

THEORETICAL STUDY OF THE A²Σ⁺-X²Π TRANSITION OF CCO⁻

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Three-dimensional potential energy functions have been generated for the A²Σ⁺ electronic state of C₂O⁻ using highly correlated electronic multi-reference configuration interaction wavefunctions. These were employed in variational calculations of the rovibrational states. The rotational constant has been calculated as $B_e = 0.3960 \text{ cm}^{-1}$, with $R_{\text{CO}}^e = 1.240 \text{ \AA}$ and $R_{\text{CC}}^e = 1.244 \text{ \AA}$. Rovibrational levels for $J = 0$ and 1 are reported for energies up to about $4\,800 \text{ cm}^{-1}$. Only weak anharmonic resonances are found in this energy region. The theoretically predicted A²Σ⁺←X²Π absorption spectrum is found to be in excellent agreement with the observed one in a neon matrix.

Keywords: Electronic calculations; Vibrational levels variational calculations; Electronic transition; Franck-Condon approximation; Electronic absorption spectroscopy; Vibrational wavefunctions; *Ab initio* calculations.

An electronic absorption spectrum of the C₂O⁻ ion has been observed in a neon matrix at 6 K, with origin at 1.516 eV and attributed to the A²Σ⁺-X²Π transition¹. The spectrum shows vibrational progressions of the fundamentals and their combinations in the upper state.

Neither experimental nor theoretical studies of the Renner-Teller effect have been reported for negative ions so far. The CCO⁻ anion appears to be one of the most suitable candidates for the investigation of this effect. As has been the case in most 15 valence electron systems, its emission spectrum could provide the necessary spectroscopic information. Our previous theoretical study dealt with the X²Π electronic ground state². In the present work large-scale *ab initio* electronic structure calculations of the potential energy function (PEF) for the A²Σ⁺ state were carried out, and its rovibrational states obtained in subsequent variational calculations. These

data were then used to predict the $A^2\Sigma^+-X^2\Pi$ absorption spectrum within the Franck–Condon approximation. The intensities and the positions of the vibrational peaks are in very good agreement with the experimental absorption spectrum¹ in a neon matrix at 6 K.

COMPUTATIONAL APPROACH

As the $X^2\Pi$ and $A^2\Sigma^+$ states both reduce to A' symmetry for the distorted nuclei geometries, it is impossible to use the RCCSD(T) method employed for the electronic ground state² to determine the $A^2\Sigma^+$ PEF. Consequently, this one was mapped by the internally contracted multireference configuration interaction (MRCI) approach^{3,4} and the MOLPRO software⁵. The AO basis set comprised the spd subset of the augcc-pVQZ basis⁶. In the complete active space self-consistent field^{7–9} (CASSCF) calculations, all valence orbitals but the highest σ orbital were active and the electronic ground and excited states were averaged with equal weights. In the subsequent MRCI calculations all CSF's of the CASSCF wavefunctions were used as a reference. The MRCI energies were calculated for 22 different geometries and fitted to a quartic polynomial expansion in displacement coordinates taking the calculated equilibrium geometry as reference

$$V(R_{CC}, R_{CO}, \Theta_{CCO}) = \sum_{ijk} C_{ijk} (q_1)^i (q_2)^j (q_3)^k$$

with

$$q_1 = R_{CC} - R_{CC}^e, \quad q_2 = R_{CO} - R_{CO}^e, \quad q_3 = \Theta_{CCO} - \Theta_{CCO}^e.$$

The explicit quartic force fields in internal and dimensionless normal coordinates obtained from this expansion are given in Table I. The variational calculations of the rovibrational states were performed for $J = 0$ and 1 using the method of Carter and Handy¹⁰, with the kinetic energy operator in bond coordinates and bisecting angle. The primitive basis set consisted of products of pre-optimized harmonic-oscillator eigenfunctions for the stretching modes, Legendre functions for the bending modes and rigid rotor eigenfunctions. The integration was performed numerically for the vibrational part, and analytically for the rotational part.

RESULTS

A rotationally resolved gas phase infrared or electronic spectrum of CCO⁻ anion is not available, so far, which could allow the determination of the equilibrium geometries and rotational spectroscopic constants. Such a set of spectroscopic constants as well as those characterizing the rovibrational levels have now been calculated by the perturbation approach¹¹ from the MRCI potential for the A²Σ⁺ state and is given in Table II. The R_{CC}^e and R_{CO}^e distances in the X²Π electronic ground state are predicted to be 1.308 and 1.221 Å, respectively. In the A²Σ⁺ state the R_{CO}^e distance is longer by 0.023 Å

TABLE I

MRCI quartic force fields of the A²Σ⁺ state in internal coordinates^a (left-hand column) and in dimensionless normal coordinates^b (right-hand column)

f_{rr}	10.0	ω_1	2 122.9
f_{RR}	13.3	ω_2	658.7
$f_{\theta\theta}$	0.8	ω_3	1 211.8
f_{rR}	0.9	Φ_{111}	-276.4
f_{rrr}	-73.4	Φ_{333}	-303.9
f_{RRR}	-79.4	Φ_{122}	76.9
f_{rrR}	-3.2	Φ_{223}	91.9
f_{rRR}	-2.1	Φ_{113}	-396.2
$f_{r\theta\theta}$	-1.3	Φ_{133}	122.7
$f_{R\theta\theta}$	-1.1	Φ_{1111}	141.4
f_{rrrr}	395.6	Φ_{2222}	21.6
f_{RRRR}	356.2	Φ_{3333}	57.0
$f_{\theta\theta\theta\theta}$	3.5	Φ_{1122}	-88.9
f_{rrrR}	1.5	Φ_{1113}	3.3
f_{rRRR}	0.1	Φ_{1223}	2.8
f_{rrRR}	2.1	Φ_{2233}	-38.2
$f_{rr\theta\theta}$	0.8	Φ_{1133}	64.4
$f_{RR\theta\theta}$	0.6	Φ_{1333}	-39.3
$f_{rR\theta\theta}$	1.7		

^a In aJ/Åⁿ; $r = R_{CO}$, $R = R_{CC}$, the bending coordinate is defined as in ref.¹¹, factorials are excluded. ^b All values in cm⁻¹.

and the R_{CC}^e distance shorter by 0.068 Å. Using a (4s3p2d1f) basis set and the CASPT2 approach, Zengin *et al.*¹² calculated the R_{CC}^e and R_{CO}^e distances to be 1.261 and 1.244 Å. Their internal force constants for the stretches $f_{\text{RR}} = 13.3 \text{ aJ/Å}^2$ and $f_{\text{TR}} = 10.4 \text{ aJ/Å}^2$ are in good agreement with our results (*cf.* Table I), though their harmonic wavenumbers $\omega_1 = 2\,218 \text{ cm}^{-1}$ and $\omega_3 = 1\,190 \text{ cm}^{-1}$ differ strongly from the calculated MRCI values in Table I. The excellent agreement with the experimental anharmonic wavenumbers (*cf.* next paragraph) shows that the present results are more accurate. The FG analysis of Wilson¹³ shows that the stretching modes have the following form

$$v_1 = -0.4736 R_{\text{CO}} + 0.8807 R_{\text{CC}}$$

$$v_3 = 0.7943 R_{\text{CO}} + 0.6076 R_{\text{CC}},$$

i.e. v_1 is more localized in the CC bond and the v_1 progression will be more intense than the v_3 one in the absorption spectrum due to the larger change in the CC distance between the $A^2\Sigma^+$ and the $X^2\Pi$ electronic states.

TABLE II

Equilibrium distances and spectroscopic constants of CCO^- in the $A^2\Sigma^+$ state calculated by perturbation theory

R_{CO}^e , Å	1.240	R_{CC}^e , Å	1.244
B_e , cm^{-1}	0.3960	B_0 , cm^{-1} ^a	0.3942
α_1 , MHz	87.6	α_2 , MHz	-13.7
α_3 , MHz	49.3	D_e , MHz	0.00498
q_f , MHz	20.8	ω_1 , cm^{-1}	2 123.1
ω_2 , cm^{-1}	658.8	ω_3 , cm^{-1}	1 211.9
x_{11} , cm^{-1}	-10.4	x_{22} , cm^{-1}	-2.2
x_{33} , cm^{-1}	-3.8	x_{12} , cm^{-1}	-10.1
x_{13} , cm^{-1}	-21.5	x_{23} , cm^{-1}	-15.3
g_{tr} , cm^{-1}	-2.558		
$G(0,0^0,0)$, cm^{-1}	2 306.9	$G(0,0^0,0)$, cm^{-1} ^a	2 312.6

^a Variational calculation.

In Table III the rovibrational levels for $J = 0$ and 1 are given for energies up to about 4 800 cm⁻¹ together with the experimental values obtained from the matrix absorption spectrum. The agreement between theory and experiment can be regarded as very good; the deviations are smaller than about 10 cm⁻¹. Anharmonic effects, such as Fermi coupling, are not important in low lying vibrational states of the A²Σ⁺ state. They start to play a

TABLE III
Rovibrational energies (in cm⁻¹) in the A²Σ⁺ state of ¹²C¹²C¹⁶O⁻

$J = 0$			$J = 1$		
Σ ⁺	Calc.	Exp. ^a	Π	Calc.	Exp. ^a
(0,0 ⁰ ,0)	0.0	0.0	(0,1 ¹ ,0)	649.9	656
(0,0 ⁰ ,1)	1 181.1	1 185	(0,1 ¹ ,1)	1 819.2	
(0,2 ⁰ ,0)	1 308.2	1 318	(0,3 ¹ ,0)	1 963.3	
(1,0 ⁰ ,0)	2 083.1	2 082	(1,1 ¹ ,0)	2 723.1	2 725
(0,0 ⁰ ,2)	2 354.5		(0,1 ¹ ,2)	2 980.6	
(0,2 ⁰ ,1)	2 469.0		(0,3 ¹ ,1)	3 115.2	
(0,4 ⁰ ,0)	2 624.4		(0,5 ¹ ,0)	3 282.1	
(1,0 ⁰ ,1)	3 245.9	3 232	(1,1 ¹ ,1)	3 874.5	
(1,2 ⁰ ,0)	3 371.5	3 381	(1,3 ¹ ,0)	4 016.9	
(0,0 ⁰ ,3)	3 520.1		(0,1 ¹ ,3)	4 134.0	
(0,2 ⁰ ,2)	3 623.0		(0,3 ¹ ,2)	4 260.3	
(0,4 ⁰ ,1)	3 768.6		(0,5 ¹ ,1)	4 418.4	
(0,6 ⁰ ,0)	3 944.3		(0,7 ¹ ,0)	4 603.0	
(2,0 ⁰ ,0)	4 148.3	4 141	(2,1 ¹ ,0)	4 778.6	4 773
(1,0 ⁰ ,2)	4 402.4				
(1,2 ⁰ ,1)	4 515.0				
(1,4 ⁰ ,0)	4 668.3				
(0,0 ⁰ ,4)	4 677.4				
(0,6 ⁰ ,1)	4 770.6				

^a Ref.¹

role for $2\nu_3 + \nu_2 = 6$. Figures 1 and 2 show the contour plots of three characteristic vibrational wavefunctions in the energy region around 3 700 and 4 100 cm^{-1} . In Fig. 1, two members of the $2\nu_3 + \nu_2 = 6$ polyad are displayed. The presence of a coupling between R_{CO} and the bending coordinate is already apparent. On the other hand, Fig. 2 shows an unperturbed vibrational wavefunction for the $(2,0^0,0)$ levels which lies above both coupled states.

Simulation of the intensities of the absorption spectrum was carried out within the Franck–Condon approximation for $J = 0$. The vibrational wavefunctions were calculated variationally: the zero-vibrational wavefunction of the $X^2\Pi$ state was determined by using the PEF of the ref.² and the vibrational wavefunctions of the $A^2\Sigma^+$ state were obtained using the present MRCI PEF. The overlap integrals were calculated numerically. The experimental and the theoretical spectra are displayed in Fig. 3. The agreement is excellent. In the absorption spectrum of CCO^- in a neon matrix at 6 K only

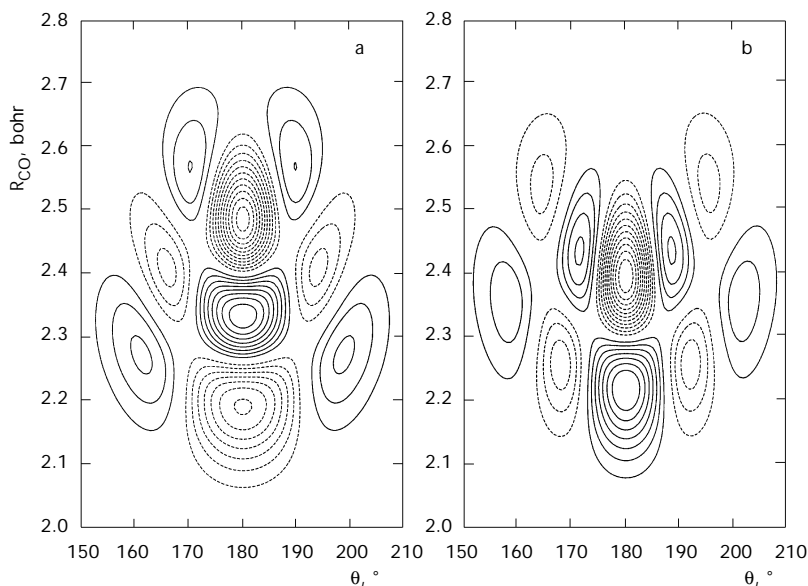


FIG. 1

Contour plots of the vibrational wavefunction for the two members of the $2\nu_3 + \nu_2 = 6$ Fermi polyad in the Σ^+ symmetry: a the level $(0,2^0,2)$ has an energy of 3 623.0 cm^{-1} above the vibrational ground state and b the level $(0,4^0,1)$ has 3 768.6 cm^{-1} . R_{CC} is fixed at its equilibrium value (2.3510 bohr). The step between the lines is 0.1. The dashed lines correspond to the negative part of the wavefunction and the full lines to the positive one

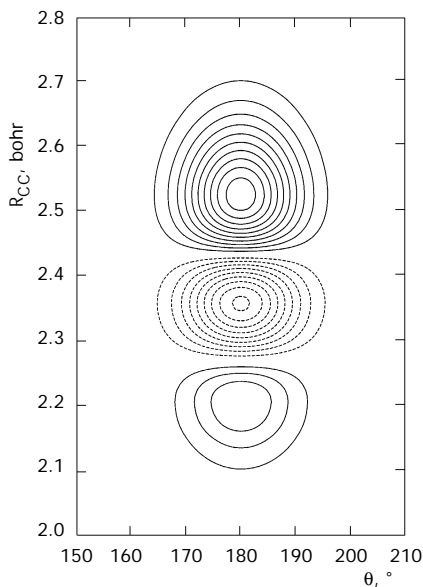


FIG. 2

Contour plots of the vibrational wavefunction of the $(2,0^0,0)$ level with an energy of $4\,148.3\text{ cm}^{-1}$. R_{CO} is fixed at its equilibrium value (2.3435 bohr). The step between the lines is 0.1. The dashed lines correspond to the negative part of the wavefunction and the full lines to the positive one

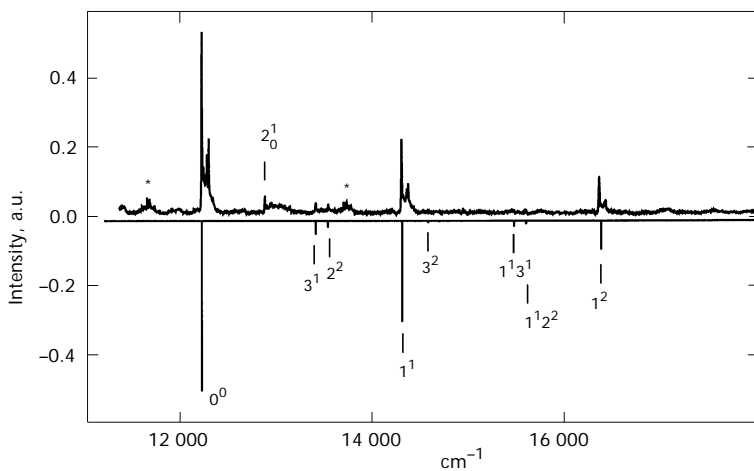


FIG. 3

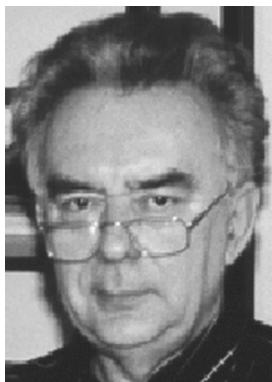
Absorption spectrum of C_2O^- in a neon matrix¹ (top) and calculated (bottom) for the $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi$ transition. Peaks marked with asterisks are due to absorptions of neutral C_2O

the lower spin-orbit component is populated. Thus the doubling of peaks in the spectrum appears to be a matrix effect.

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