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LETTERS

A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ Electronic Absorption Spectrum of CCO^- in a Neon Matrix

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An electronic absorption spectrum of CCO^- isolated in a neon matrix has been observed. The matrix was prepared by co-deposition of the mass-selected anions with excess neon at 6 K. The observed absorption spectrum is assigned to the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ electronic transition of linear CCO^- on the basis of mass-selection, photobleaching behavior, comparison with ab initio calculations, and the discernible vibrational structure. The origin band is located at 817.4(2) nm and the fundamental frequencies in the A $^2\Sigma^+$ state are $\nu_1(\sigma^+) = 2082(3)$, $\nu_2(\pi) = 656(3)$, and $\nu_3(\sigma^+) = 1185(3)$ cm^{-1}. The ν_1 fundamental in the electronic ground state has been observed at 1876.7(1.0) in the infrared spectrum.

Introduction

The C_2O molecule is a reactive intermediate taking part in many chemical reactions in the gas-phase.[1] It has also been identified in interstellar dark clouds by microwave spectroscopy.[2] The first communication on C_2O concerned its infrared spectrum in an argon matrix.[3] The frequencies of the three vibrational modes in the electronic ground state were determined. The results on isotopic substitution showed that C_2O is linear, with asymmetrical arrangement of the two carbon atoms. Several years later the electronic absorption spectrum of C_2O, produced by photolysis of carbon suboxide, was recorded in the gas-phase. Rotational analysis led to the assignment of the band system to the A $^3\Pi \leftarrow$ X $^3\Sigma^-$ electronic transition.[4] This transition was subsequently the subject of several higher resolution studies using diode lasers.[5−7] These delivered accurate information on the normal modes in the upper A $^3\Pi$ electronic state and confirmed the earlier conclusion concerning the structure of the molecule.

In contrast to the reasonably well-characterized C_2O species, information on C_2O^- is scarce. It was initially detected in flames by mass spectrometry.[8] This was succeeded by a photoelectron spectroscopic investigation,[9] which yielded 1.85 eV for the electron affinity of C_2O. The results of ab initio calculations on CCO led to the supposition that the ground electronic state of C_2O^- has X $^2\Pi$, and an excited state $^2\Sigma^+$ symmetry.[10] This was confirmed by ab initio results on CCO^- at the CASPT2 level.[11] These calculations predict the anion to be linear and asymmetric. The recent photoelectron study of CCO^- provided a new value for electron affinity, 2.29 eV.[11] The reactivity of CCO^- with various reagents has also been investigated.[12] This concluded that the CC bond is considerably weaker than the CO bond in CCO^-. In this contribution the first observation of the electronic spectrum of CCO^-, isolated in a neon matrix, is reported.

Experimental Section

The technique combining mass-selection and matrix-isolation spectroscopy has previously been used to identify the electronic spectra of carbon chain molecules.[13] C_2O^- was generated in a cesium ion sputter source that has been used to produce carbon anions.[14] By introduction of oxygen into the ion source via a small channel of 1 mm diameter drilled in the graphite cathode, C_nO^- ($n = 2-8$) anions were produced. The most intense peak in the mass spectrum was that of C_2O^-.

A beam of negative ions with $m/e = 40$ was mass-selected (20−50 nA) and co-deposited with neon for 6.5 h. The

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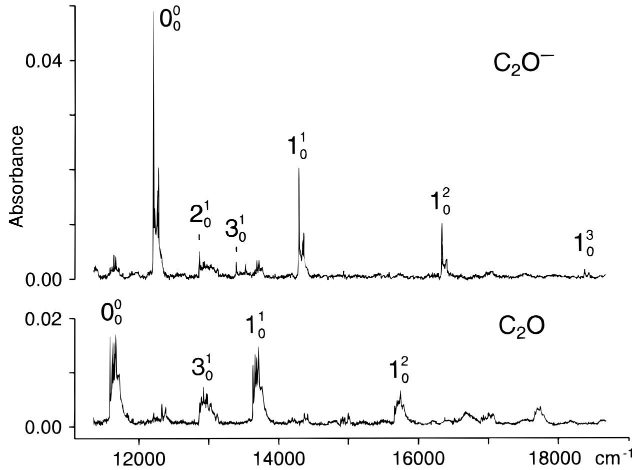

Figure 1. The A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ electronic absorption spectrum of CCO^- observed following co-deposition of mass-selected CCO^- with neon to form a 6 K matrix (top trace). The bottom trace shows the A $^3\Pi \leftarrow$ X $^3\Sigma^-$ electronic absorption spectrum of the CCO radical formed after irradiation of the matrix with UV light ($\lambda \geq 300$ nm).

TABLE 1: Band Maxima (±0.2 nm) in the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ Electronic Absorption Spectrum of CCO^- in a Neon Matrix

λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
817.4	12 234	0	0_0^0
816.2	12 252	18	site
813.8	12 288	54	site
812.6	12 306	72	site
775.8	12 890	656	2_0^1
745.2	13 419	1185	3_0^1
737.9	13 552	1318	2_0^2
698.5	14 316	2082	1_0^1
697.6	14 335	2101	site
695.8	14 372	2138	site
695.1	14 386	2153	site
668.5	14 959	2725	$1_0^1 2_0^1$
646.6	15 466	3232	$1_0^1 3_0^1$
640.4	15 615	3381	$1_0^1 2_0^2$
610.7	16 375	4141	1_0^2
608.3	16 439	4205	site
588.0	17 007	4773	$1_0^2 2_0^1$
543.0	18 416	6182	1_0^3
541.2	18 477	6244	site

deposition time was longer than the 2 h usually used and was necessary to obtain an ion concentration in the neon matrix that would be commensurate with the sensitivity of the infrared spectrometer.

After the matrix was grown, the absorption spectrum of trapped C_2O^- could be recorded in the 220−1100 nm region using the waveguide technique.[15] The spectrum in the infrared (1200−6000 cm^{-1}) was measured with 1 cm^{-1} resolution by single small-angle reflection. Photobleaching was carried out by illuminating the matrix ($\lambda \geq 300$ nm) with a high-pressure mercury lamp.

Results and Discussion

Electronic Absorption Spectrum. The absorption spectrum recorded after a 6.5 h co-deposition of mass-selected C_2O^- with neon is shown in the top trace of Figure 1. The spectrum displays one strong progression with a doublet structure. In the case of the most intense band around 12200 cm^{-1}, the doublet is further split into two more closely spaced components. At shorter wavelengths, not shown in Figure 1, an absorption band of C_2^- at 530 nm, and weaker bands at 506 and 390 nm due to C_2^+ and N_2^+, respectively, are also present. In the near-infrared a weak absorption band of C_2 at 1020 nm is apparent, and in the infrared a peak at 1876.7 cm^{-1}. The pure carbon molecules observed were formed either by photofragmentation (C_2^-), electron detachment (C_2), or ionization (C_2^+) resulting from the high kinetic energy (~60 eV) of the C_2O^- ions deposited.

Irradiation of the neon matrix containing C_2O^- with UV light ($\lambda \geq 300$ nm) resulted in the disappearance of the band system. It was gradually replaced by a different band system with a marked multiplet structure (Figure 1, bottom trace). This is the known A $^3\Pi \leftarrow$ X $^3\Sigma^-$ electronic transition of C_2O.[4] The vibrational frequencies $\nu_1 = 2045(3)$ and $\nu_3 = 1279(3)$ cm^{-1} in the A $^3\Pi$ excited state determined from this spectrum and the 0_0^0 band at 11 650(3) cm^{-1} are very similar to the values $\nu_{00} = 11\,650.8$, $\nu_1 = 2045.7$, and $\nu_3 = 1270$ cm^{-1} determined from the gas-phase spectrum.[4]

The UV irradiation also resulted in the disappearance of the IR band at 1876.7 cm^{-1} and the concomitant appearance of an absorption at 1972.5 cm^{-1}. The latter is the ν_1 fundamental of CCO, with known gas-phase (1972.5 cm^{-1})[16] and argon matrix (1969 cm^{-1})[3] values. The above observations lead to the conclusion that the absorption features in Figure 1 (top) and the infrared band at 1876.7 cm^{-1} are due to CCO^-. The irradiation process converts CCO^- into the neutral CCO molecule.

According to the ab initio calculations, the A $^2\Sigma^+$ excited-state lies 1.42 eV above the X $^2\Pi$ ground state,[11] which is consistent with the observed band origin at 1.517 eV. Thus the absorption spectrum shown at the top of Figure 1 is assigned to the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ electronic transition of CCO^-. The isoelectronic CNO radical has the origin of the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ transition at 12 612 cm^{-1} in the gas-phase.[17] The similarity of the CCO^- (A $^2\Sigma^+ \leftarrow$ X $^2\Pi$) and CCO (A $^3\Pi \leftarrow$ X $^3\Sigma^-$) band systems (Figure 1) arises because both electronic transitions involve mainly $\sigma \rightarrow \pi$ excitation between the same molecular orbitals.

The marked difference in the multiplet structure of the bands in the electronic spectra of CCO^- and CCO (Figure 1) may be correlated with the symmetry of the transitions. In the case of CCO, the site structure is richer and the absorption bands are broader than for CCO^-. The upper electronic state A $^3\Pi$ of CCO has three spin−orbit components, with constant $A \approx -35$ cm^{-1}.[5] The resulting splitting is further complicated by site structure, owing to nonequivalent orientations of the molecule trapped in the matrix. On the other hand, the upper state of CCO^- (A $^2\Sigma^+$) will only show the effects of site structure. Transitions are observed solely from the $\Omega = {}^3/_2$ component of the X $^2\Pi$ ground state at the 6 K temperature of the neon matrix. Thus it is not surprising that the bands in the A $^2\Sigma^+ \leftarrow$ X $^2\Pi_{3/2}$ transition of CCO^- show less structure.

Vibrational Structure. The energies of the bands observed in the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ spectrum of CCO^- are listed in Table 1 with suggested vibrational assignments. As all the transitions originate from the $v = 0$ level of the X $^2\Pi_{3/2}$ state, the band structure apparent corresponds to the excitation of the vibrational modes in the A $^2\Sigma^+$ excited electronic state. The most intense bands involve the ν_1 mode progression of CCO^-, enabling the harmonic frequency $\omega_1 = 2076(3)$ cm^{-1} and the anharmonic constant $\omega_e x_e = 7(1)$ cm^{-1} to be evaluated. The spectrum also shows a weak absorption band 1185 cm^{-1} above the origin band, which corresponds to the ν_3 fundamental, as well as weak features associated with the $\nu_1 + \nu_3$ combination. A small band is also apparent 656 cm^{-1} above the origin that is attributed to

TABLE 2: Vibrational Frequencies of the Normal Modes of CCO^- and CCO in the Ground and First Excited Electronic States in a Neon Matrix. Known Gas-Phase Values for CCO Are Included

		ν_1	ν_2	ν_3
CCO^-	A $^2\Sigma^+$	2082(3)	656(3)	1185(3)
	X $^2\Pi$	1876.7(1.0)		
CCO	A $^3\Pi$	2045(3)		1279(3)
		2045.7[a]	607.8[a]	1270[a]
	X $^3\Sigma^-$	1972.5(1.0)	381[b]	1074[b]
		1970.86[a]	379.4[a]	

[a] Gas-phase.[4] [b] Argon matrix.[3]

the excitation of the bending fundamental by one quantum, being symmetry-forbidden. This mode also gives rise to weak combination bands with ν_1. The symmetry forbidden ν_2 transition was also observed in the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ absorption spectrum of the isoelectronic CNO isolated in a neon matrix,[18] as well as in the gas-phase electronic spectrum of CCO.[4]

The vibrational frequencies for CCO^- in a neon matrix inferred from the electronic band system (Figure 1), and from the infrared spectrum, are summarized in Table 2. These values can be compared with the frequencies of the CCO radical. The frequency $\nu_1 = 1876.7$ cm^{-1} determined for the ground state of CCO^- is close to the value of 1900 cm^{-1} deduced from the gas-phase photoelectron spectrum,[10] although the latter value is endowed with a rather large uncertainty (±150 cm^{-1}). Ab initio calculations yield the harmonic frequency $\omega_1 = 1912$ cm^{-1},[11] close to the experimental result. For comparison, the frequency of the ν_1 mode in CCO is 1972.5 cm^{-1} in a neon matrix and 1970.86 cm^{-1} in the gas-phase.[16]

The ν_1 frequency in the A $^2\Sigma^+$ excited electronic state of CCO^- is higher than in the X $^2\Pi$ ground state. This was predicted by the CASPT2 calculations, although the value of $\omega_1 = 2218$ cm^{-1} in the A $^2\Sigma^+$ state is overestimated.[11] This change in the ν_1 frequency on passing from the ground to the excited electronic state is reflected by the intensity of the ν_1 progression in the spectrum of CCO^- (Figure 1). A similar change in the ν_1 frequency between the X $^3\Sigma^-$ ground and A $^3\Pi$ excited electronic states is observed for the CCO radical (Table 2), and the band system is also dominated by the ν_1 progression.

The 1185 cm^{-1} frequency of the ν_3 vibrational mode in the A $^2\Sigma^+$ excited electronic state of CCO^- is in accord with the ab initio result, $\omega_3 = 1190$ cm^{-1}.[11] The inferred value for the ν_2 bending mode, 654 cm^{-1}, is comparable to the ν_2 frequencies in the excited electronic states of CNO ($\nu_2 = 605$ cm^{-1})[18] and of CCO ($\nu_2 = 607.8$ cm^{-1}).[4]

Conclusion

Matrix isolation of mass-selected anions in combination with photobleaching is a powerful method to spectroscopically characterize anions and neutral species. The application of this method to the study of CCO^- allowed the identification of the A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ electronic transition and the vibrational frequencies of the normal modes to be inferred for the excited state. These results establish the basis for high-resolution studies of CCO^- in the gas-phase.

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