

Ultraviolet photoelectron spectroscopy of the chromium dioxide negative ion

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Chromium dioxide, CrO_2 , is commonly used in magnetic storage tapes and other magnetic layers. Considering its importance in audio and data storage technology, it is not surprising that the properties of bulk CrO_2 have been well studied.¹ However, despite all the work that has been done, important aspects of the electronic structure and metal/semiconductor character of CrO_2 still remain unresolved.²

While the properties of bulk phase CrO_2 have been investigated in depth, little is known about the isolated CrO_2 monomer. Vibrational spectroscopy of CrO_2 , prepared in Ar matrices from the reaction of chromium atoms with O_2 , has been reported.^{3–10} A common feature of all these studies is that the CrO_2 is generated along with many other species, including CrO_2 coordinated to other molecules such as CO. The IR spectra of these complexes are significantly perturbed from that of the isolated molecule, and the vibrational frequencies of (nearly) free CrO_2 are not well determined at the present time.

Most of the vibrational studies that have been carried out have focused on determining the value of ν_3 , the asymmetric stretching frequency, for three isotopomers of CrO_2 ($^{52}\text{Cr}^{16}\text{O}_2$, $^{52}\text{Cr}^{16}\text{O}^{18}\text{O}$, and $^{52}\text{Cr}^{18}\text{O}_2$) in order to determine the O–Cr–O bond angle. Serebrennikov and Mal'tsev³ originally reported a bond angle of 105° for CrO_2 prepared from the condensation of sputtered Cr atoms with O_2 . Almond and co-workers⁹ have obtained a bond angle of $112 \pm 2^\circ$ after a series of extensive investigations in which Cr atoms were prepared by photolysis of $\text{Cr}(\text{CO})_6$. Recently, Andrews and co-workers¹⁰ have measured a significantly higher value of $128 \pm 5^\circ$ using not only the three isotopomers listed above, but also using ν_3 for isotopomers involving ^{53}Cr and ^{54}Cr . In this study, Cr atoms were prepared by laser ablation of chromium metal, such that the CrO_2 is prepared without the presence of possible carbonyl-containing by-products. The values of ν_3 obtained in these studies range from 964 – 978 cm^{-1} , with most around 970 cm^{-1} (Table I).

While it appears the value of the asymmetric stretching frequency in CrO_2 is fairly well established, the value of ν_1 , the symmetric stretching frequency, has been controversial. Determination of this frequency using IR spectroscopy is difficult because the peak corresponding to this mode is much weaker than that for ν_3 . Serebrennikov and Mal'tsev³ originally estimated 935 cm^{-1} , while Almond and Hahne⁹ deduced a value 960 cm^{-1} , corresponding to a shoulder on the ν_3 peak. This latter value is significantly higher than the value of 914.4 cm^{-1} determined recently by Andrews and

co-workers.¹⁰ The bending frequency in CrO_2 , ν_2 , has not been measured.

The properties described above all refer to matrix isolated CrO_2 . It would be much more desirable to determine the properties of this molecule in the gas phase, but such measurements have not been available until now. We have now used negative ion photoelectron spectroscopy of mass-selected CrO_2^- ions to study the properties of gas-phase CrO_2 . From the spectrum, we obtain values for ν_1 and ν_2 for the isolated, gas-phase molecule, along with an accurate electron affinity for CrO_2 . Our data support the lower of the two matrix values for ν_1 .

The negative ion photoelectron spectrometer, the laser system, and experimental procedures used for this work have all been described previously.¹¹ Thermalized CrO_2^- ions are prepared by the reaction of O^- with $\text{Cr}(\text{CO})_6$ in the presence of oxygen in a flowing afterglow ion source. The photoelectron spectrum of CrO_2^- (Fig. 1) shows a single electronic state with extensive vibrational structure. The identity of the origin (0–0) peak of the spectrum, marked in Fig. 1, was established by cooling the flowing afterglow with liquid nitrogen. The intensities of the hot bands relative to the assigned origin decreased significantly under these conditions, providing an unequivocal assignment of the band origin and electron affinity of CrO_2 . The electron affinity of CrO_2 is found to be $2.413 \pm 0.008 \text{ eV}$, which is consistent with the previously reported value of $2.3 \pm 0.7 \text{ eV}$,¹² but substantially more precise. Two vibrational progressions are observed in the spectrum, corresponding to the symmetric stretch and bending modes, ν_1 and ν_2 . The vibrational frequency of the symmetric stretching mode, ν_1 , is $895 \pm 20 \text{ cm}^{-1}$. This is in reasonable agreement with the matrix result of Andrews and co-workers,¹⁰ but significantly lower than that reported by Almond and Hahne.⁹ The bending frequency, ν_2 , is 220

TABLE I. Summary of measured vibrational frequencies for chromium dioxide.

Method	ν_1 / cm^{-1}	ν_2 / cm^{-1}	ν_3 / cm^{-1}	Reference
Matrix IR	935		978	3
			971	4
			971	5
			964	6
			971	8
			969.8	9
NIPES	895 ± 20	220 ± 20	914.4	10
				This work

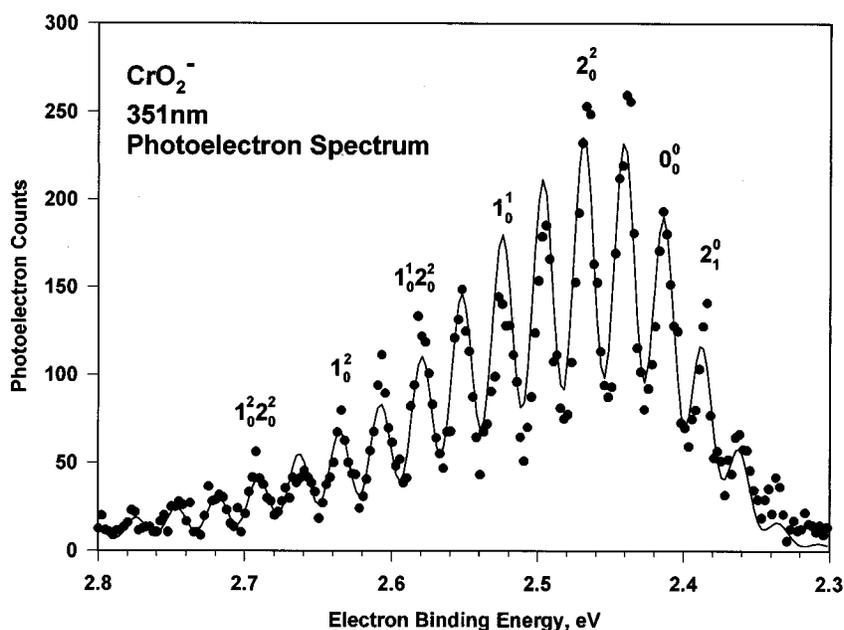


FIG. 1. The 351 nm photoelectron spectrum of chromium dioxide anion. The points (●) are the experimental spectrum while the solid line is the Franck-Condon fit to the data. See text for details.

$\pm 20 \text{ cm}^{-1}$. A summary of the data for CrO_2^- is given in Table I. From hot bands, we obtain a value of $205 \pm 40 \text{ cm}^{-1}$ for the bending mode in the negative ion.

The complex vibrational pattern in the spectrum can be accurately reproduced using a Franck-Condon analysis procedure described previously.¹¹ The calculated spectrum, shown as a solid line in Fig. 1, was obtained using vibrational frequencies of 220 and 895 cm^{-1} , with corresponding normal coordinate displacements (ΔQ_i)¹³ of 0.72 and $0.21 \text{ amu}^{1/2} \text{ \AA}$, respectively. The large geometry differences between the ion and neutral are most likely a result of a larger bond angle and longer bond lengths in the ion, better stabilizing the extra charge. The hot bands correspond to a bending frequency of 205 cm^{-1} , with an ion temperature of 360 K.

The electron detachment yield, I_θ , depends on the polarization of the laser according to the equation $I_\theta \propto 1 - \beta P_2(\cos \theta)$, where $P_2(\cos \theta)$ is the second Legendre polynomial and β is the anisotropy parameter. The value of β can be determined from the signal intensities for detachment with the laser parallel (I_0) and perpendicular (I_{90}) to the detector using the relation $\beta = (I_0 - I_{90}) / (0.5I_0 - I_{90})$,¹⁴⁻¹⁷ and be used to infer information regarding the orbital from which the electron is detached. For atomic ions, detached electrons from s -orbitals have $\beta = 2$, while detachment from p -orbitals has $\beta = -1$ at energies close to threshold. For example, detachment of Cr^- to form the 7S_3 state of Cr has $\beta = +2$, which indicates that the electron is detached from the $4s$ orbital. The interpretation of β in molecular systems is more difficult, but it has been found that β is close to $+2$ for electrons detached from highly s -like (σ) orbitals, while $\beta \leq 0$ for detachment from p -like (π) orbitals. For detachment of the ions CrO^- ¹⁸ and CrO_2^- , the corresponding

anisotropy parameters are 1.7 and 1.0 ± 0.2 , indicating that the orbital from which the electron is detached strongly resembles the Cr $4s$ orbital, but is perturbed slightly.

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