Computational Molecular Spectroscopy: Fe-containing Molecules of Astrochemical Interest

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Although Fe is known to have a large cosmic abundance comparable to those of Mg and Si, the only iron-containing molecules so far detected in the cosmic environment are FeH in sunspots [1] and FeO toward Sgr B2 [2,3]. In 1994, we made a preliminary *ab initio* calculation on FeCO as a candidate for observation in interstellar space [4], but attempts by Kasai *et al* to detect it in space failed [5,6]. Then we started *ab initio* calculations on several Fe-containing molecules of astrochemical interest, including FeC [7], FeN [8], FeS, FeCO, FeNC [9], FeCN [10], FeOH [11,12].

We discuss here the molecular properties of $\tilde{X}\ ^6\Delta$ FeNC, $\tilde{X}\ ^6\Delta$ FeCN, and $\tilde{X}\ ^6$A'($^6\Delta$) FeOH. The last two of these have not yet been observed spectroscopically, and hence the predicted spectra are shown in Fig. 1 and Fig. 2, respectively. The *ab initio* calculations are done at the level of MR-SDCI+Q+ E_{rel}/[Roos ANO (Fe), aug-cc-pVQZ (C, N, O, H)].

The equilibrium structures of FeNC and FeCN are *linear*. The equilibrium structure of FeOH is *bent* with a barrier of 273 cm^{-1} at linearity, which is just above the bending zero-point energy of 194 cm^{-1}, so that $\tilde{X}\ ^6$A' FeOH is a *quasi-linear* molecule. The geometrical constants of these molecules are given in Table 1.

The Fe atoms in these three molecules are bound to their ligands through an ionic bond, so that the bending potentials are shallow and give large amplitude bending motion. We have calculated ro-vibrationally averaged bond lengths for various

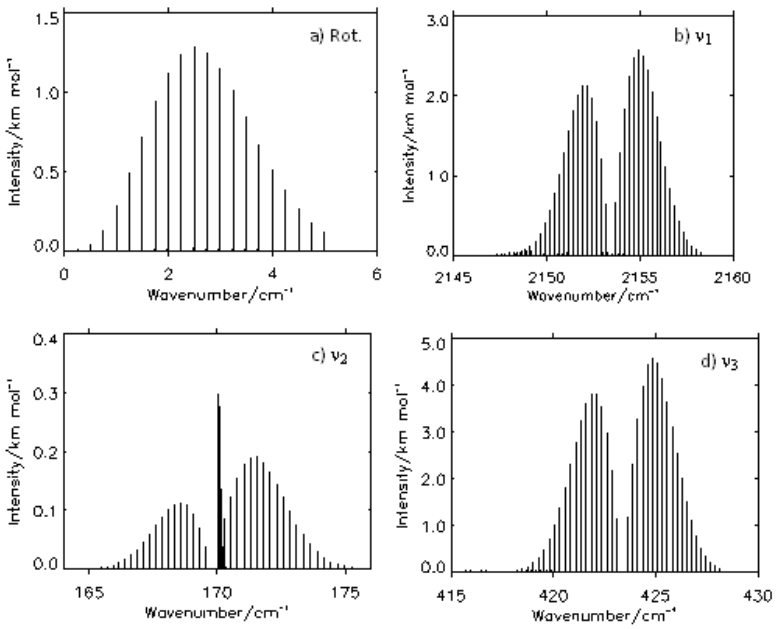

Fig. 1 Predicted spectra for the $\tilde{X}\ ^6\Delta$ FeCN: (a) rotation spectrum, (b) ν_1 (at 2153 cm^{-1}), (c) ν_2 (at 170 cm^{-1}), and (d) ν_3 (at 423 cm^{-1}), simulated at 12 K [10].

Table 1 *Ab initio* calculated molecular constants at the MR-SDCI+Q+E_{rel} level.

Molecule	B_0 /cm^{-1}	$10^8\ D_J$ /cm^{-1}	r_e(M-ligand) /Å	r_e(C-N) or r_e(O-H) / Å	Bond angle /degrees	$\langle\bar{\rho}\rangle_0$ ($\delta\bar{\rho}$) [a)] /degrees
$\tilde{X}\ ^6\Delta$ FeNC [b)]	0.14274	4.84	1.9354	1.1823	180.0	13(7)
Exp. [13]	0.14447(13)		2.01(5), r_0	1.03(8), r_0	180.0	
$\tilde{X}\ ^6\Delta$ FeCN [c)]	0.12380	4.12	2.0484	1.1681	180.0	10(5)
$\tilde{X}\ ^6$A' FeOH [d)]			1.8059	0.9520	134.2	39(14)

a) The bond angle deviation from linearity with quantum dynamical uncertainty in parentheses.
b) Ref. [9]. c) Ref. [10]. d) Refs. [11,12].

vibrational states as expectation values in terms of variational MORBID wavefunctions. The r_0 structure and the bond angle supplement $\langle\bar{\rho}\rangle_0$ (i.e. the angle deviation from linearity) thus determined are included in Table 1.

It should be noted that even for a linear molecule, whose equilibrium structure is linear, the ro-vibrationally averaged structure deviates substantially from linearity due to the large amplitude bending motion. It should also be noted that, for the quasi-linear molecule $\tilde{X}$ ^{6}A' FeOH, the $\langle\bar{\rho}\rangle_0$ value is quite close to the equilibrium bond angle. Whether the molecule is linear or quasi-linear or bent can be distinguished by the Yamada-Winnewisser quasilinearity parameter γ_0 [14],

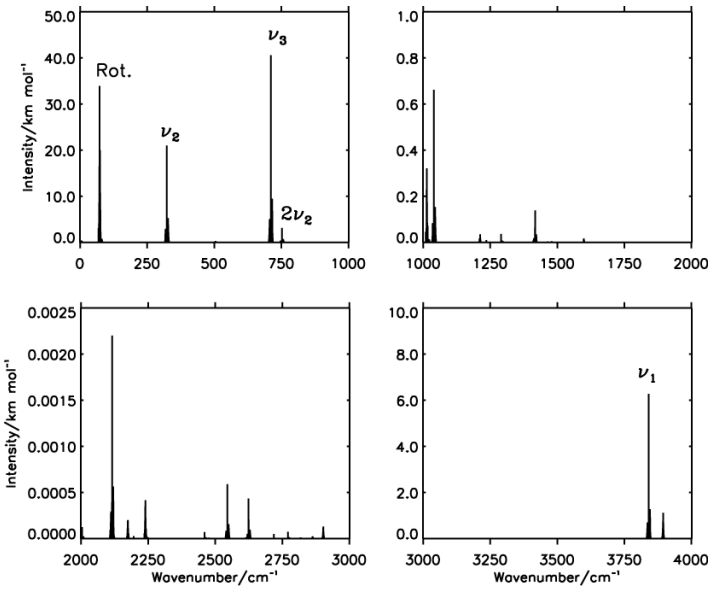

Fig. 2 Predicted spectra of the $^6A'$ ($^6\Delta$) FeOH Renner-degenerate states (at 10 K) [11].

$$\gamma_0 = 1 - 4 \times \frac{E(v_2 = |l_2| = 1) - E(v_2 = |l_2| = 0)}{E(v_2 = 2, |l_2| = 0) - E(v_2 = |l_2| = 0)} \quad .$$

It was found that for the linear molecules FeNC and FeNC, $\gamma_0 \approx -1.0$, and for the quasi-linear molecule FeOH, $\gamma_0 = 0.1$. Thus, at the early stage of the analysis of the experimentally obtained infrared spectrum, one can identify the relevant molecule being linear, or quasi-linear, or bent.

Another molecule we consider here is FeCO. Many spectroscopic studies have been reported for $\tilde{X}$ $^3\Sigma^-$ FeCO (see ref. [15], for example), but none for a $^5\Sigma^-$ FeCO. Our recent prediction at the MR-SDCI+Q+E_{rel}/[Roos ANO (Fe, C, O)] level for the a $^5\Sigma^-$ FeCO is as follows. This is a linear molecule, with equilibrium structures r_e(Fe–C) = 1.843 Å, r_e(C–O) = 1.153 Å, $\angle_e$(Fe-C-O) = 180°. The MORBID analysis gives ro-vibrationally averaged structures as r_0(Fe–C) = 1.845 Å, r_0(C–O) = 1.157 Å, and $\langle\bar{\rho}\rangle_0$ =9°(4°) with B_0 = 0.13422 cm^{-1} (4023.7 MHz). γ_0 = –1.0 as is expected for a *linear* molecule. We think that it would be worthwhile to characterize this molecule further spectroscopically and to search for it in interstellar space.

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