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High Resolution He Iα Photoelectron Spectroscopy of H_2CCO and D_2CCO Using Supersonic Molecular Beams

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Abstract

High resolution helium Iα (584 Å) photoelectron spectra of H_2CCO and D_2CCO using supersonic molecular beams are reported. The adiabatic ionization energies (**AIEs**) of the electronic first, second, and fifth excited states are determined unambiguously. The doublet-like fine structures observed in the first excited states of ketene imply the excitation of a 'soft' mode that was not observed before. Strong isotope effects are observed in the vibronic (vibrational) couplings in the ground state of ketene cations. The **AIEs** and spectroscopic constants for all six ionic states are reported to a much higher accuracy than previously available.

1. Introduction

The photoelectron spectra of ketene and d_2-ketene have been the subject of several experimental and theoretical studies. [1-5] Most of the theoretical work has been based largely on the experimental studies by Baker et al. [1], and by Hall et al.. [4] Very recently, in an *ab initio* study, Takeshita [6] has given a detailed analysis of the photoelectron spectra of ketene and d_2-ketene and of the fine structures observed in the experimental studies of Baker and Hall. However, the disparity between the experimental and theoretical results is substantial. Especially in the ionic first excited states, the sharp onset and the complex spectra observed in the photoelectron spectrum cannot be reproduced by the theoretical calculation. Very different explanations were given for the complexity of the photoelectron spectra for the ionic first excited state.

In this letter, we report the high resolution (FWHM 12 meV) helium Iα (584 Å) photoelectron spectra of H_2CCO and D_2CCO. Improved resolution and effective rotational cooling of the sample by supersonic expansion enabled us to determine the adiabatic ionization energies (**AIEs**) to a much higher accuracy ($\pm$ 3.0 meV), and to report spectroscopic constants for all six ionic states with very high accuracy ($\pm$ 0.5 meV, or 4.3 cm^{-1}).

2. Experiment

The molecular beam photoelectron spectrometer used for this study has been described previously. [7] Briefly, it consists of a supersonic molecular beam source, a windowless helium discharge lamp, a quadrupole mass spectrometer (**QMS**), 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 12 meV (**FWHM**) as measured with Ar photoelectron peaks.

Approximately 350 torr of ultra high purity helium (99.9999%, Matheson) was first passed through a U-tube kept at 77 K to remove trace amounts of water and other impurities in the carrier gas line, then bubbled through a liquid H_2CCO or D_2CCO trap kept at hexane/LN_2 slush temperature (177 K) with vapor pressure about 50 or 45 torr as measured with a **MKS** model 122AA-2000 Baratron. The pure liquid ketene or d_2-ketene was prepared following literature procedures [8,9] by thermodecomposition of acetic anhydride or d_6-acetic anhydride (Aldrich 99% D-atom) at ca. 823 K, trapping the acetic acid byproduct at 195 K using dry ice/acetone slush and trapping the ketene or d_2-ketene at 77 K. Ketene or d_2-ketene prepared in this way was vacuum distilled once from 117 K to 77 K to remove trace amounts of acetic acid left and carbon dioxide, the primary ketene decomposition byproduct. Purified ketene and d_2-ketene were kept in the dark with continuous pumping at 77 K before use. The He/H_2CCO or He/D_2CCO mixture with a total pressure of ca. 400 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 **QMS**: no polymers of H_2CCO or D_2CCO and no CO_2 decomposition byproducts were found in the beams under these experimental conditions. The rotational temperature of the beams was estimated to be ≈ 5 K as shown by laser induced fluorescence (**LIF**) measurements under similar conditions. [10-12]

3. Results and Discussions

The full photoelectron spectra of H_2CCO and D_2CCO obtained by combining five separate scans with a resolution of 12 meV **FWHM** are shown in Figure 1. Table I summarizes the measured spectroscopic constants together with results reported in the literature. [13,14] The absolute AIEs are accurate to ± 3.0 meV. The accuracy is mainly limited by the drifts and the linearity of the energy scales as discussed in previous

publications. [15] 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 $\tilde{X}$ 1^2B_1 State

The $\tilde{X}$ 1^2B_1 states of H_2CCO^+ and D_2CCO^+, with well-resolved vibrational structures, are shown in Figure 2. The present study established that three normal modes are excited in this band, this is apparent from the spectrum of D_2CCO^+. The abnormality in the intensity of the third peak for this state was not discussed by Baker et al.[1] nor by Hall et al.. [4] Takeshita [6] attributed it to the superposition of the two possible vibrational levels, $v_2 = 1$ and $v_4 = 2$, quoting $v_2 = 2v_4$ from the calculation results in the case of H_2CCO^+. The present study, however, shows that $v_2 \neq 2v_4$. We attribute this abnormality to a **Fermi** resonances, in which one peak "borrows" intensity from its nearby neighbor. Here it is the $v_2 = 1$ peak that "borrows" intensity from the $v_4 = 2$ peak. In the case of D_2CCO^+, the situations are similar, but it is the $v_3 = 2$ peak that "borrows" intensity from the $3_0^1 4_0^1$ peak. Since $v_3 \approx v_4$, the doublet structures observed in the second, the fourth, the sixth and the eighth peaks in the D_2CCO^+ spectrum agree with the theoretical calculations which are due to the excitation of the v_3 and v_4 modes along with the v_2 mode excitations. Strong isotope effects on vibronic (vibrational) couplings in this band are apparent from the present spectra.

3.2   The Second Band, the $\tilde{A}$ 1^2B_2 State

The $\tilde{A}$ 1^2B_2 states of H_2CCO^+ and D_2CCO^+ with well-resolved vibrational fine structures, albeit the heavy overlap with the $\tilde{B}$ 2^2B_1 state, are presented in Figure 3, which shows the $\tilde{B}$ 2^2B_1 state for both isotopic species as well. The complexity of this band from previous measurements was attributed to the possible predissociation of this band. [4] The

ab initio calculated spectra [6] for this band, however, showed much simpler vibrational progressions. The disparity between the calculated and observed spectra was attributed [6] to the possible contamination from the CO_2^+ $\tilde{X}\,^2\Pi_g$ band near 13.8 eV and from the overlapping with the $\tilde{B}\,2^2B_1$ band of ketene above 14.6 eV. We can eliminate the possibility of contamination from CO_2, since the **AIE** for the CO_2^+ $\tilde{X}\,^2\Pi_g$ state is 13.7778[18] ($\pm$4.0 meV) and the 20 meV spin-orbit splittings in this band would have been evident. The contributions from the $\tilde{B}\,2^2B_1$ band of ketene can be rejected because the very distinct long vibrational progressions observed for the $\tilde{B}\,2^2B_1$ bands in both isotopic species cannot possibly broaden or complicate the vibrational progressions in the $\tilde{A}\,1^2B_2$ state. We tentatively attribute the complexity of this band to the combination of the weak excitations of a 'soft' mode with the strong excitations of the ν_2 and ν_4 modes, and possible predissociation of this band in the **Franck-Condon** region. The soft mode is assigned as the ν_5 mode, which is characterized by the CH_2 (CD_2) group out-of-plane wagging motion following the convention of Duncan et al. [14], based largely on the reduction in frequencies upon deuteration. In separate publications, [16,17] we have calculated the vibrational autocorrelation function for this band. The results support that this state is subject to lifetime (possibly due to predissociation) broadening effects.

3.3 The Third Band, the $\tilde{B}\,2^2B_1$ State

The $\tilde{B}\,2^2B_1$ states of ketene and d_2-ketene, with fully resolved vibrational structures, were presented in Figure 3 together with the $\tilde{A}\,1^2B_2$ states. The **AIEs** are established to be 14.6089 $\pm$0.003 eV and 14.6106$\pm$0.003 eV for H_2CCO and D_2CCO by this study. Takeshita, however, has placed the **AIEs** for this band around 14.38 eV, based on the **Franck-Condon** factor (**FCF**) analysis. Referring to the H_2CCO^+ spectrum of this band, if the **AIEs** were lower than 14.609 eV, we would have seen

another sharp peak in the spectrum near 14.50 eV that would stand out compared with contributions from the $\tilde{A}$ 1^2B_2 band. The observed abnormality in intensity in the fifth peak of the H_2CCO^+ spectrum might be attributed to a **Fermi** resonances. There is another much weaker progression in H_2CCO^+ with similar spacing to the main progression which is assigned to the v_4 mode. The weaker progression is assigned to the excitation of another 'soft' mode v_6, which is characterized by the C=C=O skeleton out-of-plane bending, based largely on the insensitivity of this splitting to deuteration. The D_2CCO^+ spectrum, however, in addition to those observed in the H_2CCO^+ spectrum, showed more fine structures than those observed previously. The assignment was based largely on the *ab initio* calculations of Takeshita. The excitations of four normal modes in this band make the definitive assignment extremely difficult. The full nature of this band awaits further scrutiny both theoretically and experimentally.

3.4   The Fourth and the Fifth bands, the $\tilde{C}$ 2^2B_2 and the $\tilde{D}$ 1^2A_1 State

The photoelectron spectra of these two bands, as shown in Figure 4, overlapped heavily. The major vibrational progressions in the $\tilde{C}$ 2^2B_2 states, upon deuteration, have large reductions in frequency and were assigned to the v_3 mode, in agreement with the assignment of Hall et al.. [4] Takeshita, [6] however, assigned the progression to the v_4 mode. As discussed by Duncan et al. [14] in their investigation of the neutral ketene spectra, the strong coupling and mixing among different normal modes in ketene make the assignment only tentative without rotationally resolved studies. The gradually rising 'background' toward higher ionization energies of the $\tilde{C}$ 2^2B_2 states are mostly attributed to contributions from the overlapping, dissociative $\tilde{D}$ 1^2A_1 state. The **AIEs** for the $\tilde{D}$ 1^2A_1 states can only be regarded as the best estimate because of the completely dissociative nature of this state in the **Frank-Condon** region. The qualitative disagreements between the calculated [6] and the present spectra for the $\tilde{D}$ 1^2A_1 states, however, imply that the

potential energy surfaces (**PES**) must be very different from that of the neutral ground state and have a rather large anharmonicity.

3.5 The Sixth Band, the $\tilde{E}$ 2^2A_1 State

The photoelectron spectra of the $\tilde{E}$ 2^2A_1 states are shown in Figure 5. Previous experimental studies on this band had been impeded by the presence of CO_2 impurity and by the possible overlapping from the CO_2^+ $\tilde{B}$ $2\Sigma_u^+$ state, even the **AIEs** are not precisely known because of this. The present spectra, free of CO_2 contributions, give the **AIEs** to be 18.0897 ± 0.010 eV and 18.0734 ± 0.010 eV for H_2CCO and D_2CCO, respectively. The **FWHM** of the adiabatic peaks are almost 40 meV, which are much broader than the instrumental resolution and cannot be accounted for by invoking rotational broadening, and the asymmetric peak shapes as well as the absence of any major vibrational progressions, implied that dissociation and other intramolecular processes were at play here. There were no available theoretical calculations on the **PES** for this state, the vibrational assignments can only be regarded as tentative at best. Further high level theoretical exploration involving multimode coupled vibronic and anharmonic effects will be especially desirable to understand the details of this band.

In conclusion, we have obtained high resolution photoelectron spectra of ketene and d_2-ketene using supersonic molecular beams. The **AIEs** and spectroscopic constants for all six ionic states accessible by the helium Iα (584 Å) radiation are reported to a much higher accuracy than previously available.

Acknowledgment

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References:

1.   A. D. Baker and D. W. Turner, **Chem. Comm.**, 480(1969).

2.   D. W. Turner, Phil. Trans. R. Soc., London Ser., **A7**, 268(1970).

3.   D. W. Turner, A. D. Baker, and C. R. Brundle, <u>**Molecular Photoelectron Spectroscopy**</u>, John Wiley & Sons, London, 139(1970).

4.   D. Hall, J. P. Maier, and P. Rosmus, Chem. Phys., **373**, 24(1977).

5.   D. P. Chong, Theoretical Chim. Acta., **181**, 50(1978).

6.   K. Takeshita, J. Chem. Phys., **96(2)**, 1199(1992).

7.   J. E. Pollard, D. J. Trevor, Y. T. Lee, and D. A. Shirley, Rev. Sci. Instrum., **52**, 1837(1081).

8.   G. J. Fisher, A. F. Maclean, and A. W. Schwizer, **J. Org. Chem.**, 1055(1952).

9.   B. I. Sonobe and R. N. Rosenfeld, **JACS**, **105**, 7582(1983).

10.   H. Bitto, D. R. Guyer, W. F. Polik, and C. B. Moore, Faraday Trans. Dis. Chem. Soc., **81**, 149(1986).

11.   I-Chia Chen, W. H. Green, Jr., and C. B. Moore, J. Chem. Phys., **89(1)**, 314(1988).

12.   I-Chia Chen and C. B. Moore, J. Phys. Chem., **94**, 263,269(1990).

13.   C. B. Moore and G. Pimentel, J. Chem. Phys., **38(12)**, 2816(1963).

14.   J. L. Duncan, A. M. Ferguson, J. Harpper, and K. H. Tong, J. Mol. Spect., **122**, 72-93(1987), and **125**, 196-213(1987).

15.   Baohua Niu, David A. Shirley, and Ying Bai, submitted to J. Chem. Phys..

16.   Baohua Niu, Ph.D. Thesis, The University of California at Berkeley, Berkeley, CA94720, USA.

17.   Baohua Niu, Ying Bai, and David A. Shirley, in preparation.

18.   L. S. Wang, J. E. Reutt, Y. T. Lee, and D. A. Shirley, J. Elect. Spect. and Related Phenomena, **47**, 167-186(1988).

Table I. Ionization Potentials & Vibrational Frequencies (cm^{-1}) Observed

Ionic States	AIE[a] (eV)	ν_1, $\omega_e x_e$	ν_2, $\omega_e x_e$	ν_3, $\omega_e x_e$	ν_4, $\omega_e x_e$	ν_5, $\omega_e x_e$	ν_6, $\omega_e x_e$
H_2CCO[b] $\tilde{X}$ $^1A_1$		3070.4	2152.6	1387.5	1116.0	587.4	528.4
H_2CCO^+ $\tilde{X}$ 1^2B_2	9.6191(4)		2263.4 (4.3), 17.4 (4.3)	1378.6 (4.3)	1226.9 (4.3), 99.8 (4.3)		
$\tilde{A}$ 1^2B_2	13.7967(3)		1527.9 (4.3), -61.7 (4.3)		1164.2 (4.3), 21.1 (4.3)	460.7 (4.3)[d]	689.8(4.3)
$\tilde{B}$ 2^2B_1	14.6089(8)		2001.2 (4.3), 15.8 (4.3)		1000.8 (4.3), 4.8 (4.3)		346.7 (4.3)
$\tilde{C}$ 2^2B_2	16.0687(8)		1697.1 (4.3), -1.4 (4.3)	1086.6 (4.3), 7.8 (4.3)			
$\tilde{D}$ 1^2A_1	16.2393(3)[c]		1488.0 (4.3), -19.5 (4.3)	1164.3 (4.3), 11.5 (4.3)	708.9 (4.3), 4.5 (4.3)		
$\tilde{E}$ 2^2A_1	18.0897(10)			1177.4 (4.3), 15.0 (4.3)	670.6 (4.3), -4.3 (4.3)		396.9 (4.3), -23.9 (4.3)

TABLE I. Continued

Ionic States	AIE[a] (eV)	$\nu_1, \omega_e x_e$	$\nu_2, \omega_e x_e$	$\nu_3, \omega_e x_e$	$\nu_4, \omega_e x_e$	$\nu_5, \omega_e x_e$	$\nu_6, \omega_e x_e$
D_2CCO^b $\tilde{X}$ $^1A_1$		2267.3	2120.5	1225.1	924.7	541.2	434.7
D_2CCO^+ $\tilde{X}$ 1^2B_2	9.6130(3)		2285.6 (4.3), 20.8 (4.3)	1090.9 (4.3), -6.9 (4.3)	924.7 (4.3), -82.2 (4.3)		
$\tilde{A}$ 1^2B_2	13.8366(8)		2140.4 (4.3), 5.2 (4.3)		1006.6 (4.3), -12.8 (4.3)	299.3 (4.3)[d]	105.8 (4.3)
$\tilde{B}$ 2^2B_1	14.4942(7)		1732.3 (4.3)	848.4 (4.3)	1056.1 (4.3), 0.5 (4.3)		
$\tilde{C}$ 2^2B_2	16.0856(1)		1101.7 (4.3)	799.8 (4.3), 2.1 (4.3)			
$\tilde{D}$ 1^2A_1	16.3204(2)[c]	1266.7 (4.3)	1204.0 (4.3), 8.2 (4.3)	1168.8 (4.3), 13.6 (4.3)			
$\tilde{E}$ 2^2A_1	18.0734(10)	1133.3 (4.3), 12.4 (4.3)	834.4 (4.3)				

(a) The absolute AIEs are accurate to ± 3meV as discussed in the main text. Other spectroscopic constants, however, are obtained as line splittings, and can thus be reported to a much higher accuracy of ±0.5 meV (e.g. ±4.3 cm^{-1}). (b) From ref. 13, 14. (c) Best estimate only. (d) From the splitting in the first two peaks of the $\tilde{A}$ 1^2B_2 state. Numbers in parenthese indicate the uncertanties in the last digit.

Figure Captions:

Figure 1.   The full spectrum of ketene and d_2-ketene with a resolution of 12 meV **FWHM.** The designation of the ionic states assumes that the ions have C_{2v} symmetry.

Figure 2.   The photoelectron spectrum of the $\tilde{X}$ 1^2B_1 state of ketene and d_2-ketene. The vibrational progressions are labeled according to the C_{2v} geometry and 2_0^n stands for the transition of

$$M^+ (v_2 = n) + e \leftarrow M (v_2 = 0) + \hbar\omega$$

following standard spectroscopic notations.

Figure 3.   The photoelectron spectrum of the $\tilde{A}$ 1^2B_2 and $\tilde{B}$ 2^2B_1 states of ketene and d_2-ketene. Note the details of the vibrational progressions in the $\tilde{A}$ 1^2B_2 state are fully resolved here for the first time.

Figure 4.   The photoelectron spectrum of the $\tilde{C}$ 2^2B_2 and $\tilde{D}$ 1^2A_1 states of ketene and d_2-ketene. The major vibrational progressions are attributed to the $\tilde{C}$ 2^2B_2 state.

Figure 5.   The photoelectron spectrum of the $\tilde{E}$ 2^2A_1 state of ketene and d_2-ketene. The very broad adiabatic peak and the asymmetric line shapes imply that ketene cations in the **Franck-Condon** part of the **PES** are subject to lifetime broadening effects.
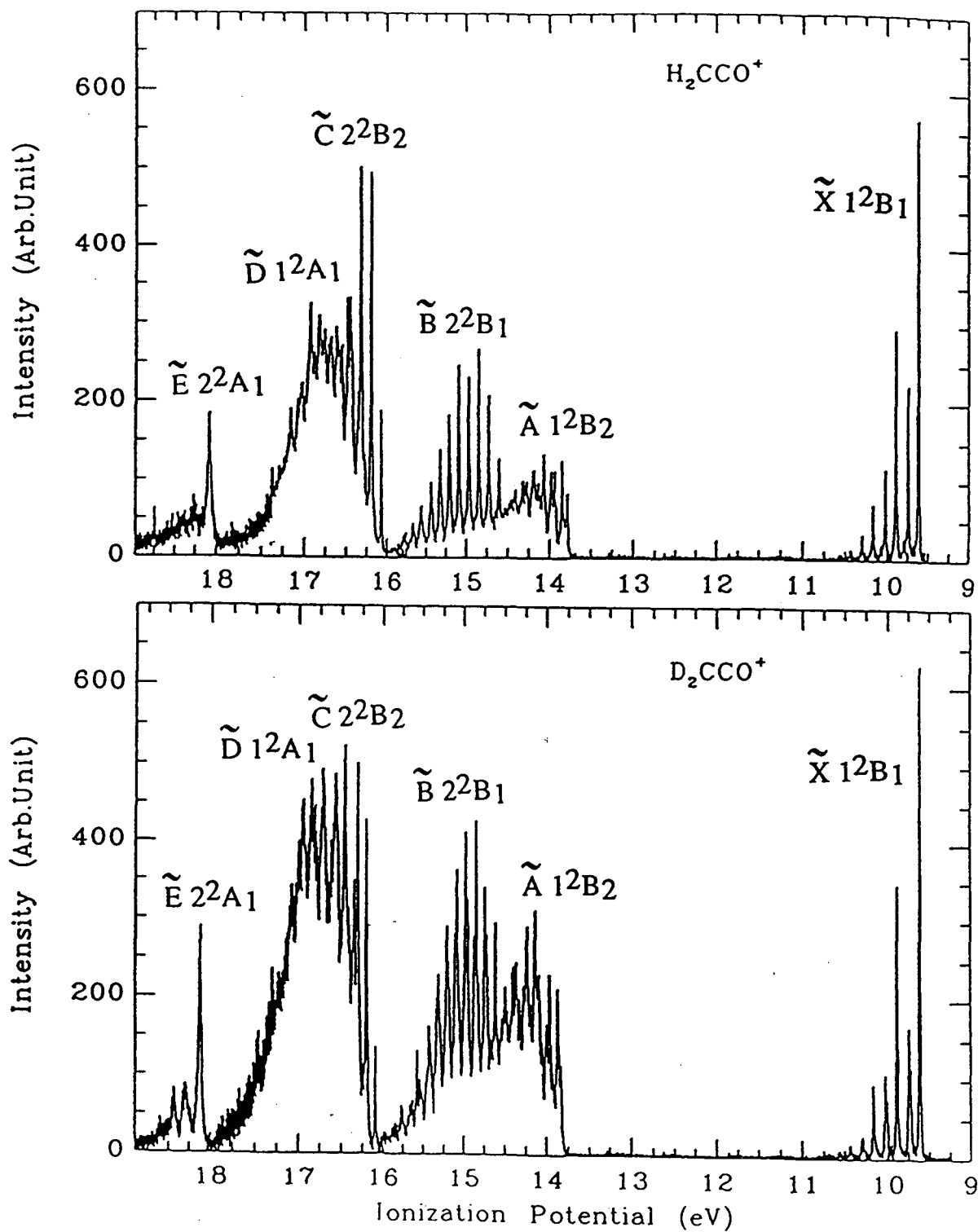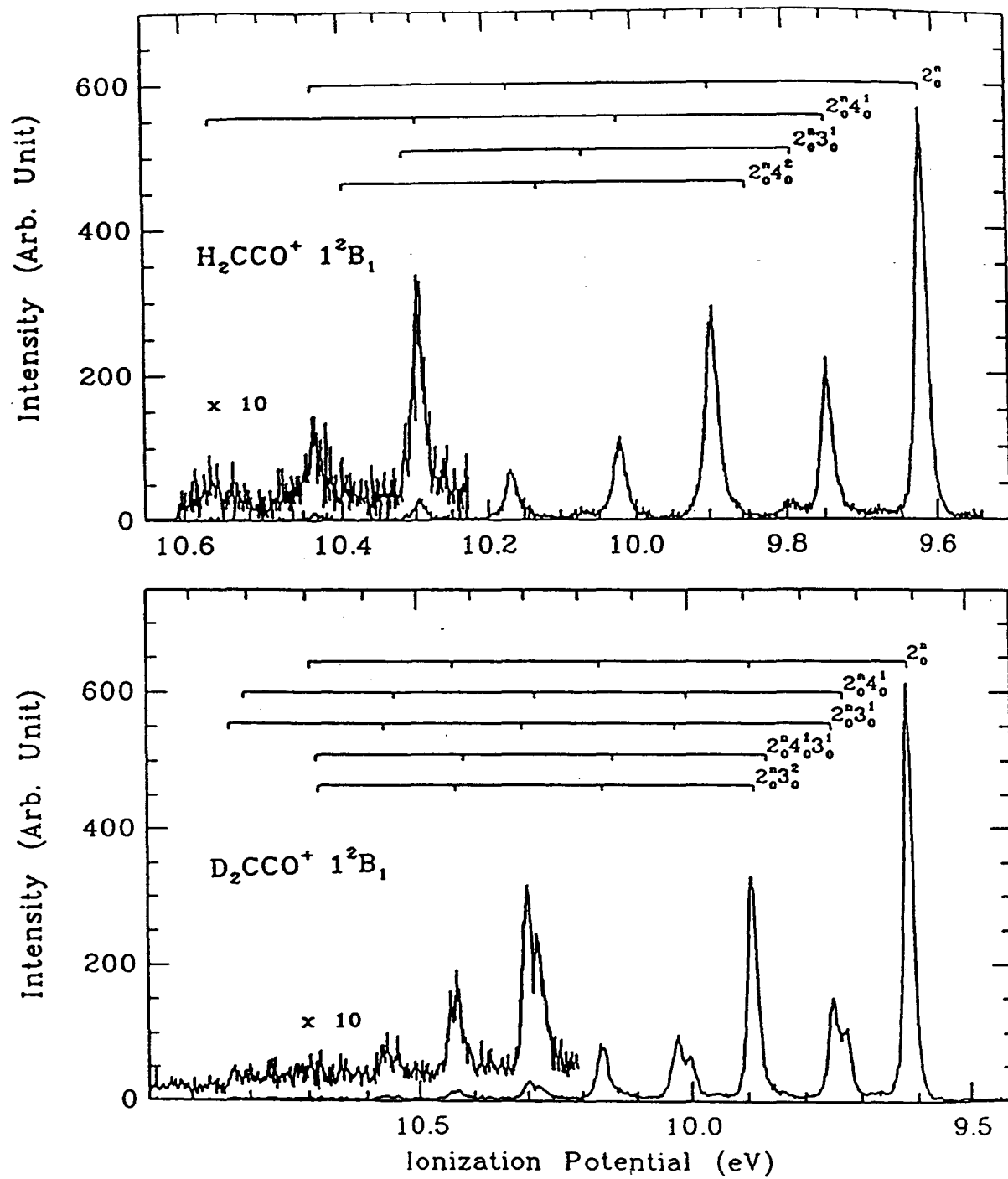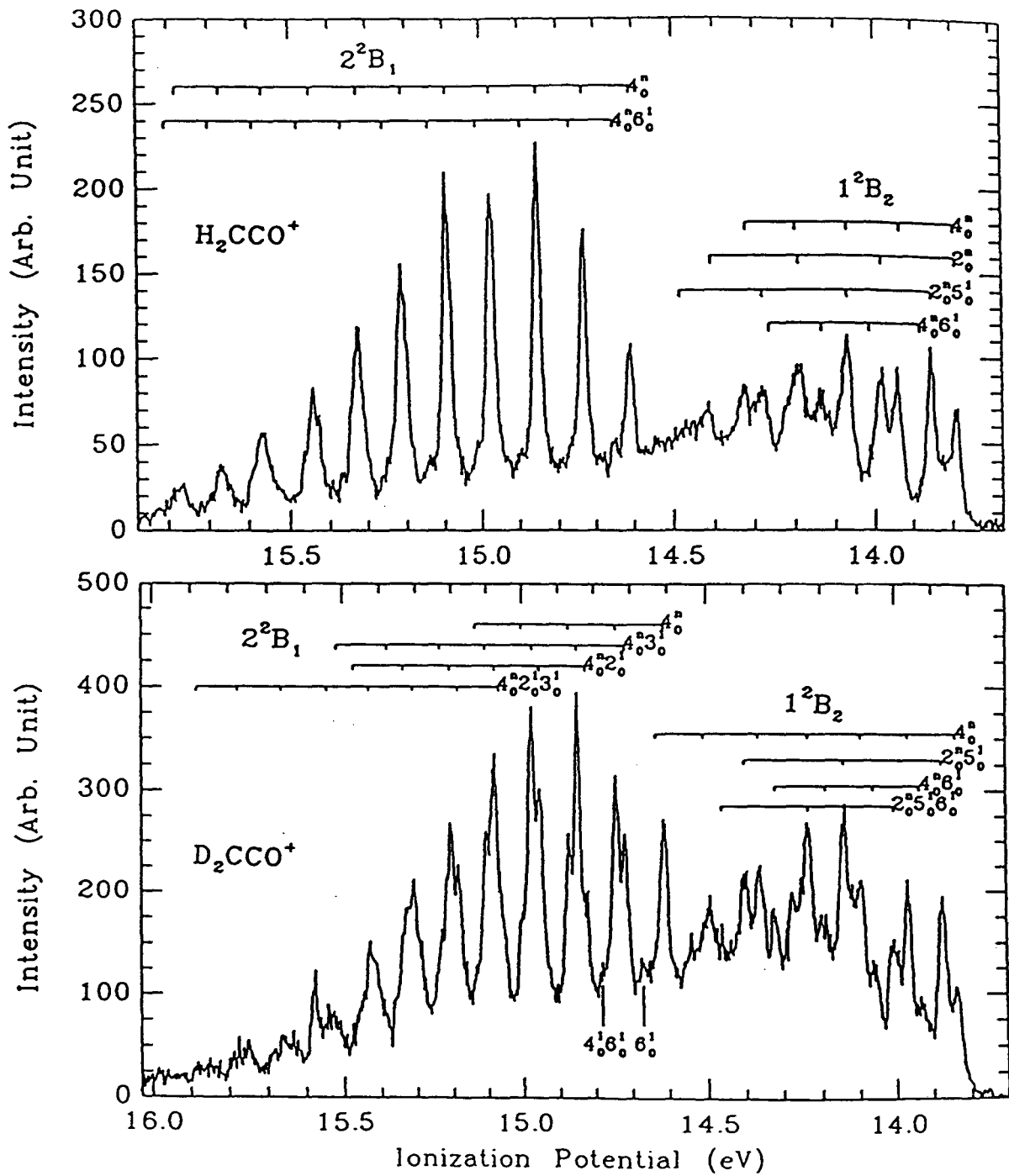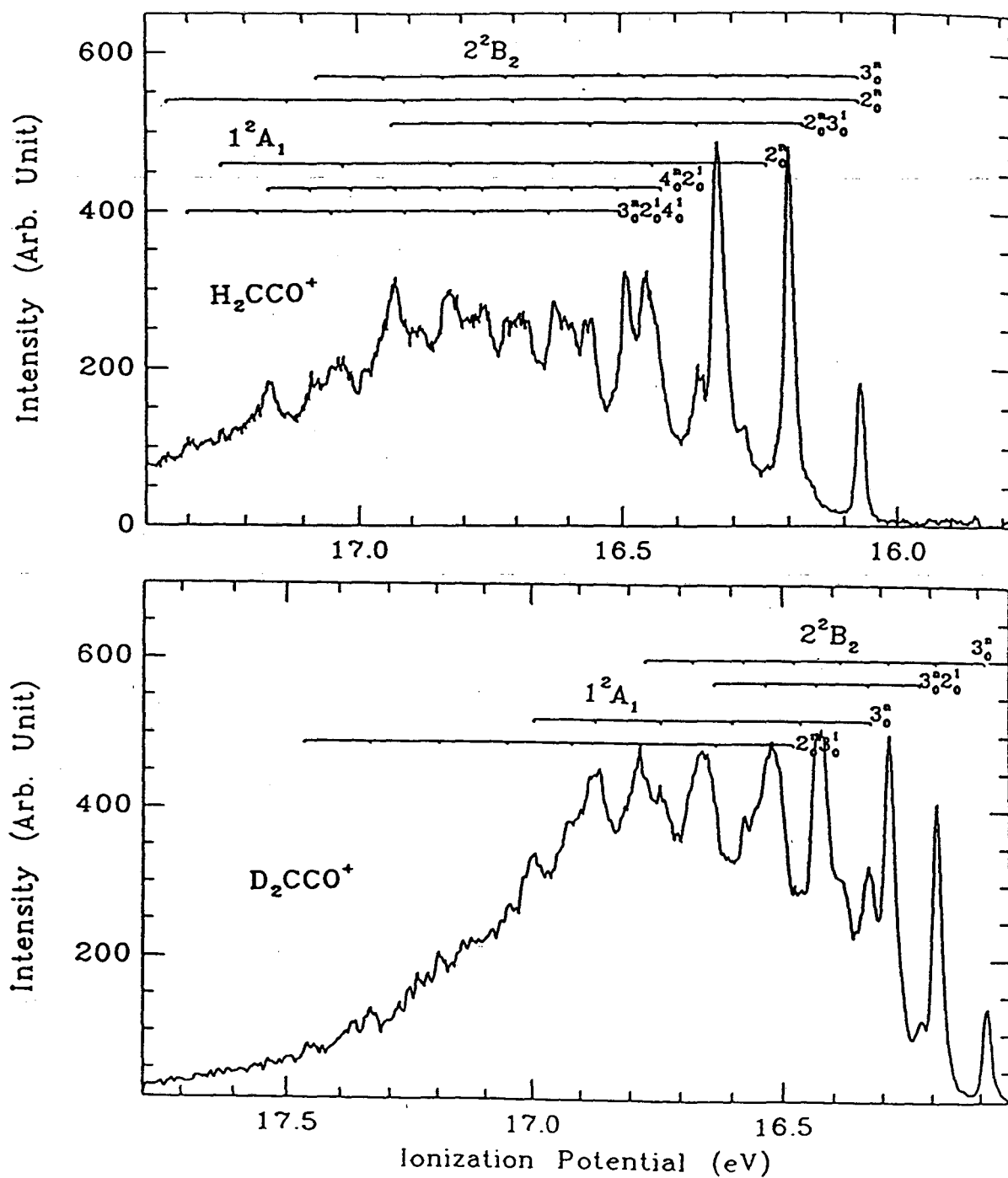
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5