatomic molecule, especially carbon mono-fluoride (CF), has been experimentally investigated by many researchers. For instance, a rotational analysis of four bands of *A–X* transition and the vibrational analysis of the *B–X* system was conducted, and the rotational constants were also estimated from band-head separations by Andrews and Barrow [11, 12]. Dunning [13] performed the multi-configuration Hartree–Fock calculations for the low-lying valence states of the CF molecule. Hartree–Fock and multi-configuration Hartree–Fock calculations were performed by White et al. [14] for some low-lying Rydberg states of the CF molecule. Porter et al. [15] investigated the *A–X* band system of the CF molecule with high dispersion in the region of 2190–2965 Å and analyzed the rotational structure of 18 bands. Adiabatic potential energy curves of ground and 12-doublet excited electronic states of the CF molecule were constructed by Petsalakis [16] using multi-reference single- and double-excitation configuration interaction (MRDCI) calculations.

However, in the literature there is a lack of investigation of the CF molecule towards the identification of the CF molecule in a celestial environment. This may be because of the scarcity of an extensive set of spectroscopic parameters of the CF molecule derived from both theoretical and experimental observations. Hence, there is a need for a theoretical background of ground electronic state properties and transition probability parameters for the band systems of *D–X*, *A–X*, and *B–X* of the CF molecule, which is believed to be the key component found in celestial objects such as the sun, stars, comets, and ISM. Keeping this in mind, the ground-state molecular parameters such as bond length, dipole moment, harmonic frequency, vibrational temperature, and the transition probability parameters such as Franck–Condon factors (FCFs) and *r*-centroids for three band systems have been evaluated in the present study by using the density functional theory (DFT) along with a suitable numerical integration method.

Computational procedure. To study the effect of the basis set on the spectroscopic constants, theoretical calculations were done by using DFT methods with a series of basis sets. The hybrid density functional B3LYP procedure was formulated to provide a clear picture of the molecular properties of the interstellar molecule CF. Computations were carried out using three different basis sets 3-21G, 6-31G, and 6-311G. The molecular structure of CF was optimized under tight convergence criteria and frequency computations were executed to verify the nature of the stationary points. All computations were pursued using a suite of Gauss View 3.0 software [17]. The molecular parameters such as bond length, dipole moment, rotational constant, harmonic frequency, IR intensity, and vibrational temperature were derived. Using the turning points and energy values obtained from the three different basis sets, the potential energy (PE) curves were constructed for the ground electronic state of the CF molecule.

The probability of a vibronic transition is mainly decided by the overlapping amongst the vibrational wave functions of the ground and excited states and the square modulus of the vibrational overlap integral yields the FCF, which can be written as [18]:

$$q_{v'v''} = |\langle \Psi_{v'} | \Psi_{v''} \rangle|^2, \tag{1}$$

where v' and v'' are the upper and lower vibrational quantum numbers, and $\Psi_{v'}$ and $\Psi_{v''}$ are the vibrational wave functions of the excited (upper) and ground (lower) states, respectively. The *r*-centroid ($\tilde{r}_{v'v''}$) is seen to be the weighted average with respect to $\Psi_{v'}\Psi_{v''}$ of the range of r values experienced by the molecule in both states of the $v' - v''$ transition. The form of $\tilde{r}_{v'v''}$ can be expressed as [19]:

$$\tilde{r}_{v'v''} = \frac{\langle \Psi_{v'} | r | \Psi_{v''} \rangle}{\langle \Psi_{v'} | \Psi_{v''} \rangle}. \tag{2}$$

As the wave functions $\Psi_{v'}$ and $\Psi_{v''}$ rely accurately on PE curves, it is essential to involve the proper PE curves for the electronic states in the transition. For the calculation of FCFs and *r*-centroids, the Morse potential function is the best-known empirical potential function, owing to its simple form, among the various empirical models available in the literature. In most of the cases, the Morse approach always gives reliable FCFs and *r*-centroids. The Morse procedure [20] was therefore adopted to obtain the potential energy curves for the electronic states involved in the present study. From the dataset of potential energy curves, the values of maximum and minimum inter-nuclear separation were noted for all the experimentally observed vibrational levels involved in the electronic transitions. The vibrational wave functions for all the vibrational levels in the electronic states involved in the present study were estimated at an interval of 0.01 Å. FCFs and *r*-centroids were then evaluated by adopting a more reliable numerical integration method [18, 21] using the molecular constants available in [22].

Results and discussion. The geometrical optimization was done and the single point energy of the CF molecule in the ground state was calculated at B3LYP/3-21G, B3LYP/6-31G, and B3LYP/6-311G levels. The spectroscopic constants obtained through the DFT approach were given in Table 1. Of all the obtained values of bond length from all three basis sets, some were found to deviate from the theoretically obtained values available in the literature. On the other hand, the bond length value obtained based on the 6-311G set coincides well with the experimental value. The dipole moments obtained from the basis sets of 3-21G and 6-31G deviated more from the experimental value, whereas the assessment achieved from the set of 6-311G shows only 20% inconsistency from the experimental value. There is a slight mismatching of harmonic frequency too; however, the deviation is very small, i.e., the percentage error for the harmonic frequency in the 3-21G set is very small (about 4%). It is very clear that all these three basis sets give a reliable and contented value for the rotational constant. As mentioned in the computation procedure, using optimized geometry of CF, the potential energy has been constructed as shown in Fig. 1. It is obvious from the potential energy curve diagram that the potential energy curves coincide in the lower region of r values whereas the curve obtained from the 3-21G basis set deviates from other two curves for the higher values of r. The other values such as bond length, dipole moment, etc., also lie closer to the experimental values, which are given

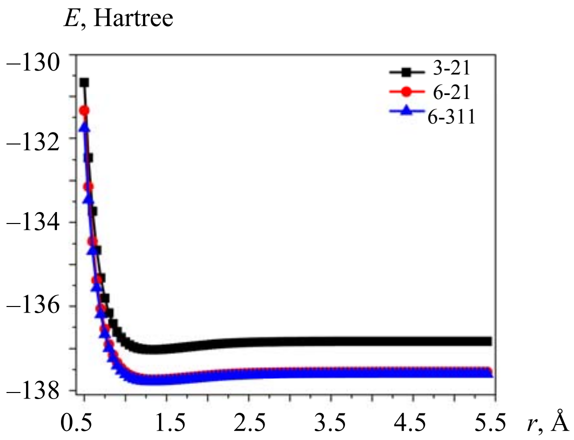

Fig. 1. Potential energy curve for the ground state of the CF molecule, obtained using three different basis sets.

in Table 1. Another interesting observation made at this stage is that the vibrational temperature obtained for the ground electronic state of the CF molecule is around 1500 K, which is generally the accepted favorable temperature of an interstellar medium for the formation of molecules.

TABLE 1. Molecular Parameters for the Ground State of the CF Molecule

Basis set	Bond length, μm	Dipole moment, debye	Rotational constant, GHz	Harmonic frequency, cm^{-1}	IR intensity (km/mol)	Vibrational temperature, K	CPU time, s
3-21G	1.3286	0.1713	38.9286	1249.4263	105.2500	1797.64	19
6-31G	1.3465	0.1701	37.8979	1155.5559	149.2694	1662.59	18
6-311G	1.3439	0.1957	38.0463	1103.5845	166.0459	1587.81	26
Literature	1.3500 [23] 1.2860 [13]	0.2450 [24]	42.4700 [25]	1307.9925 [25] 1292.0000 [13]	–	–	–

TABLE 2. Franck–Condon Factors (FCF) and r-Centroids (Å) of the A–X Band System of the CF Molecule

ν'	0	1	2	3	4	5	6	7	8	9	10	11	12	13
$\nu' = 0$														
FCF	0.1107	0.2093	0.2265	0.1828	0.1240	0.0734	0.0393	0.0194	0.0090	0.0039	*	*	*	*
r	1.2154	1.1917	1.1703	1.1505	1.1318	1.1139	1.0966	1.0795	1.0624	1.0450				
$\nu' = 1$														
FCF	0.3053	1.1550	0.0095	0.0230	0.0879	0.1199	0.1104	0.0812	0.0513	0.0290	0.0149	0.0070	0.0030	*
r	1.2473	1.2181	1.1838	1.1839	1.1596	1.1400	1.1218	1.1045	1.0876	1.0709	1.0541	1.0367	1.0178	
$\nu' = 2$														
FCF	0.3391	*	0.1227	0.1007	0.0152	0.0065	0.0495	0.0842	0.0891	0.0728	0.0501	0.0302	0.0163	0.078
r	1.2822		1.2310	1.2031	1.1754	1.1754	1.1486	1.1296	1.1121	1.0954	1.0791	1.0627	1.0459	1.028

* FCF nearly equal to zero.

TABLE 3. Franck–Condon Factors (FCF) and r-Centroids (Å) of the B–X Band System of the CF Molecule

ν'	0	1	2	3	4	5	6	7
$\nu' = 0$								
FCF	0.7345	0.2370	0.0284	0.0021	*	*	*	*
r	1.3010	1.3837	1.4796	1.5566				
$\nu' = 1$								
FCF	0.2110	0.3215	0.3721	0.0863	0.0104	*	*	*
r	1.2292	1.3172	1.3933	1.4852	1.5614			
$\nu' = 2$								
FCF	0.0444	0.2897	0.0787	0.3918	0.1634	0.0299	0.0035	*
r	1.1674	1.2470	1.3394	1.4036	1.4920	1.5671	1.6262	

* FCF nearly equal to zero.

The evaluated FCFs and r-centroids for the band systems of the CF molecule are given in Tables 2–4. To disseminate the chance of errors in FCFs as a conclusion of the breakdown of the r-centroid approximation [26], FCFs smaller than 0.001 are eliminated and they are considered as zero.

The FCFs for the A–X band system of the CF molecule divulge that the (1, 1), (1, 0), (0, 1), and (0, 2) bands are more intense bands and all other bands are relatively less intense. The FCFs manifest that the bands (0, 0), (1, 1), (1, 2), (2, 1), and (2, 3) of the B–X band system are relatively more intense. For the D–X system, FCFs predict that the (0, 2), (0, 3), (2, 0), and (3, 0) bands are intense compared with other bands.

The estimated r-centroid values of the D–X band system of the CF molecule are found to decrease with the increase of a wavelength following $r'_e < r''_e$, which indicates that the bands are blue shifted. Here, r'_e and r''_e are the equilibrium internuclear distance for upper and lower electronic states. In the case of the A–X and B–X band systems, r-centroid values are decreasing with the increase of wavelengths (when $r'_e < r''_e$) which normally occurs in the red-shifted band system [27]. The r-centroid values of the (0,0) band of all the investigated band systems are greater than $(r'_e + r''_e)/2$ and the difference between them is approximately 0.01 Å.

TABLE 4. Franck–Condon Factors (FCF) and *r*-Centroids of the *D–X* Band System of the CF Molecule

ν'	0	1	2	3	4	5	6	7	8	9	10	11	12
$\nu' = 0$													
FCF	0.0677	0.1642	0.2122	0.1958	0.1461	0.0945	0.0554	0.0305	0.0161	0.0083	0.0042	0.0022	0.0011
r	1.2067	1.1886	1.1704	1.1521	1.1340	1.1164	1.0995	1.0837	1.0690	1.0555	1.0432	1.0322	1.0222
$\nu' = 1$													
FCF	0.1656	0.1807	0.0596	*	0.0360	0.0925	0.1182	0.1103	0.0859	0.0597	0.0386	0.0237	0.0142
r	1.2321	1.2152	1.1981		1.1617	1.1444	1.1272	1.1105	1.0945	1.0796	1.0657	1.0529	1.0414
$\nu' = 2$													
FCF	0.2119	0.0582	0.0115	0.0955	0.0931	0.0281	*	0.0235	0.0605	0.0823	0.0837	0.0720	0.0558
r	1.2565	1.2427	1.2149	1.2038	1.1872	1.1691		1.1406	1.1229	1.1066	1.0913	1.0770	1.0638
$\nu' = 3$													
FCF	0.1966	*	0.0944	0.0658	*	0.0434	0.0836	0.0571	0.0135	*	0.0175	0.0429	0.0603
r	1.2794		1.2454	1.2321		1.1938	1.1784	1.1612	1.1405		1.1234	1.1055	1.0902
$\nu' = 4$													
FCF	0.1462	0.0360	0.0895	*	0.0605	0.0670	0.0078	0.0128	0.0566	0.0656	0.0372	0.0081	*
r	1.3006	1.2806	1.2711		1.2353	1.1225	1.2118	1.1849	1.1715	1.1552	1.1374	1.1139	
$\nu' = 5$													
FCF	0.0955	0.0929	0.0264	0.0410	0.0655	*	0.0391	0.0653	0.0224	*	0.0272	0.0548	0.0519
r	1.3203	1.3039	1.2970	1.2723	1.2632		1.2259	1.2140	1.2004		1.1665	1.1511	1.1348
$\nu' = 6$													
FCF	0.0564	0.1205	*	0.0786	0.0078	0.0374	0.0567	0.0039	0.0212	0.0576	0.0380	0.0043	0.0057
r	1.3386	1.3240		1.2973	1.2970	1.2642	1.2556	1.2576	1.2169	1.2066	1.1928	1.1773	1.1652

* FCF nearly equal to zero.

As the difference is very small, the potential energy curves are not so anharmonic. The sequence difference of *r*-centroid values for all the band systems analyzed here are found to be around 0.03 Å, which shows that the potential energy curves are not so wide. The results of the present study reveal that an extensive experimental investigation of a vibrational and rotational spectrum is needed for the CF molecule. Once the complete set of rotational lines for a band system is available, the FCFs and *r*-centroids obtained in the present study along with the rotational dataset will be very helpful for the identification of the CF molecule in various astrophysical sources, using the line identification technique available in [28–30].

Conclusions. To summarize the work performed in the present study, the DFT analysis employing the B3LYP method with 3-21G, 6-31G, and 6-311G basis sets was carried out for the ground state of the carbon mono-fluoride molecule. Molecular optimization was done prior to the calculation of spectral parameters. After achieving the optimized geometries of the carbon mono-fluoride molecule, the potential energy curves of the ground state and various parameters such as bond length, dipole moment, rotational constant, harmonic frequency, IR intensity, and vibrational temperature were obtained. The observed spectroscopic constants using the DFT analysis were compared with the values already reported for better justification. The Franck–Condon factor values of various bands of electronic transitions of *A–X*, *B–X*, and *D–X* were evaluated using the numerical integration method. The physical and astrophysical significance of the obtained Frank–Condon factors and *r*-centroids were discussed. The vibrational temperature obtained using the DFT approach provides additional support in expecting the existence of the carbon mono-fluoride molecule in a sunspot where several diatomic molecules are found in low-temperature regions. Hence, the present study is a first step toward the prediction, search, and identification of the carbon mono-fluoride molecule in a sunspot.

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REFERENCES

1. Yongliang Hao, et al., *J. Chem. Phys*., **151**, 034302 (2019).
2. John R. Daniel, Chen Wang, Kayla Rodriguez, Boerge Hemmerling, Taylor N. Lewis, Christopher Bardeen, Alexander Teplukhin, Brian K. Kendrick, *Phys. Rev. A*, Accepted 23 June 2021 (2021).
3. Amal Moussa, Nayla El-Kork, Mahmoud Korek, *New J. Phys*., **23**, 013017 (2021).
4. Xiangyue Liu, Gerard Meijer, Jesús Pérez-Ríos, *RSC Adv*., Issue 24, Issue in Progress (2021), doi: 10.1039/D1RA02061G.
5. B. Barbuy, J. Trevisan, A. de Almeida, *Publ. Astron. Soc. Australia*, **35**, e046(1–9) (2018), doi: 10.1017/pasa.2018.33.
6. M. G. Tarallo, G. Z. Iwata, T. Zelevinsky, *Phys. Rev. A*, **93**, 032509 (2016).
7. L. E. Berg, K. Ekvall, A. Hishikawa, S. Kelly, *Phys. Scr.*, **55**, 269–272 (1997).
8. S. Schlemmer, H. Mutschke, T. Giesen, C. Jäger, *Laboratory Astrochemistry: from Molecules Through Nanoparticles to Grains*, John Wiley & Sons Publication (2014).
9. Anna-Maree Syme, Laura K. McKemmish*, Res. Notes AAS*, **4**, 139 (2020).
10. V. A. Sre´ckovi´c, L. M. Ignjatovi´c, M. S. Dimitrijevi´c, *Molecules*, **26**, 151 (2021).
11. E. B. Andrews, R. F. Barrow, *Nature* (London), **165**, 890 (1950).
12. E. B. Andrews, R. F. Barrow, *Proc. Phys. Sot. London Sec. A*, **64**, 481–492 (1951).
13. T. H. Dunning, Jr., *J. Mol. Spectrosc*., **75**, 297–317 (1979).
14. W. P. White, M. Russel, C. Pitzer, W. Mathews, T. H. Dunning, Jr., *J. Mol. Spectrosc*., **75**, 318–326 (1979).
15. T. L. Porter, D. E. Mann, N. E. Aquista, *J. Mol. Spectrosc*., **16**, 228–263 (1965).
16. I. D. Petsalakis, *J. Chem. Phys*., **110**, 10730–10737 (1999).
17. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT (2004).
18. D. R. Bates, *Proc. R. Soc. A*, **196**, 217–250 (1949).
19. R. W. Nicholls, W. R. Jarmain, *Proc. Roy. Phys. Soc*., **69**, 253–264 (1956).
20. P. M. Morse, *Phys. Rev*., **34**, 57–64 (1929).
21. B. Karthikeyan, *Studies on Molecular Species Identified in Solar and Allied Spectra by Spectroscopic Techniques*, Ph.D. Thesis, MKU (2008).
22. K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure: IV Costants of Diatomic Molecules*, New York. Van Nostrand Reinhold Co. (1979).
23. B. de B. Darwent, *National Standard Reference Data Series, National Bureau of Standards*, No. 31, Washington, DC (1970).
24. R. L. David, *Handbook of Chemistry and Physics*, 85th ed., CRC Press, USA (2004).
25. M. A. Gondal, W. Rohrbech, W. Urban, *J. Mol. Spectrosc.*, **100**, 290–302 (1983).
26. C. A. Mahon, A. Stampanoni, J. Luque, *J. Mol. Spectrosc*., **183**, 18–24 (1997).
27. O. Launilla, J. Jonsson, *J. Mol. Spectrosc*., **168**, 483–493 (1994).
28. B. Karthikeyan, S. P. Bagare, N. Rajamanickam, V. Raja, *Astropart. Phys*., **31**, 6–12 (2009).
29. B. Karthikeyan, N. Rajamanickam, S. P. Bagare, *Solar Phys*., **264**, 279–285 (2010).
30. G. Shanmugapriya, B. Karthikeyan, K. Balachandrakumar, N. Rajamanickam, S. P. Bagare, *Solar Phys*., **290**, 1569–1579 (2015).