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CCSD(T) Determination of the Vibrational Structure in the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ Spectrum of CCO^-

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An ab-inito quartic force field of CCO− in its first excited state $\tilde{A}^2\Sigma^+$ is calculated from an aug-cc-VTZ basis set at CCSD(T) level of theory in order to compute the vibrational energy levels in the range 600−4800 cm^{-1}. A variational-perturbational approach is used to diagonalize the most important vibrational configurations constructed from harmonic vibrational wave functions. The result agree well with the most reliable experimental values studied in a neon matrix and predict as yet unobserved overtones bands in the vibrational structure of the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ spectrum of CCO^-.

1. Introduction

In contrast to the well-characterized C_2O species, information on the negative ion CCO^- remain a long time rather scarce. Initially detected in flames by mass-spectrometry,[1] CCO^- was then studied by photoelectron spectroscopy[2−4] and its $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ electronic absorption spectrum[5] has been observed very recently in a neon matrix. Concurrently to these spectroscopic studies several works using various techniques of molecular electronic structure theory have been published lately.[3,6,7] It is well-established that the ground $\tilde{X}^2\Pi$ and the first $\tilde{A}^2\Sigma^+$ states are linear[3] and that the ground state is unperturbed by vibronic coupling with $\tilde{A}^2\Sigma^+$, situated 1.517 eV[5] above. Although a three-dimensional potential energy function has been calculated by Panten et al.,[8] for the $\tilde{X}^2\Pi$ electronic ground state to analyze the rovibronic levels of this Renner−Teller system, little is known theoretically about the $\tilde{A}^2\Sigma^+$ state. The goal of the present study is to provide theoretical spectroscopic data on the anharmonic vibrational spectra of CCO^- ($\tilde{A}^2\Sigma^+$) in the medium IR region, to analyze and to complement the assignments of the vibrational structure in the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ electronic absorption spectrum. This letter is laid out as follows: in section 2 we briefly present the computational details. All results are presented, discussed, and compared with the experimental data in section 3.

2. Method and Computational Details

The method used to calculate the anharmonic wavenumbers of CCO^- ($\tilde{A}^2\Sigma^+$) in the medium IR region stems from a configuration interaction treatment based on a variation−perturbation approach similar to that developed in the CIPSI algorithm[9] and described in detail elsewhere.[10,11] The quartic force field needed for the anharmonic energy levels calculations was set up from a least-squares fit to energies on a grid of 81 points corresponding to the distorted structures generated by bond and angular displacements of 0.01 Å and 0.2 rad around the equilibrium structure. All energies were calculated at the coupled cluster singles and doubles level of theory[12,13] including a perturbative estimation of connected triples (CCSD(T))[14] using the aug-cc-pVTZ [5s,4p,3d,2f] basis set of Dunning and coworkers.[15,16] Because the states studied to determine the energy of the $\tilde{A}^2\Sigma^+$ state of CCO- with regard to the ground state of CCO^- ($\tilde{X}^2\Pi$) and CCO ($\tilde{X}^3\Sigma^+$) are strongly dominated by the SCF configuration, the choice of CCSD(T) methods appears judicious and coherent to calculate transition energies, electron affinity, and structural and spectroscopic data for these systems.

All the molecular electronic wave function calculations were performed using the GAUSSIAN 98 package.[17]

On the basis of curvilinear coordinates S_k and their conjugate moments p_{s_k}, the quantum mechanical pure vibrational Hamiltonian is written

$$H = \frac{1}{2}\sum_{i,j} g_{ij}(s) p_{s_i} p_{s_j} + V(s)$$

where g_{ij} is the element of the G matrix described by Wilson et al.[18] and $V(s)$ the potential function expressed from a complete set of quadratic, cubic, and quartic force constants by:

$$V(s) = \frac{1}{2}\sum_{i,j} f_{ij}\, S_i\, S_j + \frac{1}{6}\sum_{i,j,k} f_{ijk}\, S_i\, S_j\, S_k + \frac{1}{24}\sum_{i,j,k,l} f_{ijkl}\, S_i\, S_j\, S_k\, S_l$$

Like the potential function $V(s)$, the kinetic part of the Hamiltonian can be written as a Taylor expansion in terms of the curvilinear displacement coordinates set:

$$T = \frac{1}{2}\sum_{i,j} g_{ij}(0)\; P_{S_i} P_{S_j} + \frac{1}{2}\sum_{i,j,k} g_{ijk}\; P_{S_i}\, S_k\, P_{S_j} + \ldots$$

$$g_{ij}(s) = g_{ij}(0) + \sum_{k} g_{ijk}\, s_k + \frac{1}{2}\sum_{k,l} g_{ijkl}\, s_k\, s_l + \ldots$$

$$\text{where } g_{ijk} = \left(\frac{\partial g_{ij}}{\partial s_k}\right)_0 \text{ and } g_{ijkl} = \left(\frac{\partial^2 g_{ij}}{\partial s_k \partial s_l}\right)_0$$

In the harmonic approximation, only the first term $g_{ij}(0)$ is considered, whereas in the anharmonic approach involving large amplitude displacements, higher order terms have to be retained for both the kinetic and the potential operators.

In our calculations, both the kinetic and the potential parts of the vibrational Hamiltonian are expressed in the basis of

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dimensionless normal coordinates q_i and conjugate momentum operators P_{q_i}. The anharmonic energy levels are calculated from a configuration interaction treatment based on a variation−perturbation approach. In our method, the vibrational Hamiltonian representation is “in fine” diagonalized in a subspace built iteratively by means of a second-order Rayleigh−Schrödinger perturbation theory. Only configurations with weights greater than a given threshold are included in the primary subspace for the following iterations. The multireference vibrational function is then corrected to first order by the remaining states, which interact weakly. The eigenvalues and eigenvectors of the corresponding vibrational levels are obtained by diagonalizing the Hamiltonian with Davidson’s procedure[19] in a subspace generated by our algorithm. This extensive configuration selection method can be compared with those developed by Dunn et al.[20,21] About 700 functions are needed to obtain the first 30 eigenvalues converged to an accuracy of 1 cm^{-1}. In our problem, harmonic oscillator functions are used as expansion functions. The values of the quadratic, cubic, and quartic terms in curvilinear coordinates are obtained from a fourth order polynomial fit. The rms error and the maximum absolute error of the fit were [1.38;8.81] μE_H for the $\tilde{A}^2\Sigma^+$ state of CCO$^-$ particulary considered. To calculate the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ electronic spectrum of CCO$^-$ and the electron affinity, the structural parameters and the spectroscopic data for the $\tilde{X}^2\Pi$ state of the anion and the ground state of CCO are calculated at the same level of theory with the same basis set. In these two cases, the anharmonicity is roughly estimated by a perturbational approach and the Renner−Teller effect (weak[8]) is not taken into consideration for the ground state of the anion.

3. Results and Discussion

The optimized structures, corresponding energies, quadratic force constants, and harmonic and anharmonic wavenumbers of both species for CCO ($\tilde{X}^3\Sigma^-$) and CCO$^-$ [($\tilde{X}^2\Pi$) and ($\tilde{A}^2\Sigma^+$)] are reported in Table 1.

Optimized bond lengths calculated for these linear species shows that compared to the ground state of CCO, the CC bond length is shorter, and the CO distance longer in the anion. For the $\tilde{A}^2\Sigma^+$ state of CCO$^-$, it should be emphasized that the two bondings are very close: the CC distance (1.243 Å) being found 0.005 Å shorter than CO (1.248 Å). Our CCSD(T) equilibrium distances, in agreement with those published by Panten et al.[8] at the same level of theory, are respectively shorter by about 0.018 Å for CC and longer by about 0.004 Å for CO than the theoretical values reported by Zengin et al.[3] from a CASPT2 method.

The quadratic force field was also calculated for both species. The Renner−Teller effect is not taken into account in our calculation of the ground state of the anion ($\tilde{X}^2\Pi$) giving only the lower component for the bending force constant and the corresponding harmonic wavenumber. A comparison of the quadratic force constants in the series reveals the increase of the bending ($f_{\alpha\alpha}$) and carbon−carbon stretching (f_{rr}) values from the neutral CCO molecule to the anions: the values relative to $\tilde{A}^2\Sigma^+$ are larger than those calculated for $\tilde{X}^2\Pi$. This trend for the CC stretching can easily be explained by the decrease of the CC distance in the series. The carbon−oxygen stretching constant (f_{RR}) decreases from the neutral to the anion. But in this case, unlike the CO bending, the corresponding force constants for the two states of CCO$^-$, are not directly connected with the difference in calculated bond length. If we turn our attention to the $f_{CO/CC}$ interaction constant, we find that they are in general comparable for the three systems. For the $\tilde{A}^2\Sigma^+$ state, our $f_{CO/CO}$ CCSD(T) value (13.48 mdyn Å^{-2}) is practically identical with the CASPT2 result (13.3 mdyn Å^{-2}) and our $f_{CC/CC}$ value (10.19 mdyn Å^{-2}) is found about 2% smaller than the CASPT2 constant (10.4 mdyn Å^{-2}). Our harmonic wavenumbers respectively calculated at 654, 1219, and 2116 cm^{-1} for the bending and the ω_{CC} and ω_{CO} stretching modes, in good agreement with the observed data (656, 1185, and 2082 cm^{-1}), differ respectively for the stretching vibrations by about 4.3% and 4.8% with the CASPT2 results (1190 and 2218 cm^{-1}). Anharmonic corrections calculated from cubic and quartic force constant[22] reduce by about 50, 32, and 39 cm^{-1} the ν_{CO} mode and by about 20, 12, and 36 cm^{-1} the ν_{CC} mode from CCO ($\tilde{X}^3\Sigma^-$) to CCO$^-$ ($\tilde{X}^2\Pi$) and ($\tilde{A}^2\Sigma^+$), respectively. The negligible influence of the anharmonic correction for the bending mode should be noted. Our anharmonic fundamental vibrations for the three systems agree very well with the observed data, the discrepancy being the range between 2 to 23 cm^{-1}. From our CCSD(T) energy values and the knowledge of zero point energy at the anharmonic level, we have calculated the electron affinity of CCO as well as the adiabatic excitation energy for the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ transition of the anion. Our calculated electron affinity (2.23 eV), that agrees well with the CASPT2 result (2.22 eV) published by Zengin et al,[3] is only 0.06 eV lower than the measured value. As for the adiabatic transition $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$, our CCSD(T) calculation gives a T_0 value (1.572 eV) consistent with the observed band origin at 1.517 eV.[5]

TABLE 1: Calculated Equilibrium Bond Lengths (Å), Energies (H), Quadratic Force Field (aJ/Å^2 for Strech-Strech; AJ for Bend-bend), Harmonic and Anharmonic Wavenumbers (cm^{-1}) for CCO ($\tilde{X}^3\Sigma^-$) and CCO$^-$ [($\tilde{X}^2\Pi$) and ($\tilde{A}^2\Sigma^+$)]

	CCO	CCO$^-$	
	$\tilde{X}^3\Sigma^-$	$\tilde{X}^2\Pi$	$\tilde{A}^2\Sigma^+$
R(CO)	1.164	1.226	1.248
r(CC)	1.372	1.309	1.243
E_H	−151.026624	−151.108731	−151.051883
$f_{22} = f_{\alpha\alpha}$	0.29	0.41	0.77
$f_{33} = f_{rr}$	6.20	9.02	10.19
$f_{13} = f_{rR}$	1.11	0.87	1.19
$f_{11} = f_{RR}$	15.41	11.12	13.48
ω_1 (CO)	2026	1928	2116
ω_2 (α)	382	455	654
ω_3 (CC)	1071	1157	1219
ν_1 (CO)	1976 (1971−1973)[b],(1978)[a]	1896 *(1877)*[d]	2077 *(2082)*[d]
ν_2 (α)	383 *(379−381)*[a,c]	456	652 *(656)*[d]
ν_3 (CC)	1051 *(1074)*[a]	1145	1183 *(1185)*[d]

R, r, and α are respectively CO, CC, and bending coordinates. Experimental values in brakets. [a] Jacox, M. E.; Milligan, D. E.; Moll, N. G.; Thompson, W. E. *J. Chem. Phys.* **1965**, *43*, 3734. Matrix-isolation Infrared spectrum.[23] [b] Moazzen-Ahmadi, M.; Boere, R. T. *J. Chem. Phys.* **1998**, *108*, 6588.[24] Yamada, C.; Kanamori, H.; Horiguchi, H.; Tsuchiya, S.; Hirota, E. *J. Chem. Phys.* **1986**, *84*, 2573.[25] [c] Ohashi, N.; Kiryu, R.; Okino, S.; Fujitake, M. *J. Mol. Spect.* **1993**, *50*, 157.[26] Devillers, C.; Ramsay, D. A. *Can. J. Phys.* **1971**, *49*, 2839.[27] [d] Fulara, J.; Grutter, M.; Wyss, M.; Maier, J. P. *J. Phys. Chem. A* **1998**, *102*, 3459. Electronic absorption spectrum of CCO− isolated in a neon matrix.[5]

Table 2 reports for CCO$^-$ ($\tilde{A}^2\Sigma^+$) our quartic force field expressed in curvilinear coordinates. The large values obtained for the diagonal cubic and quartic terms relative to the stretching coordinates confirm the great importance of the anharmonic corrections for their determination. This great influence is corroborated by the analysis of the anharmonic force constants expressed in the dimensionless normal coordinate system reported in Table 3. The coefficients involving the CO and CC

TABLE 2: Quartic Force Force Field Calculated for C_2O^- in its First Excited State ($\tilde{A}^2\Sigma^+$) at CCSD(T) Level of Theory

parameter	our value (cm^{-1})
F_{RR}	13.483
F_{Rr}	1.193
F_{rr}	10.191
$F_{\alpha\alpha}$	0.770
F_{RRR}	−75.356
F_{RRr}	−2.226
F_{Rrr}	−1.017
F_{rrr}	−67.406
$F_{\alpha\alpha R}$	−1.870
$F_{\alpha\alpha r}$	−2.413
F_{RRRR}	303.15
F_{RRRr}	0.766
F_{RRrr}	0.708
F_{Rrrr}	0.712
F_{rrrr}	555.90
$F_{\alpha\alpha RR}$	0.215
$F_{\alpha\alpha Rr}$	1.681
$F_{\alpha\alpha rr}$	0.229
$F_{\alpha\alpha\alpha\alpha}$	4.864

R, r, and α are respectively CO, CC and bending coordinates. Units are consistent with energy measured in aJ.

TABLE 3: Cubic and Quartic Force Constants (cm^{-1}) for the ($\tilde{A}^2\Sigma^+$) State of CCO$^-$ with Respect to Dimensionless normal Coordinates[a]

parameter	calculated value (cm^{-1})	parameter	calculated value (cm^{-1})
ϕ_{111}	−279.44	ϕ_{3333}	48.7
ϕ_{113}	−372.75	ϕ_{1111}	68.3
ϕ_{122}	76.7	ϕ_{2233}	−61.9
ϕ_{133}	121.59	ϕ_{1122}	−181.8
ϕ_{223}	112.40	ϕ_{1133}	79.0
ϕ_{333}	−262.64	ϕ_{1333}	−122.0
		ϕ_{1113}	17.6
		ϕ_{1223}	6.3
		ϕ_{2222}	65.6

[a] Sign convention adopted for ϕ are consistent with a positive value for the eigenvectors L_{1k}.

stretching and their coupling are particularly strong through the ϕ_{111}, ϕ_{333}, and ϕ_{113} parameters.

Table 4 reports for CCO$^-$ ($\tilde{A}^2\Sigma^+$) our calculated anharmonic wavenumbers in the medium IR region and compares them with the available experimental data arising from the vibrational structures in the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ spectrum observed in a neon matrix. Calculated transition wavenumbers are complemented by the description of the configurational contributions in order to specify the assignment. The symmetry forbidden ν_2 transition calculated at 652 cm^{-1} corresponds to the bending mode that gives rise to the small band observed 4 cm^{-1} higher at 656 cm^{-1}. The first harmonic $2\nu_2$ and the $\nu_2 + \nu_1$ combinations are calculated respectively at 1310 and 2724 cm^{-1} and can be associated with the very weak absorption bands observed 8 and 1 cm^{-1} higher at 1318 and 2725 cm^{-1}. The ν_{CO} (ν_1) and ν_{CC} (ν_2) stretching modes are found respectively at 2077 and 1183 cm^{-1}, in perfect agreement with the intense and the weak absorption bands respectively observed at 2082 and 1185 cm^{-1}. Our calculations also prove the assignments proposed for the $\nu_1 + 2\nu_2$, $\nu_1 + \nu_3$, $2\nu_1$ and $2\nu_1 + \nu_2$ bands observed around 3381, 3232, 4141, and 4773 cm^{-1} and respectively calculated at 3374, 3255, 4154, and 4800 cm^{-1}. It is worth noticing that the agreement between the calculated and the observed data is remarkably good, better than 0.3% for the fundamental bands and better than 0.4% for overtones and combinations. This good agreement should be emphasized because the calculated vibrational frequencies are often shifted from the gas phase values particularly for ions. All other overtones and combinations bands calculated in the range 1800−4800 cm^{-1} are not observed experimentally. Our calculations predict wavenumbers around 1827, 1964, and 2362 cm^{-1} assigned to the $\nu_2 + \nu_3$, $3\nu_2$, and $2\nu_3$ combinations with present despite any coupling a dominant contribution making easier the assignment.

TABLE 4: Computed Transition Energies and Dominant Contributions Calculated between 300 and 4800 cm^{-1}

label	wave − number (cm^{-1})		description
	CCSD(T)	observed[a]	
ν_1	2077.0	2082[a]	$0.92\vert\nu_1\rangle$
ν_3	1183.4	1185[a]	$0.93\vert\nu_3\rangle$
ν_2	652.1	656[a]	$0.96\vert\nu_2\rangle$
$2\nu_2$	1310	1318[a]	$0.91\vert 2\nu_2\rangle$
$\nu_2 + \nu_3$	1827		$0.84\vert\nu_2 + \nu_3\rangle + 0.05\vert\nu_2 + 2\nu_3\rangle$
$3\nu_2$	1964		$0.75\vert 3\nu_2\rangle + 0.12\vert 2\nu_2 + \nu_3\rangle$
$2\nu_3$	2362		$0.79\vert 2\nu_3\rangle + 0.10\vert 3\nu_3\rangle$
$\nu_3 + 2\nu_2$	2480		$0.62\vert 2\nu_2 + \nu_3\rangle + 0.12\vert 3\nu_2\rangle + 0.07\vert\nu_2 + 2\nu_3\rangle$
$3\nu_2$	2624		$0.71\vert 4\nu_2\rangle + 0.14\vert 2\nu_2 + \nu_3\rangle + 0.11\vert\nu_2 + 2\nu_3\rangle$
$\nu_1 + \nu_2$	2724	2725[a]	$0.89\vert\nu_1 + \nu_2\rangle$
$2\nu_3 + \nu_2$	3001		$0.66\vert\nu_2 + 2\nu_3\rangle + 0.16\vert\nu_3\rangle + 0.08\vert 2\nu_2 + \nu_3\rangle + 0.10\vert\nu_2 + 3\nu_3\rangle$
$\nu_3 + 3\nu_2$	3130		$0.60\vert 3\nu_2 + \nu_3\rangle + 0.11\vert\nu_2 + 2\nu_3\rangle$
$\nu_1 + \nu_3$	3255	3232[a]	$0.771\vert\nu_1 + \nu_3\rangle + 0.11\vert\nu_1 + 2\nu_3\rangle$
$\nu_1 + 2\nu_2$	3374	3381[a]	$0.81\vert\nu_1 + 2\nu_2\rangle + 0.23\vert\nu_1 + \nu_3\rangle$
$3\nu_3$	3536		$0.68\vert 3\nu_3\rangle + 0.12\vert 4\nu_3\rangle + 0.10\vert 2\nu_3\rangle$
$2\nu_3 + 2\nu_2$	3645		$0.60\vert 2\nu_2 + 2\nu_3\rangle + 0.14\vert 3\nu_2 + \nu_3\rangle + 0.06\vert\nu_1 + \nu_2 + \nu_3\rangle$
$\nu_1 + \nu_2 + \nu_3$	3887		$0.48\vert\nu_1 + \nu_2 + \nu_3\rangle + 0.10\vert\nu_1 + \nu_2 + 2\nu_3\rangle$
$\nu_1 + 3\nu_2$	4023		$0.63\vert\nu_1 + 3\nu_2\rangle + 0.09\vert\nu_1 + 2\nu_2 + \nu_3\rangle$
$2\nu_1$	4154	4141[a]	$0.14\vert 2\nu_1 + \nu_3\rangle + 0.83\vert 2\nu_1\rangle$
$\nu_2 + 3\nu_3$	4160		$0.50\vert\nu_2 + 3\nu_3\rangle + 0.08\vert\nu_2 + \nu_3\rangle + 0.10\vert\nu_2 + 4\nu_3\rangle$
$\nu_1 + 2\nu_3$	4424		$0.56\vert\nu_1 + 2\nu_3\rangle + 0.16\vert\nu_1 + 3\nu_2\rangle + 0.11\vert\nu_1 + \nu_3\rangle$
$\nu_1 + 2\nu_2 + \nu_3$	4533		$0.63\vert\nu_1 + 2\nu_2 + \nu_3\rangle + 0.10\vert\nu_1 + 2\nu_2 + 2\nu_3\rangle + 0.11\vert\nu_1 + 2\nu_3\rangle$
$2\nu_1 + \nu_2$	4800	4773[a]	$0.67\vert 2\nu_1 + \nu_2\rangle + 0.07\vert 2\nu_1 + \nu_2 + \nu_3\rangle$

[a] Fulara, J.; Grutter, M.; Wyss, M.; Maier, J. P. *J. Phys. Chem. A* **1998**, *102*, 3459.[5]

In summary, our calculated anharmonic force field leads to results which show an excellent agreement with the most reliable experimental data proposed by Fulara et al.[5] This potential function also allows to assignment of combination and overtone bands not observed yet. We hope they may stimulate further experimental work determine the vibrational structure of the $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ electronic absorption spectrum of CCO$^-$.

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