THE ASTROPHYSICAL JOURNAL, **220**: 739–741, 1978 March 1

THEORETICAL STUDY OF THE THIOFORMYL ION

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Received 1977 July 18; accepted 1977 September 2

ABSTRACT

The equilibrium structure of the thioformyl ion has been determined from an *ab initio* matrix Hartree-Fock calculation and an estimated rotation constant has been derived. For HCS^+ we obtain $B_e = 21.7$ GHz, while for DCS^+ $B_e = 18.3$ GHz. If the vibration-rotation interaction constants for HCS^+ are assumed to be the same as those for HCP, then $B_0 = 21.6$ GHz, while the vibration-rotation constants of DCP give $B_0 = 18.3$ GHz for DCS^+.

Subject headings: interstellar: molecules — molecular processes — quantum mechanics

In this paper we report a quantum-mechanical determination of the equilibrium geometry and the rotation constant of the thioformyl ion, HSC^+.

A number of molecules have been detected in space in which the group VI atom of the first row of the periodic table, oxygen, has been replaced by the corresponding second-row atom, sulfur. In addition to the diatomic species CO (Wilson, Jefferts, and Penzias 1970) and CS (Penzias *et al.* 1971), SiO (Wilson *et al.* 1971) and SiS (Morris *et al.* 1975), the polyatomic molecules H_2O (Cheung *et al.* 1969) and H_2S (Thaddeus *et al.* 1972), H_2CO (Snyder *et al.* 1969) and H_2CS (Sinclair *et al.* 1971) have been detected in space. Molecules such as SO (Gottlieb and Ball 1973) and OCS (Jefferts *et al.* 1971), which contain both oxygen and sulfur, are also present. HCS^+ and the astronomically abundant HCO^+ are isovalent. It is probable that the formyl ion plays an important part in molecule-formation processes in space (Herbst and Klemperer 1973).

Quantum-mechanical calculations have played a key role in the identification of several molecules in the interstellar medium. These studies were particularly useful in the case of species such as HCO^+ (Wahlgren *et al.* 1973; Kraemer and Diercksen 1976; Bruna 1975), N_2H^+ (Green, Montgomery, and Thaddeus 1974), HNC (Pearson *et al.* 1973), and C_3N (Wilson and Green 1977) which had not been observed in the laboratory when first detected in space.

We employed the matrix Hartree-Fock model, with a basis set of Slater exponential functions, to perform the calculations reported in this work. HCS^+ was assumed to be linear, and calculations were performed to determine the optimum bond lengths. A rotation constant was derived from the equilibrium structural parameters. Vibration-rotation interaction constants were estimated from studies of the isoelectronic HCP molecule (Strey and Mills 1973), and thus a rotation constant B_0 is suggested. Similar studies for the CO, CS, and HCO^+ molecules are reported. These calculations not only enable us to make a qualitative estimate of the accuracy of the present calculations but also allow an empirical correction to the calculated bond lengths to be made.

The results of the matrix Hartree-Fock calculations for the formyl and thioformyl ions are given in Table 1. The calculations for the CO and CS molecules are described elsewhere (Wilson 1977*a*, *b*). Interpolation of the calculated points on the potential energy curves and surfaces leads to the following equilibrium bond distances:

$$\text{CO:} \quad r(\text{CO}) = 1.102\ \text{Å}\,,$$

$$\text{CS:} \quad r(\text{CS}) = 1.504\ \text{Å}\,,$$

$$\text{HCO}^+\text{:} \quad r(\text{CH}) = 1.085\ \text{Å}\,; \quad r(\text{CO}) = 1.078\ \text{Å}\,,$$

$$\text{HCS}^+\text{:} \quad r(\text{CH}) = 1.071\ \text{Å}\,; \quad r(\text{CS}) = 1.456\ \text{Å}\,.$$

The theoretically determined bond lengths for carbon monoxide and carbon monosulfide should be compared with the experimentally determined values of 1.128_3 Å and 1.534_9 Å (Mills 1974), respectively. The ratio of the theoretical value to the experimental value in these two isovalent molecules is 0.977 and 0.980 for CO and CS, respectively. Assuming that the same ratio applies for the corresponding bonds in the formyl and thioformyl ions, we obtain the empirically corrected bond lengths:

$$\text{HCO}^+\text{:} \quad r(\text{CO}) = 1.103\ \text{Å}\,,$$

$$\text{HCS}^+\text{:} \quad r(\text{CS}) = 1.486\ \text{Å}\,.$$

For HCO^+ Kraemer and Diercksen (1976) empirically corrected a configuration interaction study to obtain $r(\text{CO}) = 1.101$ Å, which is within 0.2% of the corrected value given above. Kraemer and Diercksen (1976) obtained a CH bond length of 1.090 Å in HCO^+, which is within 0.46% of the present value.

B_0 is related to B_e by

$$B_0 = B_e - \tfrac{1}{2}\alpha_1 - \alpha_2 - \tfrac{1}{2}\alpha_3\,,$$

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[*] National Research Council Resident Research Associate, supported by the National Aeronautics and Space Administration.

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TABLE 1

DETAILS OF GEOMETRY OPTIMIZATION FOR HCX^+ (X = O, S)*

Ion	r(CH)†	r(CX)†	$-E$‡
HCO^+......	2.012	2.034	113.0216724
	2.062	1.984	113.0193906
	2.062	2.034	113.0219217
	2.062	2.084	113.0198467
	2.112	2.034	113.0212697
HCS^+......	1.967	2.744	435.6578374
	2.017	2.694	435.6583959
	2.017	2.744	435.6584884
	2.017	2.794	435.6564268
	2.067	2.744	435.6581025

* Basis set of Slater exponential functions:
H: $1s$ (0.97155, 1.23206), $2p_\sigma$ (1.37568), $3d_\sigma$ (1.7), $2p_\pi$ (0.79006), $3d_\pi$ (2.2).
C: $1s$ (5.3767, 8.982), $2s$ (2.0131, 5.6319, 1.3089), $2p_\sigma$ (1.8076, 2.2398, 0.9554, 0.63438), $3d_\sigma$ (2.65), $4f_\sigma$ (2.06), $2p_\pi$ (1.4209, 2.5873, 0.9554, 6.3438), $3d_\pi$ (2.207), $4f_\pi$ (2.9).
O: $1s$ (7.6063, 13.224), $2s$ (3.11196, 6.3783, 1.80848), $2p_\sigma$ (1.796, 3.3379, 1.1536, 7.907), $3d_\sigma$ (2.1144), $4f_\sigma$ (2.5), $2p_\pi$ (1.8171, 3.4379, 1.1536, 7.907), $3d_\pi$ (2.2297), $4f_\pi$ (2.482).
S: $1s$ (13.7174, 17.6913), $2s$ (6.7527, 14.0693), $3s$ (2.6107, 1.6426, 5.7425), $2p_\sigma$ (7.1763, 13.53), $3p_\sigma$ (2.3277, 1.3194, 5.4397), $3d_\sigma$ (2.9), $4f_\sigma$ (2.1), $2p_\pi$ (7.1763, 13.5), $3p_\pi$ (2.3277, 1.3194, 5.4397), $3d_\pi$ (2.9), $4f_\pi$ (2.1).

† In bohr; 1 bohr (atomic unit of length), $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2 \sim 0.529177 \times 10^{-10}$ m.

‡ In Hartree; 1 Hartree (atomic unit of energy) $= \hbar^2/m_e a_0^2 \sim 4.359814$ aJ.

where the α's are vibration-rotation interaction constants. We shall use the values of these constants derived from experimental data (Strey and Mills 1973) for HCN and HCP to estimate the B_0 constants for HCO^+ and HCS^+. Thus for HCO^+ we have for the $J = 0 \leftarrow 1$ rotational transition

$$\nu_0 = 2B_e - 398.6 \text{ MHz},$$

while for HCS^+ we obtain

$$\nu_0 = 2B_e - 184.1 \text{ MHz}.$$

By using the calculated equilibrium geometry for HCO^+, we obtain $\nu_0 = 93.39$ GHz, which is within 4.7% of the experimentally observed value of $\nu_0 = 89.19$ GHz (Woods *et al.* 1975). Introduction of the empirical correction to the CO bond length leads to $\nu_0 = 89.80$ GHz, which is within 0.69% of the observed value.

In Table 2 we present both the calculated and the empirically corrected rotation constants for the formyl ion and the thioformyl ion. Since these molecules are isovalent, we expect the accuracy achieved in our study of the thio-species to be comparable with that obtained for the oxy-ion.

DCO^+ has been detected in space (Hollis *et al.* 1976). From the work of Strey and Mills (1973), we estimate, for DCO^+,

$$\nu_0 = 2B_e - 263.2 \text{ MHz},$$

and, for DCS^+,

$$\nu_0 = 2B_e - 48.0 \text{ MHz}.$$

Table 2 contains calculated and empirically corrected rotation constants for these deuterated species.

While quantum-mechanical calculations cannot, at present, provide the basis for a definitive identification of interstellar molecular species, they are useful, particularly in the case of radicals and ions, such as the thioformyl ion, which have not been observed in the laboratory. Theoretical calculations can provide a sound basis for rejecting certain molecules in the consideration of unassigned lines. By performing calculations for a series of related molecules, for some of which experimental data are available, we have attempted to empirically adjust the calculated bond lengths to correct for the errors which are known to be associated with the particular theoretical model employed in this work.

The estimated frequencies given in Table 2 are for the $J = 0 \leftarrow 1$ transition. The $J = 1 \leftarrow 2$ and $J = 2 \leftarrow 3$ transitions are more likely to be observed in space; they lie at 86.2 GHz and 129.3 GHz, respectively, for HCS^+ and at 73.0 GHz and 109.5 GHz for DCS^+.

Constructive criticism of the manuscript by Dr. P. Thaddeus is appreciated.

TABLE 2

ROTATION CONSTANTS FOR THE FORMYL AND THIOFORMYL IONS

Ion	B_e (calculated) (MHz)	B_e (adjusted) (MHz)	Estimated Frequency* $J = 0 \leftarrow 1$ MHz
HCO^+.......	46894	45101	89803 (89189)
HCS^+.......	22451	21650	43116
DCO^+.......	37718	36431	72599 (72039)
DCS^+.......	18908	18280	36512

* The observed frequency is given in parentheses when it is known.

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