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**High Resolution He I α Photoelectron Spectroscopy of
H₂CO and D₂CO Using Supersonic Molecular Beams**

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Abstract

High resolution helium I α (584 Å) photoelectron spectra of H₂CO and D₂CO using supersonic molecular beams are reported. The excitation of the ν_4 out-of-plane bending mode in the ionic ground state and the first excited state imply that formaldehyde cations in these states might have non-planar equilibrium geometries. The different vibrational progressions observed in the first and second excited states indicate strong isotope effects on vibrational (vibronic) couplings. The AIEs and spectroscopic constants for all four ionic states are reported to a much higher accuracy than previously available.

1. Introduction

The photoelectron spectroscopy of H_2CO and D_2CO has been the subject of extensive experimental and theoretical investigations.¹⁻¹⁰ Most of the theoretical work has been based on the early experimental studies by Turner et al,¹ and by Baker et al.² The assignment of the four outermost valence states' adiabatic ionization energies (AIEs) by Turner et al has been the subject of some theoretical calculations, especially on the ordering of the third and fourth ionic states. The vibrational fine structures observed in these lower-resolution works have been studied extensively by theoretical calculations. Although the vibrational structures seemed well resolved and relatively simple in most of the electronic states, their interpretation has caused considerable difficulty.^{11, 12} Cederbaum et al^{6,7} used a many-body approach to the vibrational structures in formaldehyde, and cautioned that the vibrational couplings could be very different for different isotopic species. There were also disagreements between the theoretical and experimental results regarding the vibrational assignments.¹³

In this letter, we report high-resolution (FWHM 11 meV) helium $\text{I}\alpha$ (584 Å) photoelectron spectra of H_2CO and D_2CO . Improved resolution and effective cooling of the sample by supersonic expansion enabled us to determine the AIEs to a much higher accuracy (± 3 meV), and to report spectroscopic constants for all four ionic states with very high accuracy (± 0.5 meV, e.g. 4.3 cm^{-1}).

2. Experiment

The molecular beam photoelectron spectrometer used for this study has been described previously.¹⁴ Briefly, it consists of a supersonic molecular beam source, a windowless helium discharge lamp, a quadrupole mass spectrometer, and a high-resolution electron-energy analyzer consisting of a 90° spherical sector prefilter and a 180° hemispherical analyzer equipped with a multichannel detector. The energy resolution was 11 meV (FWHM) as calibrated by Ar photoelectron peaks.

Approximately 300 torr of ultra high purity helium (99.9999%, Matheson) was first passed through a U-tube maintained at 77 K to remove trace amounts of water in the carrier gas line, then bubbled through a liquid monomer of H₂CO or D₂CO trap maintained at acetone/dry ice slush temperature (195 K) with vapor pressures about 35 and 30 torr as measured with an MKS model 122AA-2000 Baratron. The monomer H₂CO or D₂CO was prepared following a literature procedure¹⁵ by thermocracking paraformaldehyde (95%) and fully deuterated paraformaldehyde (MSD Isotopes 99% D-atom) at ca. 393 K, fractioning (at 195 K) and trapping the monomer (at 77 K) and storing it in the dark with continuous pumping at 77 K before use. The He/H₂CO or He/D₂CO mixture, at a total pressure of ca. 350 torr, was expanded through a 70 μm diameter nozzle held at room temperature, and skimmed by a 0.858 mm diameter, 6.4 mm tall conical skimmer. Beam compositions were checked using the quadrupole mass spectrometer. No polymers of H₂CO or D₂CO were found under these experimental conditions. The rotational temperature in the beams was

estimated to be <10 K as shown by laser induced fluorescence (LIF) measurements under similar conditions.¹⁶

3. Results and Discussions

The full photoelectron spectra of H₂CO and D₂CO obtained by combining four separate scans with a resolution of 11 meV FWHM are shown in Figure 1. Table I summarizes the measured spectroscopic constants together with results reported in the literature.^{17,18} The absolute AIEs are accurate to ± 3.0 meV. This accuracy is mainly limited by the drifts and the linearity of the energy scales as will be discussed in forthcoming publications.^{19,20} Other spectroscopic constants, however, were obtained as line splittings, and are reported to a much higher accuracy of ± 0.5 meV (4.3 cm⁻¹).

3.1 The First Band, the \tilde{X}^1B_2 state

The \tilde{X}^1B_2 states of both H₂CO⁺ and D₂CO⁺, with well-resolved vibrational structures, are shown in Figure 2. The weak excitation of the ν_4 out-of-plane bending mode is an indication that formaldehyde cations might have non-planar equilibrium geometries. The \tilde{X}^1B_2 state corresponds to the removal of an electron from the b_2 (n_O) orbital, thus reducing the stabilization energy gained by having two electrons in the planar form. This also reduces the repulsion between the hydrogen atoms and the oxygen atom. MO calculations have indicated that, in the \tilde{X}^1B_2 state of H₂CO⁺ and D₂CO⁺, the HCO angle decreases slightly ($\sim 5^\circ$) from the neutral \tilde{X}^1A_1 state. Buenker and Peyerimhoff concluded from their *ab initio* calculations that molecules with 10 and 11 valence electrons are less strongly planar compared to those with 12

upon electron removal from the n non-bonding orbitals. We expect the deviation from the planar equilibrium geometry to be very small. The present assignments of the vibrational progressions agree with the theoretical calculations by Domcke et al,⁷ but not with the results of the calculation by Takeshita¹³ concerning the excitation of the ν_1 mode in H_2CO^+ . The anharmonicity would be too big if we assigned the feature at 11.2086 eV as the $\nu_2 = 2$ peak.

3.2 The Second Band, the $\tilde{\text{A}}^2\text{B}_1$ State

The photoelectron spectra of the $\tilde{\text{A}}^2\text{B}_1$ states of H_2CO^+ and D_2CO^+ , are shown in Figure 3. The different vibrational progressions are fully resolved here for the first time. In both isotopic compounds the major progression are assigned to the excitation of the ν_2 mode but, as discussed first by Domcke et al, the vibrational couplings are different for the isotopic compounds. In H_2CO^+ the vibrational progressions observed are attributed to the excitation of the ν_2 mode, with several quanta of the ν_3 mode excited as well. In D_2CO^+ , however, it is the ν_1 mode that gets excited along with the major excitation of the ν_2 mode. These agree fairly well with the theoretical calculations by Domcke et al⁷, when many-body effects are included. This is expected, since the vibrational coupling coefficients are mass-dependent (the kinematic matrix, which transforms from normal to internal coordinates, of D_2CO differs considerably from that of H_2CO). But without rotationally resolved studies on individual features presented in the current spectrum, the assignment of excitation of the ν_1 or ν_3 mode in both isotopic compounds cannot be regarded as definitive.

3.3 The Third Band, the \tilde{B}^2A_1 State

The third bands of H_2CO^+ and D_2CO^+ are shown in Figure 4. The simplicity of the \tilde{B}^2A_1 state spectrum in H_2CO^+ was attributed to the accidental degeneracy of the ν_2 and ν_3 modes in previous experimental and theoretical studies.¹⁻¹⁰ The removal of this degeneracy in D_2CO^+ was used to support this interpretation. Here we note that the different vibrational progression patterns observed in H_2CO^+ and D_2CO^+ in the \tilde{B}^2A_1 states might be due to differences in vibrational couplings, according to the many-body approach calculation by Domcke et al.⁷ This is supported by the FWHM observed in the present spectra. In H_2CO^+ the FWHM is close to 12 meV, and in D_2CO^+ it is slightly broader than 12 meV, with both being very close to the instrumental resolution. Unless ν_2 and ν_3 are truly degenerate to within 1 meV or less, we would have seen a broadening of the peaks in the H_2CO^+ spectrum. We tentatively assigned the vibrational progression in the \tilde{B}^2A_1 state of H_2CO^+ to the ν_2 mode only. The present assignment of the AIEs and vibrational progressions definitely support the assignment of Brundle et al.¹² and all theoretical calculations³⁻¹³ available: i.e. that this band is the \tilde{B}^2A_1 state of formaldehyde.

3.4 The Fourth Band, the \tilde{C}^2B_2 State

The fourth band of H_2CO^+ was shown in Figure 4 together with the third band. The fourth band of D_2CO^+ is shown in Figure 5 separately. Even with supersonic cooling in the present high-resolution study, the complexity of this band for both isotopic compounds cannot be fully untangled. As pointed out by Turner et al in their original studies, the complexity might have

been caused by the crossing of another repulsive state with the $\tilde{C} 2^2B_2$ state. In separate publications,^{19,20} we have calculated the vibrational autocorrelation function for this band. The results support that this state is subject to lifetime (dissociation and predissociation) broadening effects. The AIEs and the vibrational progression assignments for this band could only be regarded as tentative, especially in the case of D_2CO^+ . The vibrational assignments are based largely on the theoretical analysis of Domcke et al.⁷

In conclusion, we have obtained high resolution photoelectron spectra of formaldehyde and deuterated formaldehyde using supersonic molecular beams. The AIEs and spectroscopic constants for all four ionic states accessible by the helium Ia (584 Å) radiation are reported to a much higher accuracy than previously available.

Acknowledgment

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Table I. Adiabatic Ionization Energies (eV) & Vibrational Frequencies (cm⁻¹) Observed

Ionic States	AIE ^a (eV)	$\nu_1, \omega_e X_e$ (cm ⁻¹)	$\nu_2, \omega_e X_e$ (cm ⁻¹)	$\nu_3, \omega_e X_e$ (cm ⁻¹)	$\nu_4, \omega_e X_e$ (cm ⁻¹)
H ₂ CO ^f \tilde{X} 1A ₁		2782.5	1746.0	1500.2	1167.3
H ₂ CO ⁺ \tilde{X} 1 ² B ₂	10.8887(4)	2580.2(4.3)	1674.8, 19.0 (4.3)	1210.2, 6.1 (4.3)	777.1, 13.3 (4.3)
\tilde{A} 2B ₁	14.1024(2)		1250.5, 10.0 (4.3)	1487.7, 0.6 (4.3)	262.8 ^c (4.3)
\tilde{B} 2A ₁	15.8375(3)		1304.5, 12.6 (4.3)	1304 (20)	
\tilde{C} 2 ² B ₂	16.2395(10)	1894.9 ^d , 11.3 (4.3)		1411.7 ^d , 12.5 (4.3)	

Ionic States	AIE ^a (eV)	$\nu_1, \omega_e X_e$ (cm ⁻¹)	$\nu_2, \omega_e X_e$ (cm ⁻¹)	$\nu_3, \omega_e X_e$ (cm ⁻¹)	$\nu_4, \omega_e X_e$ (cm ⁻¹)
D ₂ CO ^f \tilde{X} 1A ₁		2055.8	1701.6	1105.7	938.0
D ₂ CO ⁺ \tilde{X} 1 ² B ₂	10.9076(4)	1948.2, 28.6 (4.3)	1656.7, 11.3 (4.3)	919.9, 31.1 (4.3)	648.1, 8.9 (4.3)
\tilde{A} 2B ₁	14.0999(5)	1064.5, 10.0 (4.3)	1281.6, 5.7 (4.3)		776.6 ^e (4.3)
\tilde{B} 2A ₁	15.8425(2)		1311.1, 15.3 (4.3)	957.3, 3.4 (4.3)	
\tilde{C} 2 ² B ₂	16.4350(200) ^b	1604.4 ^d , 22.3 (4.3)	943.4 ^d , -12.7 (4.3)	818.7 ^d , -11.8 (4.3)	

(a) The absolute AIEs are accurate to ± 3.0 meV as discussed in the main text. Other spectroscopic quantities, however, were obtained as line splittings, and can be reported to higher accuracy of ± 0.5 meV (4.3 cm⁻¹). (b) This value is the best estimate. (c) the value of $\nu_4=1,0$ splitting. (d) These values are estimates only. (e) The average value of $\nu_4=2, 1, 0$ splittings. (f) From ref. 17, 18. Number in parentheses indicate the uncertainties in the last digit.

Figure Captions:

- Figure 1. The full spectra of H_2CO and D_2CO . The designation of the ionic states is based on C_{2v} symmetry.
- Figure 2. The $\tilde{\text{X}}\ 1^2\text{B}_2$ states of H_2CO^+ and D_2CO^+ . The designation of the vibrational progression 2_0^n stands for the following transition:

$$\text{M}^+(\nu_2 = n) + e^- \leftarrow \text{M}(\nu_2 = 0) + h\nu$$
in accordance with standard spectroscopic notations.
- Figure 3. The $\tilde{\text{A}}\ 2^2\text{B}_1$ states of H_2CO^+ and D_2CO^+ , here hb stands for hot band. The presence of the nitrogen peak makes the absolute AIE of the $\text{D}_2\text{CO}^+\ \tilde{\text{A}}\ 2^2\text{B}_1$ state reportable to an accuracy of ± 1.0 meV.
- Figure 4. The $\tilde{\text{B}}\ 2^2\text{A}_1$ and $\tilde{\text{C}}\ 2^2\text{B}_2$ states of H_2CO^+ , and the $\tilde{\text{B}}\ 2^2\text{A}_1$ state of D_2CO^+ . The presence of the Ar peaks in this band makes the absolute AIEs reportable to an accuracy of ± 1.0 meV.
- Figure 5. The $\tilde{\text{C}}\ 2^2\text{B}_2$ state of D_2CO^+ .

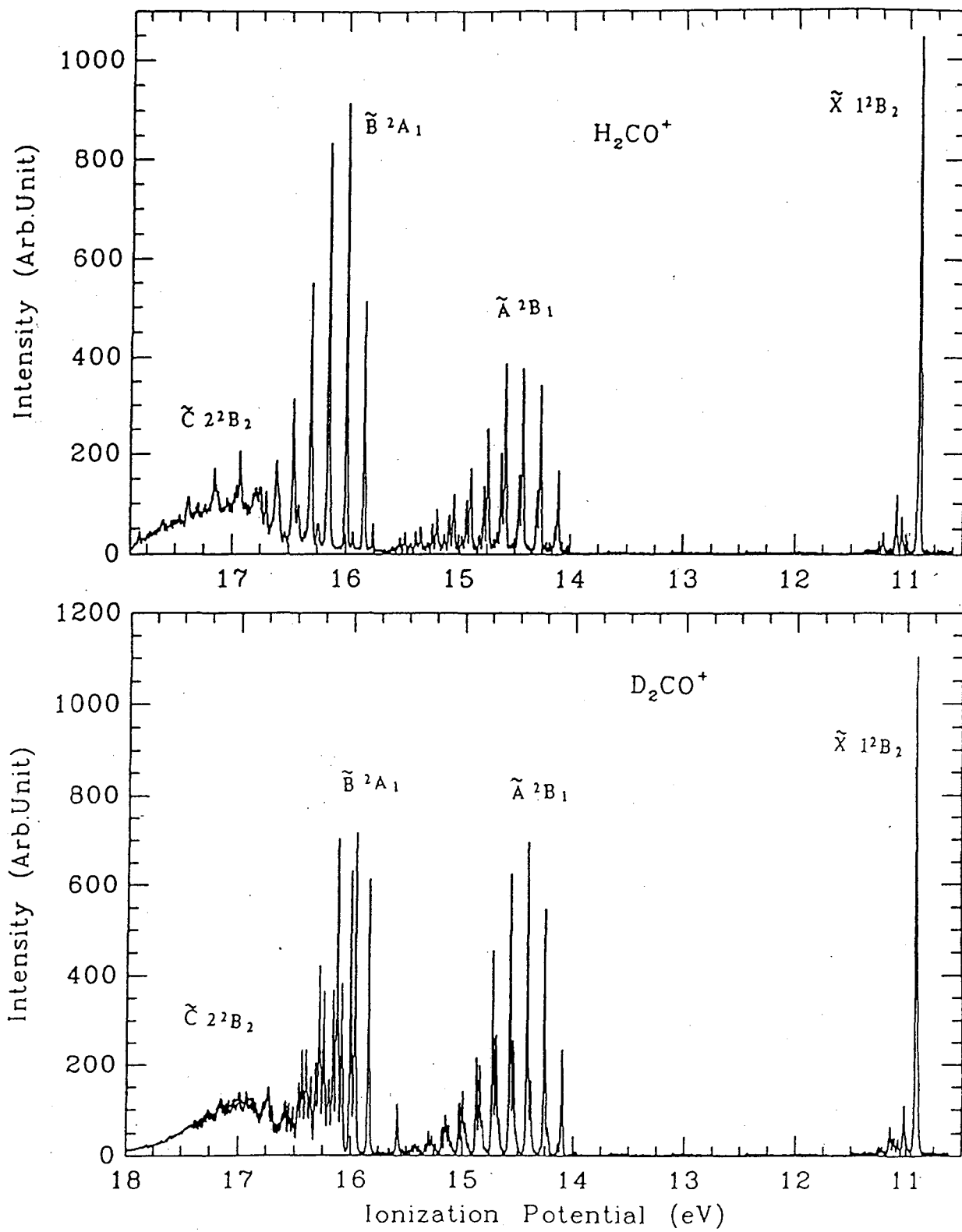


Figure 1

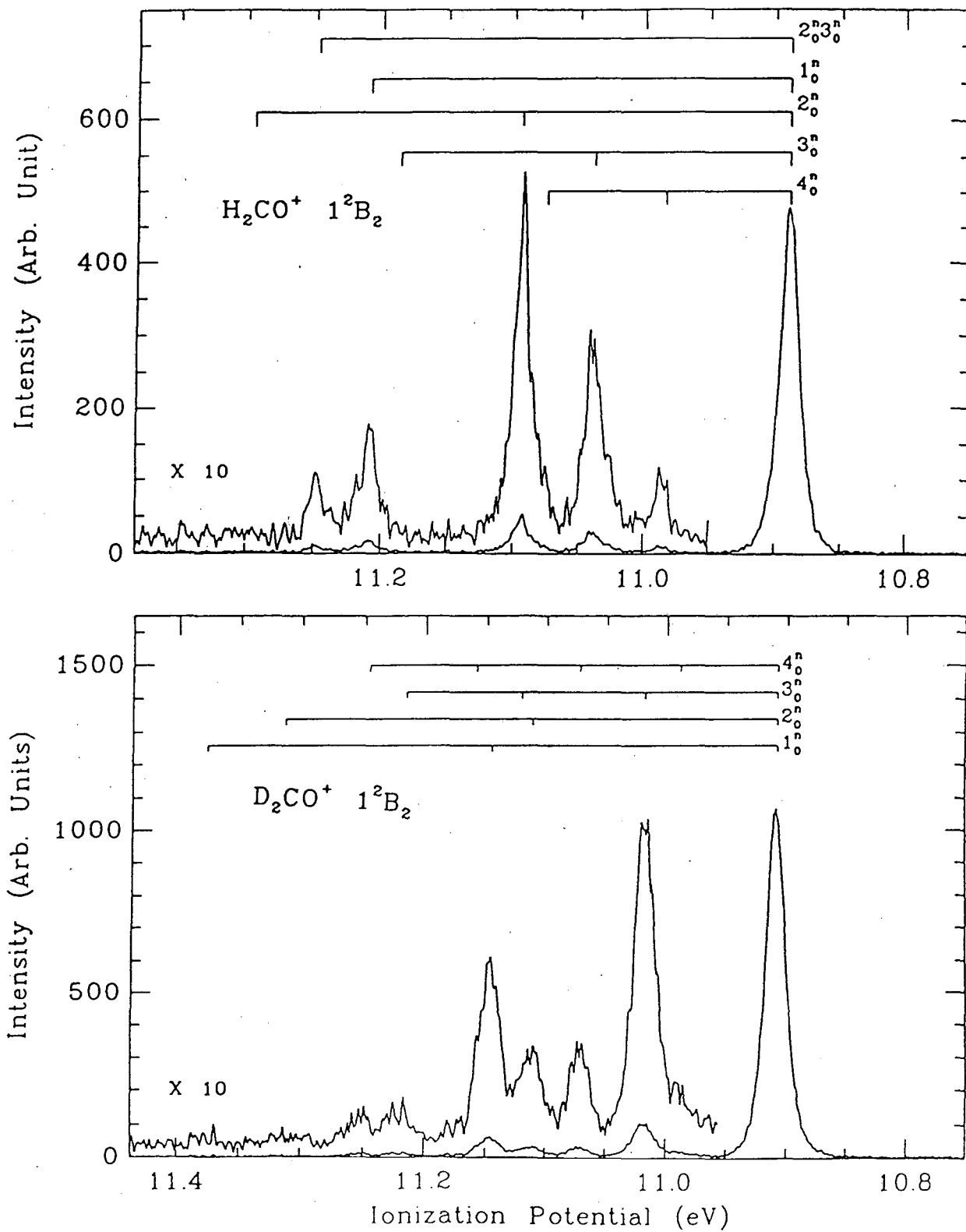


Figure 2

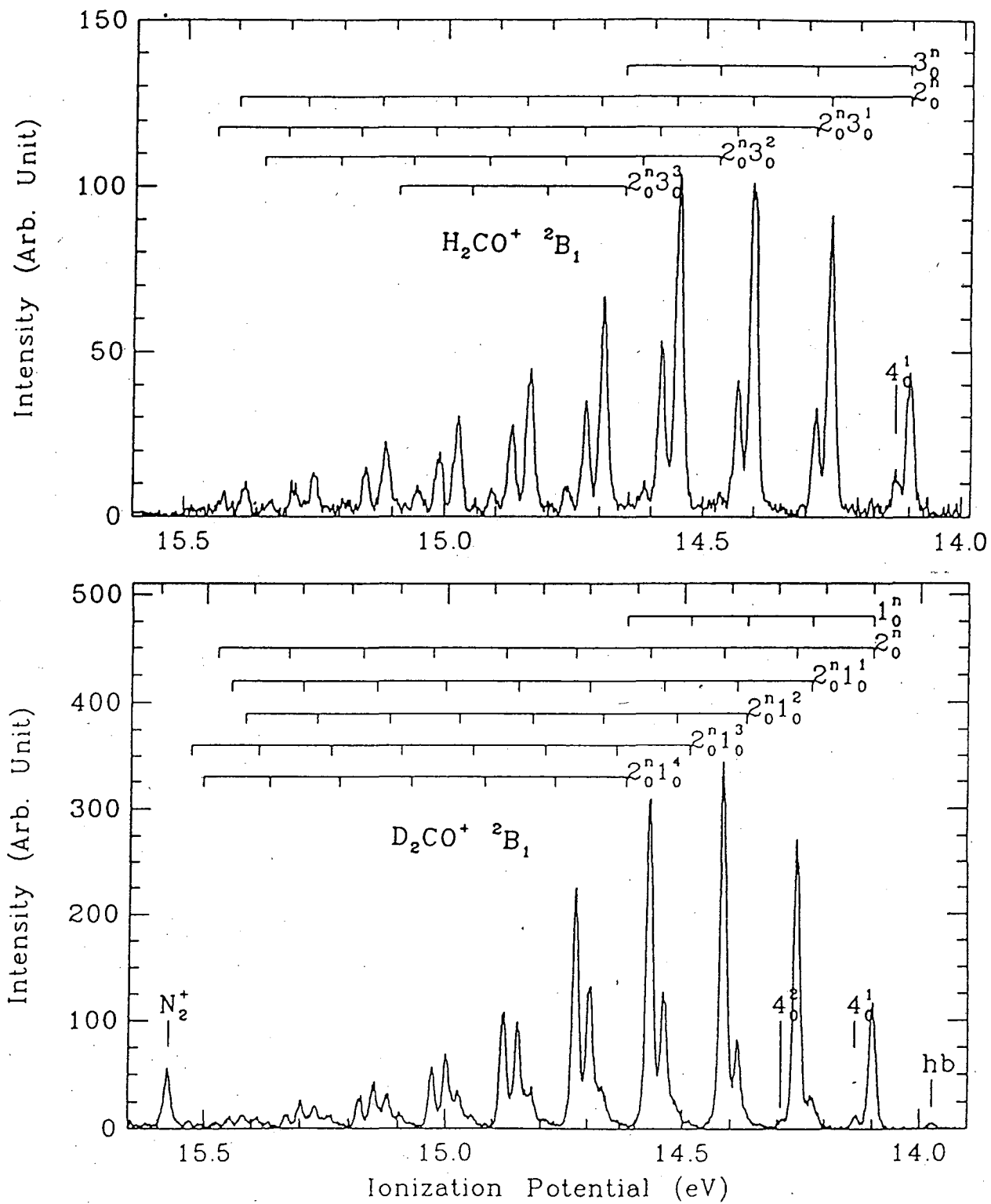


Figure 3

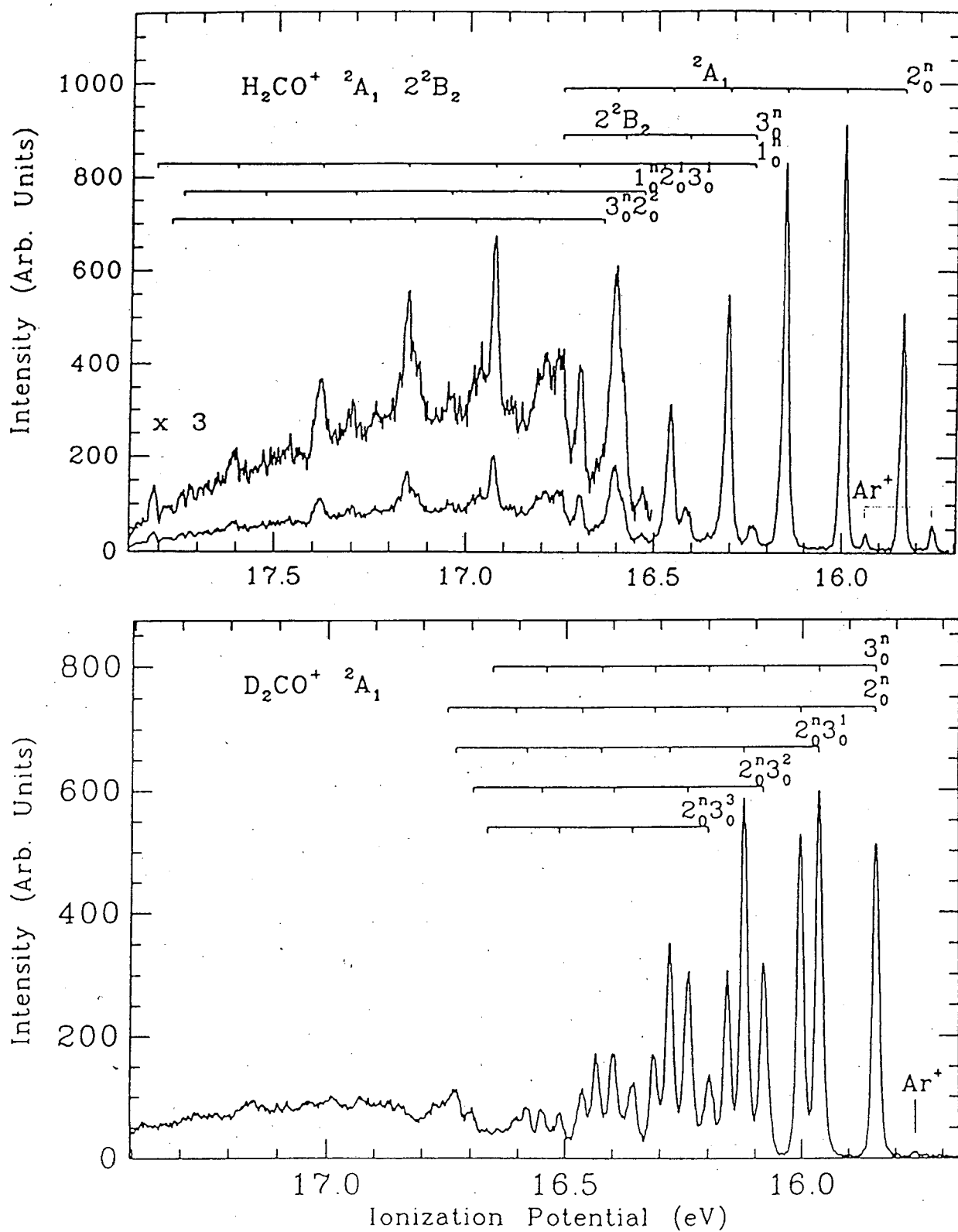


Figure 4

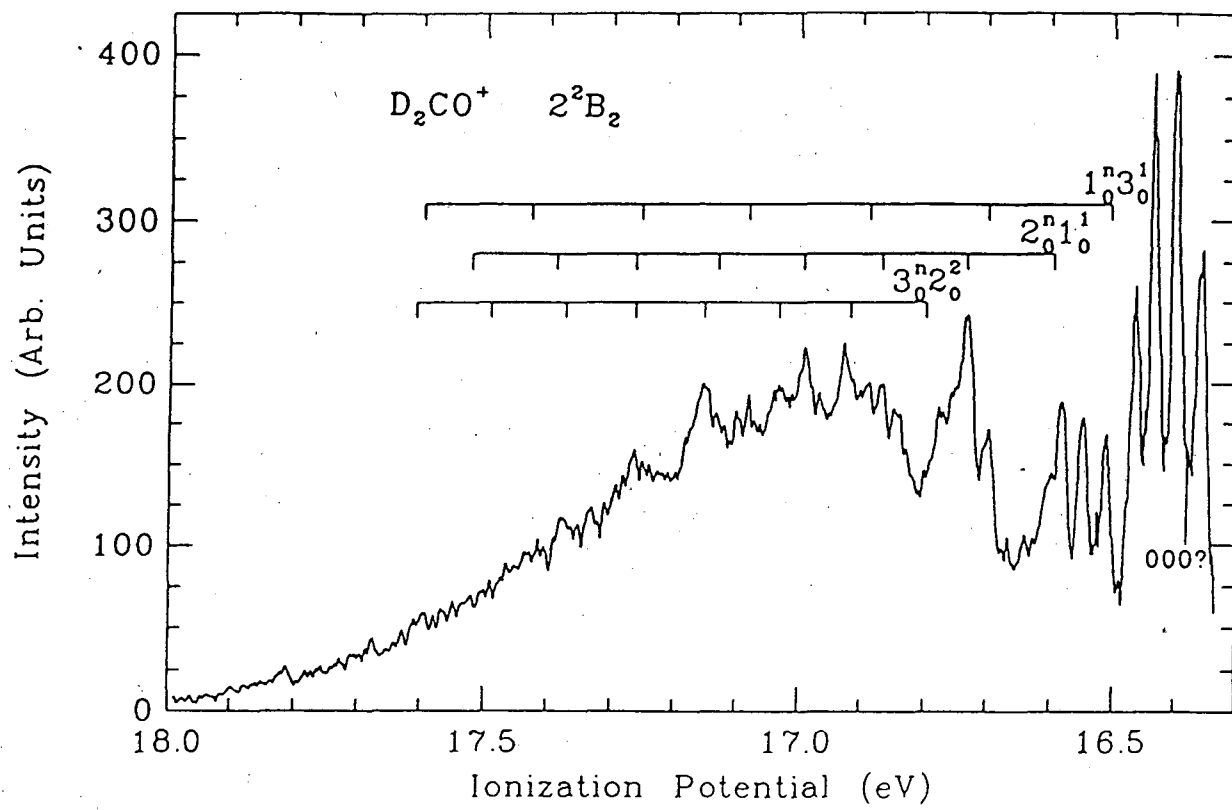


Figure 5

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