

TRIPLET STATES OF THE AMIDE GROUP.  
TRAPPED ELECTRON SPECTRA OF FORMAMIDE AND RELATED MOLECULES

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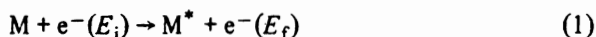
Trapped electron (TE) spectra are obtained using ion cyclotron resonance detection of scavenged electrons. The lowest singlet-triplet transitions,  $^3(n \rightarrow \pi^*)$ , in formamide (HCONH<sub>2</sub>) and N,N-dimethyl formamide (HCONMe<sub>2</sub>) are found at vertical energies of 5.30 and 5.00 eV, respectively. An unresolved band containing the  $^3(\pi \rightarrow \pi^*)$  and  $^3(n \rightarrow 3s)$  states appears at higher energies, centered at 6.60 and 6.00 eV, respectively. The TE spectra of formaldehyde (HCHO), acetaldehyde (MeCHO) and acetone (Me<sub>2</sub>CO) are obtained for comparison and are used along with results from ab initio theoretical calculations in establishing assignments. Singlet-triplet transitions dominate the spectra of all of these carbonyl containing molecules, to the exclusion of low lying singlet-singlet transitions. This is in agreement with other TE spectra and the expectation that  $(d\sigma/dE)$  will be higher near threshold for singlet-triplet as compared to singlet-singlet transitions.

## 1. Introduction

The amide functional group has singular importance as a basic structural unit in protein molecules. It is only recently, however, that many of the features of the spectra and low lying electronic states of the simplest member of this group of compounds, formamide (HCONH<sub>2</sub>), have been elucidated. Harding and Goddard have computed wavefunctions for the valence states of formamide using ab initio generalized valence bond (GVB) and configuration interaction (GVB-CI) methods [1]. The calculated vertical excitation energies to the  $^3(n \rightarrow \pi^*)$ ,  $^1(n \rightarrow \pi^*)$ , and  $^3(\pi \rightarrow \pi^*)$  states are 5.39, 5.65, and 6.19 eV [1]. Optical spectra reveal the  $^1(n \rightarrow \pi^*)$  excitation at 5.65 eV [2], in excellent agreement with the calculated energy. We wish to report experimental results for the lowest triplet state of formamide, determined using the trapped electron (TE) method [3-6] in conjunction with ion cyclotron resonance (ICR) detection of

scavenged electrons [5,6].

The basic experimental method has been previously described [5,6]. The sample gas is admitted to the ICR cell at a pressure of  $10^{-5}$ – $10^{-4}$  torr. Threshold excitation of an excited electronic state (eq. 1,  $E_f = 0$ )



leaves electrons with insufficient translational excitation to escape the trapping well (typically 0.15–0.20 eV in the present experiments). Trapped electrons are scavenged using SF<sub>6</sub> with a pressure of  $10^{-7}$  torr being sufficient to detect all of the scattered electrons. The spread in electron energies is estimated to be 0.4 eV†. This is sufficient to determine vertical excitation energies with an accuracy of  $\pm 0.1$  eV. The electron energy scale is calibrated by locating the sharp peak at 11.82 eV (the E  $^3\Sigma_g^+$  state) in N<sub>2</sub> [3-6].

One of the difficulties with interpreting TE spectra is the absence of rigorous selection rules which can be applied in a straightforward manner to assign bands. Electron exchange allows for the excitation and observation of triplet states, and combined with optical spectra and

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† The observed halfwidth at half-height for the  $1^1S \rightarrow 2^3S$  transition at 19.82 eV in He is 0.4 eV.

theoretical calculations, the lowest states observed in TE spectra can often be assigned. A general feature of triplet states is that, relative to singlet states, their excitation cross sections peak at low electron energies [3,4,7]. As a result it can be expected that the derivative of the cross section with respect to electron energy evaluated at threshold,  $(d\sigma/dE)_0$ , will be larger for triplet states than for singlet states. This conjecture has been experimentally verified in several instances [3-6, 8]. A necessary but not sufficient condition for an intense peak in the TE spectrum is that  $(d\sigma/dE)_0$  be large. Thus it is not surprising that triplet states are often dominant features of such spectra. Rather than rely entirely on this expectation, however, we have in the present work considered a range of carbonyl compounds, including formaldehyde, acetaldehyde, and acetone, where other studies are useful in identifying the observed bands [4,8-11]. This provides an underlying basis for assigning the spectrum of formamide.

## 2. Experimental

The techniques and instrumentation used in these experiments have been previously described [5,6,12]. Formaldehyde was freshly prepared by heating para-formaldehyde. Other chemicals were obtained from commercial sources and degassed with freeze-pump-thaw cycles before use. Purities as ascertained by mass spectrometric analysis were acceptable.

## 3. Results and discussion

The TE spectra of formaldehyde, acetaldehyde, and acetone are shown in fig. 1. While the spectrum of formaldehyde has not been previously reported, the spectra of the latter two compounds are in reasonable agreement with previously published results [4,8]. The low energy peaks observed in the energy range between 0 and 2 eV correspond to transient negative ions. The remaining peaks correspond to electronically excited states, the vertical excitation energies for which are summarized in table 1.

In the case of formaldehyde the lowest observed excitations correspond closely to the  $^3(n \rightarrow \pi^*)$  and  $^3(\pi \rightarrow \pi^*)$  excitations previously identified (table 1)

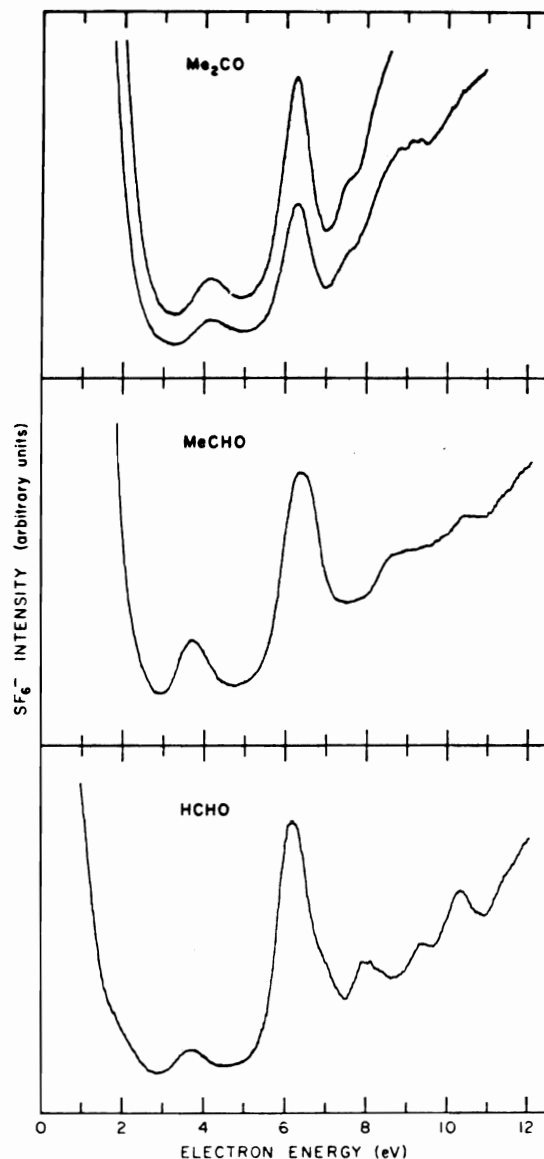


Fig. 1. TE spectra of acetone ( $\text{Me}_2\text{CO}$ ), acetaldehyde ( $\text{MeCHO}$ ), and formaldehyde ( $\text{HCHO}$ ).

[10,11]. A reproducible shoulder on the  $^3(\pi \rightarrow \pi^*)$  excitation at 7.0 eV corresponds closely to the third triplet state,  $^3(n \rightarrow 3s)$ . Significantly, there is no evidence for excitation of the two lowest singlet states,  $^1(n \rightarrow \pi^*)$  and  $^1(n \rightarrow 3s)$  in the TE spectrum. The TE spectra of acetaldehyde and acetone are similar to formaldehyde. The lowest excitation is assigned to the  $^3(n \rightarrow \pi^*)$  state, and the second peak corresponds

Table 1  
Comparison of vertical excitation energies for formamide and related molecules in the gas phase a)

Molecule	State	This work b)	Other TE spectra	Electron impact	Optical	Calculated
HCHO	$^3(n \rightarrow \pi^*)$	3.75		3.5 c)		3.62 d)
	$^1(n \rightarrow \pi^*)$			4.1 e)	4.20 f)	4.09 d)
	$^3(\pi \rightarrow \pi^*)$	6.20		6.0 c)		5.95 d)
	$^3(n \rightarrow 3s)$	7.00(s)		6.7–7.0 c)		
	$^1(n \rightarrow 3s)$			7.10 c)	7.09 g)	
MeCHO	$^3(n \rightarrow \pi^*)$	3.75	3.8 h)			
	$^1(n \rightarrow \pi^*)$				4.3 f)	
	$^3(\pi \rightarrow \pi^*)$	6.40(u)	6.35 h)			
	$^3(n \rightarrow 3s)$		6.62 h)			
$^1(n \rightarrow 3s)$				6.84 i)		
Me <sub>2</sub> CO	$^3(n \rightarrow \pi^*)$	4.15	4.15 h)j)	4.16 k)		
	$^1(n \rightarrow \pi^*)$			4.37 k)	4.5 l)	
	$^3(\pi \rightarrow \pi^*)$	6.25(u)	6.25(u) j)	5.8(u) k)	6.3 l)	
	$^3(n \rightarrow 3s)$					
$^1(n \rightarrow 3s)$			6.35 k)			
HCONH <sub>2</sub>	$^3(n \rightarrow \pi^*)$	5.30				5.39 m)
	$^1(n \rightarrow \pi^*)$				5.65 n)	5.65 m)
	$^3(\pi \rightarrow \pi^*)$	6.60(u)				6.19 m)
	$^3(n \rightarrow 3s)$					
$^1(n \rightarrow 3s)$				6.7 o)		
HCONMe <sub>2</sub>	$^3(n \rightarrow \pi^*)$	5.00(s)				
	$^1(n \rightarrow \pi^*)$					
	$^3(\pi \rightarrow \pi^*)$	6.00(u)				
	$^3(n \rightarrow 3s)$					
	$^1(n \rightarrow 3s)$				6.27 p)	

a) All data in eV. b) (s) denotes a partially resolved shoulder and (u) denotes an unresolved peak. c) Ref. [10]. d) Ref. [11]. e) Ref. [18]. f) Ref. [19]. g) Ref. [20]. h) Ref. [8]. i) Ref. [21]. j) Ref. [4]. k) Ref. [9]. l) Ref. [22]. m) Ref. [1]. n) Ref. [2]. o) Ref. [13]. p) Ref. [23].

to the unresolved  $^3(\pi \rightarrow \pi^*)$  and  $^3(n \rightarrow 3s)$  excitations. The present results for acetone are in good agreement with previous electron impact energy loss spectra [9] and TE results [8].

The TE spectra of formamide and N,N-dimethyl formamide are shown in fig. 2. Based on the results obtained with the carbonyl compounds, it is expected that the lowest  $^3(n \rightarrow \pi^*)$  excitation should be observed. Indeed a peak is observed at 5.30 eV, which is below the  $^1(n \rightarrow \pi^*)$  state observed optically at 5.65 eV [2]. This is assigned to the lowest  $^3(n \rightarrow \pi^*)$  state, in excellent agreement with the vertical excitation energy of 5.39 eV predicted from GVB–Cl calculations [1]. The broad feature between 6 and 8 eV corresponds to the unresolved admixture of the  $^3(\pi \rightarrow \pi^*)$  and  $^3(n \rightarrow 3s)$  excitations. A constant difference of

0.1–0.2 eV is found for the triplet–singlet energy separation of the  $n \rightarrow 3s$  transition in the series formaldehyde, acetaldehyde, acetone. The peak maximum at 6.60 eV is thus most consistent with the expected position of the  $^3(n \rightarrow 3s)$  excitation, 0.1 eV below the  $n \rightarrow 3s$  singlet which has been located at 6.7 eV from optical spectra [13]. The  $^3(\pi \rightarrow \pi^*)$  excitation predicted by the GVB–Cl results to have a vertical excitation energy of 6.19 eV is not observed as a sharp feature. This is not unreasonable, however. Available heats of formation give  $D(\text{CHO}–\text{NH}_2) = 4.1 \text{ eV}^\dagger$ . The  $^3(\pi \rightarrow \pi^*)$  state at 6.19 eV dissociates smoothly to the ground

<sup>†</sup>  $\Delta H_{f,298}^0(\text{NH}_2) = 40.1 \pm 3 \text{ kcal/mole}$  from ref. [14];  $\Delta H_f^0(\text{HCONH}_2) = -44.5 \text{ kcal/mole}$  from ref. [15];  $\Delta H_f^0(\text{HCO}) = 10.4 \text{ kcal/mole}$  from ref. [16].

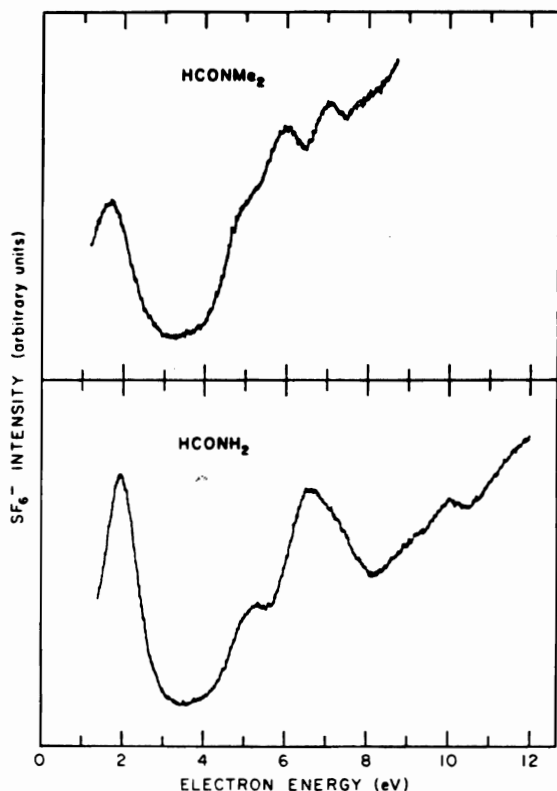


Fig. 2. TE spectra of N,N-dimethyl formamide (HCONMe<sub>2</sub>) and formamide (HCONH<sub>2</sub>).

states of CHO and NH<sub>2</sub> dropping 2.1 eV along a totally repulsive potential surface [1]. Hence this state is not bound with respect to dissociation of the CHO-NH<sub>2</sub> bond and may be particularly broad or weak.

The spectrum of N,N-dimethyl formamide is similar in appearance to the spectrum of formamide and is assigned in an analogous fashion. It is noted, however, that photoelectron spectra of the series of methyl-substituted formamides indicate that substitution of the methyl groups on nitrogen has the effect of raising the energy of the n-orbital relative to the  $\pi$ -orbital [17]. The effect is substantial, the differential change being about 0.7 eV in comparing the n- and  $\pi$ -orbitals of formamide and N,N-dimethyl formamide. Such changes should decrease significantly the  $^3(n \rightarrow \pi^*)$ ,  $^3(\pi \rightarrow \pi^*)$  separation and could possibly push the  $^3(n \rightarrow \pi^*)$  state above the  $^3(\pi \rightarrow \pi^*)$  state; however, our results do not provide the relative positions of these states.

In conclusion it appears that the TE method is a very sensitive method for determining the energies of the lowest triplet states associated with excitation of the carbonyl functional group. Interestingly, triplet states dominate the low energy portion of the spectra, to the apparent exclusion of low lying singlet excitations. Since the singlet states are prominent a few eV above threshold, we conclude for carbonyl compounds that  $(d\sigma/dE)$  for the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excitations must be much larger for the triplet as opposed to the singlet excitations near threshold.

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