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Using Supersonic Molecular Beams

**Permalink**
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**Journal**
Chemical Physics Letters, 201(1,2,3,4,)

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**Publication Date**
1992-08-01
Submitted to Chemical Physics Letters

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High Resolution He Iα Photoelectron Spectroscopy of H$_2$CO and D$_2$CO Using Supersonic Molecular Beams

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Abstract

High resolution helium Iα (584 Å) photoelectron spectra of H₂CO and D₂CO using supersonic molecular beams are reported. The excitation of the ν₄ 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 H₂CO and D₂CO 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 Iα (584 Å) photoelectron spectra of H₂CO and D₂CO. 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. 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 H$_2$CO or D$_2$CO 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 H$_2$CO or D$_2$CO was prepared following a literature procedure 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/H$_2$CO or He/D$_2$CO 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 H$_2$CO or D$_2$CO 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 constant, 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 \( \tilde{X} 1^2B_2 \) state

The \( \tilde{X} 1^2B_2 \) states of both H₂CO⁺ and D₂CO⁺, with well-resolved vibrational structures, are shown in Figure 2. The weak excitation of the \( v_4 \) out-of-plane bending mode is an indication that formaldehyde cations might have non-planar equilibrium geometries. The \( \tilde{X} 1^2B_2 \) state corresponds to the removal of an electron from the \( b_2 \) (\( n_0 \)) 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 \( \tilde{X} 1^2B_2 \) state of H₂CO⁺ and D₂CO⁺, the HCO angle decreases slightly (~5°) from the neutral \( \tilde{X} 1^A_1 \) state. Buenker and Peyerimhoff concluded from their \textit{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, but not with the results of the calculation by Takeshita concerning the excitation of the \( v_1 \) mode in \( H_2CO^+ \). The anharmonicity would be too big if we assigned the feature at 11.2086 eV as the \( v_2 = 2 \) peak.

3.2 The Second Band, the \( \tilde{A}^2B_1 \) State

The photoelectron spectra of the \( \tilde{A}^2B_1 \) 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 \( v_2 \) 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 \( v_2 \) mode, with several quanta of the \( v_3 \) mode excited as well. In \( D_2CO^+ \), however, it is the \( v_1 \) mode that gets excited along with the major excitation of the \( v_2 \) mode. These agree fairly well with the theoretical calculations by Domcke et al, 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 \( v_1 \) or \( v_3 \) mode in both isotopic compounds cannot be regarded as definitive.
3.3 The Third Band, the B 2A1 State

The third bands of H2CO+ and D2CO+ are shown in Figure 4. The simplicity of the B 2A1 state spectrum in H2CO+ was attributed to the accident degeneracy of the v2 and v3 modes in previous experimental and theoretical studies. 1-10 The removal of this degeneracy in D2CO+ was used to support this interpretation. Here we note that the different vibrational progression patterns observed in H2CO+ and D2CO+ in the B 2A1 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 H2CO+ the FWHM is close to 12 meV, and in D2CO+ it is slightly broader than 12 meV, with both being very close to the instrumental resolution. Unless v2 and v3 are truly degenerate to within 1 meV or less, we would have seen a broadening of the peaks in the H2CO+ spectrum. We tentatively assigned the vibrational progression in the B 2A1 state of H2CO+ to the v2 mode only. The present assignment of the AIEs and vibrational progressions definitely support the assignment of Brundle et al 12 and all theoretical calculations 3-13 available: i.e. that this band is the B 2A1 state of formaldehyde.

3.4 The Fourth Band, the C 2B2 State

The fourth band of H2CO+ was shown in Figure 4 together with the third band. The fourth band of D2CO+ is show 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 ($584 \, \text{Å}$) radiation are reported to a much higher accuracy than previously available.
Acknowledgment

This work was supported by the director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
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References:


16.  W. E. Polik, Ph.D. Thesis, Department of Chemistry, The University of California at Berkeley, Berkeley, CA 94720, USA


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

<table>
<thead>
<tr>
<th>Ionic States</th>
<th>AIEa (eV)</th>
<th>V₁, ωeXₑ (cm⁻¹)</th>
<th>V₂, ωeXₑ (cm⁻¹)</th>
<th>V₃, ωeXₑ (cm⁻¹)</th>
<th>V₄, ωeXₑ (cm⁻¹)</th>
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<tbody>
<tr>
<td>H₂CO⁺ X 1A₁</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂CO⁺ X 1B₂</td>
<td>10.8887(4)</td>
<td>2580.2(4.3)</td>
<td>1674.8, 19.0 (4.3)</td>
<td>1210.2, 6.1 (4.3)</td>
<td>777.1, 13.3 (4.3)</td>
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<tr>
<td>A 2B₁</td>
<td>14.1024(2)</td>
<td></td>
<td>1250.5, 10.0 (4.3)</td>
<td>1487.7, 0.6 (4.3)</td>
<td>262.8c (4.3)</td>
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<tr>
<td>b 2A₁</td>
<td>15.8375(3)</td>
<td></td>
<td>1304.5, 12.6 (4.3)</td>
<td></td>
<td>1304 (20)</td>
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<tr>
<td>C 2B₂</td>
<td>16.2395(10)</td>
<td>1894.9d, 11.3 (4.3)</td>
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<td>1411.7d, 12.5 (4.3)</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Ionic States</th>
<th>AIEa (eV)</th>
<th>V₁, ωeXₑ (cm⁻¹)</th>
<th>V₂, ωeXₑ (cm⁻¹)</th>
<th>V₃, ωeXₑ (cm⁻¹)</th>
<th>V₄, ωeXₑ (cm⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>D₂CO⁺ X 1A₁</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>D₂CO⁺ X 1B₂</td>
<td>10.9076(4)</td>
<td>1948.2, 28.6 (4.3)</td>
<td>1656.7, 11.3 (4.3)</td>
<td>919.9, 31.1 (4.3)</td>
<td>648.1, 8.9 (4.3)</td>
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<td>A 2B₁</td>
<td>14.0999(5)</td>
<td>≈1064.5, 10.0 (4.3)</td>
<td>1281.6, 5.7 (4.3)</td>
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<td>776.6e (4.3)</td>
</tr>
<tr>
<td>b 2A₁</td>
<td>15.8425(2)</td>
<td></td>
<td>1311.1, 15.3 (4.3)</td>
<td>957.3, 3.4 (4.3)</td>
<td></td>
</tr>
<tr>
<td>C 2B₂</td>
<td>16.4350(200)b</td>
<td>1604.4d, 22.3 (4.3)</td>
<td>943.4d, -12.7 (4.3)</td>
<td>818.7d, -11.8 (4.3)</td>
<td></td>
</tr>
</tbody>
</table>

(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 V₄=1,0 splitting. (d) These values are estimates only. (e) The average value of V₄=2, 1, 0 splittings. (f) From ref. 17, 18. Number in parenthesis indicate the uncertainties in the last digit.
Figure Captions:

Figure 1. The full spectra of H₂CO and D₂CO. The designation of the ionic states is based on C₂ᵥ symmetry.

Figure 2. The X 1²B₂ states of H₂CO⁺ and D₂CO⁺. The designation of the vibrational progression 2₀ⁿ stands for the following transition:

\[ M^+ (ν₂ = n) + e^- \rightarrow M (ν₂ = 0) + hν \]

in accordance with standard spectroscopic notations.

Figure 3. The \( A 2^2B_1 \) states of H₂CO⁺ and D₂CO⁺, here hb stands for hot band.

The presence of the nitrogen peak makes the absolute AIE of the D₂CO⁺ \( A 2^2B_1 \) state reportable to an accuracy of ±1.0 meV.

Figure 4. The \( B 2^2A_1 \) and \( C 2^2B_2 \) states of H₂CO⁺, and the \( B 2^2A_1 \) state of D₂CO⁺. The presence of the Ar peaks in this band makes the absolute AIEs reportable to an accuracy of ±1.0 meV.

Figure 5. The \( C 2^2B_2 \) state of D₂CO⁺.
Figure 1
Figure 2

Ionization Potential (eV)

Intensity (Arb. Unit)

H$_2$CO$^+$ $1^2B_2$

D$_2$CO$^+$ $1^2B_2$
Figure 3
Figure 4
Figure 5