

Variable angle electron-impact excitation of nitromethane^{a)}

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The electron-impact excitation of nitromethane has been studied at incident electron energies of 25, 55, and 90 eV, at scattering angles from 6° to 80°. The lowest-lying inelastic process which is observed is a previously unreported feature with a maximum intensity at 3.8 eV energy loss. This feature represents at least one singlet→triplet transition. It is likely that this 3.8 eV triplet feature plays a central role in the gas phase photolysis of nitromethane. A weak inelastic process with a peak at 4.45 eV has also been observed, as has a strong transition at 6.23 eV. Both of these excitations are well known from optical spectra, and they are generally believed to represent spin-allowed $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. Their assignments are discussed in detail. In addition, seven other transitions, several of which have not been reported previously, have been detected in the 7–12 eV energy-loss range. Three of these transitions, at 8.3, 8.85, and 11.73 eV energy loss, are tentatively assigned to Rydberg excitations of increasingly tightly bound electrons into a $3s$ Rydberg orbital.

I. INTRODUCTION

The nitroalkanes are a rather interesting group of molecules with some unusual chemical and physical properties. Essential ingredients in a variety of propellants and explosives, they also contribute significantly to air pollution and have a complex photochemistry.^{1,2} The parent compound, nitromethane, has an unusually large dipole moment (3.5 D),³ and exhibits "pseudo-acid"-type acid-base behavior.⁴

Since a knowledge of the excited electronic states of the nitroalkanes may prove useful in elucidating some of their photochemistry, it is important to attempt to understand the electronic spectrum of the prototype, nitromethane. However, investigation of the electronic states of this molecule has been hampered by the diffuse, heavily overlapped nature of many of the optical absorption bands,^{5,6} and by the fact that neither fluorescence nor phosphorescence has been observed from nitromethane.² In addition, although several semiempirical theoretical calculations^{7–10} have been performed on the electronic states of nitromethane, only one *ab initio* calculation¹¹ on the ground state has appeared, and no such calculations on the excited electronic states are available.

Many studies of the UV absorption of nitromethane have been published,^{5,6,12–21} but these have been limited to transition energies below 7.5 eV. One threshold excitation electron-impact investigation,²² which included higher energy-loss processes, has appeared, but the resolution of the reported spectrum is rather low. Most importantly, neither previous optical studies nor the

threshold electron-impact spectrum has revealed the location of low-lying triplet states in nitromethane.

Low energy, variable angle, electron-impact spectroscopy^{23–25} has proved to be a powerful tool for the detection and identification of previously unobserved transitions, both optically allowed and optically forbidden, in atoms and molecules. By means of this technique, various low-lying spin-forbidden transitions were first observed in molecules such as NO,²⁶ CO₂,²⁷ acetylene,²⁸ ketene,²⁹ and furan, thiophene, and pyrrole.³⁰ In this paper, we report the results of a variable angle electron-impact investigation of the nitromethane electronic spectrum. Of primary interest is our detection of a spin-forbidden feature at 3.8 eV energy loss.

In the following sections, we summarize previous theoretical and experimental studies of the electronic states of nitromethane; describe the experimental methods used in this study; present the results and discussion; and give final conclusions.

II. PREVIOUS STUDIES OF THE ELECTRONIC STATES OF NITROMETHANE

A. Theoretical calculations

The ground electronic state of nitromethane has been the subject of a number of theoretical investigations. Published semiempirical calculations include a Pariser-Parr-Pople study by McEwen,⁷ more recent CNDO/S-CI studies by Tinland⁸ and Harris,¹⁰ and an INDO calculation by Rabalais.⁹ An *ab initio* SCF study was performed by Murrell, Vidal, and Guest,¹¹ who employed a double zeta basis set. In Table I we list the calculated orbital energies, which are frequently correlated with experimental ionization energies via Koopmans' theorem. According to these theoretical analyses, the nitromethane molecular orbitals (MO's) blur the distinctions among the classic paradigms of σ bonding, π bonding, and n (lone-pair) nonbonding orbitals.

In all of these calculations, the occupied orbital with the smallest orbital energy has π character and a_2 symmetry in C_{2v} notation. Although the molecular point group of nitromethane is C_s , it is common practice to

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TABLE I. Ground state orbitals of nitromethane.

Symmetry ^a	Calculated orbital energy (eV)				Vertical photoelectron ionization energy (eV)		
	McEwen ^b	Rabalais ^c	Harris ^d	Murrell <i>et al.</i> ^e	Rabalais ^c	Kobayashi and Nagakura ^f	Rao ^g
a_1	11.94	10.9	12.30	12.39	11.32	11.31	11.35
a_2	11.34	10.6	12.14	10.95	11.73	11.81	11.85
b_2	11.99	11.9	12.80	12.27	14.73	14.50	
b_1	17.59	13.8	17.11	15.87	15.75	15.65	

^aSymmetry designations are those of the C_{2v} point group, appropriate for the nitro group.

^bReference 7.

^cReference 9.

^dReference 10.

^eReference 11.

^fReference 31.

^gReference 32.

designate the MO's by C_{2v} symmetry labels, which refer to the appropriate point group for the nitro ($-\text{NO}_2$) moiety. It seems generally agreed that the $a_2(\pi)$ orbital is weakly bonding or nonbonding.^{9,11,31} Larger orbital energies are calculated for MO's of a_1 and b_2 symmetry. These MO's are formed from the "lone-pair" $2p\sigma$ orbitals on the oxygen atoms of the nitro group. Although Harris¹⁰ refers to the a_1 orbital as σ (bonding) and the b_2 orbital as n (nonbonding), Rabalais⁹ designates both as σ orbitals, with the a_1 being strongly NO_2 -bonding and the b_2 strongly NO_2 -antibonding. McEwen,⁷ Kobayashi and Nagakura,³¹ and Rao³² refer to both the a_1 and b_2 orbitals as n^* or n . For the sake of clarity in the following discussion, we will refer to the highest occupied nitromethane orbitals as $a_2(\pi)$, $a_1(\sigma)$, and $b_2(n)$. The lowest unfilled (virtual) orbital is $b_1(\pi^*)$.

Two calculations,^{7,10} both semiempirical in nature, of nitromethane excited electronic states are available. Although the errors in the calculated transition energies (see Table II) are probably no more than 0.5–1.0 eV, only two experimental values have been available for comparison. Both the calculations of Harris¹⁰ and McEwen⁷ predict that the most intense transition is the $\bar{X}^1A_1 \rightarrow 1^1B_2 (\pi \rightarrow \pi^*)$ excitation. The theoretical vertical transition energies, 5.80 eV⁷ and 6.43 eV,¹⁰ are in relatively good agreement with the experimental value of 6.26 eV in the optical spectrum.¹⁸ The $\pi \rightarrow \pi^*$ assignment is widely accepted, although an alternative assignment, $\bar{X}^1A_1 \rightarrow 1^1B_1 (\sigma \rightarrow \pi^*)$ was made by Rabalais,⁹ based on his INDO calculations of the ground electronic state. However, it is by no means clear that the oscillator strength of such a $\sigma \rightarrow \pi^*$ transition would correspond to the observed value of 0.16.²⁰ Most other theoretical calculations indicate that both the $\bar{X}^1A_1 \rightarrow 1^1B_1 (\sigma \rightarrow \pi^*)$ and $\bar{X}^1A_1 \rightarrow 1^1A_2 (n \rightarrow \pi^*)$ excitations are weak transitions which lie near each other at an energy significantly lower than 6.26 eV, and that it is the electric dipole-allowed $\bar{X}^1A_1 \rightarrow 1^1B_1$ transition which contributes most of the intensity in the 3.5–5 eV region of the optical spectrum.⁷

Even less theoretical information is available about the locations and relative ordering of triplet states. A large singlet–triplet splitting (~ 3 eV) is predicted for the $1^3B_2(\pi, \pi^*)$ states, whereas a much smaller singlet–

triplet splitting (~ 0.5 eV) probably characterizes the $1^3B_1(\sigma, \pi^*)$ and the $1^3A_2(n, \pi^*)$ states.^{7,10} The calculated positions of the 1^3B_2 state are undoubtedly too low, as we feel confident that there are no transitions with peaks near 3 eV (see Sec. IV.A). As a result, we might expect that transitions to all three triplet states would occur in the 3.5–4.0 eV transition energy region.

TABLE II. Excited electronic states of nitromethane.

State ^a	Vertical transition energy (eV)		
	Theoretical ^b	Previous experimental	Present experiments ^c
$1^3B_2 (\pi, \pi^*)$	3.01, ^d 3.13 ^e		
$1^3B_1 (\sigma, \pi^*)$	3.71 ^d		3.8 ± 0.1 ^f
$1^3A_2 (n, \pi^*)$	4.60 ^d		
$1^1B_1 (\sigma, \pi^*)$	3.41, ^e 4.41 ^d		
$1^1A_2 (n, \pi^*)$	3.86, ^e 4.56 ^d	4.3, ^g 4.43, ^h 4.49 ¹	4.45 ^f
$1^1B_2 (\pi, \pi^*)$	5.80, ^d 6.43 ^e	6.1, ^g 6.26 ^j	6.23
$1^2A_1 (\pi_{\text{CH}_3}, \pi^*)$	7.64, ^d 8.49 ^e		
$2^1A_1 (\pi_{\text{CH}_3}, \pi^*)$			7.8 ± 0.1
Rydberg $^1(x_1, 3s)^k$		8.2 ^g	8.3 ± 0.1
Rydberg $^1(x_2, 3s)^k$			8.85
$^1A_1 (\sigma, \sigma^*)$	9.70 ^e	9.3 ^g	9.43
Singlet		10.5 ^g	10.35
Singlet			10.91
Rydberg $^1(x_3, 3s)^k$			11.73 ^l

^aThe proposed assignments are tentative; none of the experimental features has been definitively analyzed.

^bThe semiempirical methods used to calculate these transition energies probably have an inherent accuracy on the order of 0.5–1.0 eV.

^cThe estimated uncertainty in the transition energies is ±0.05 eV, unless otherwise indicated.

^dReference 7.

^eReference 10.

^fSee text for discussion of the assignment of this feature.

^gReference 22.

^hReference 21.

ⁱReference 20.

^jReference 18.

^kThe symbol $^1(x_n, 3s)$ is used to represent a Rydberg singlet state produced by promotion of an electron from the n th highest occupied orbital to a 3s Rydberg orbital.

^lThis is a superexcited state.

B. Photoelectron spectroscopy

Photoelectron spectra of nitromethane have been obtained by Rabalais,⁹ Kobayashi and Nagakura,³¹ and Rao.³² The results of these investigations are included in Table I for comparison with theoretical orbital energies. The two lowest vertical ionization energies of nitromethane occur at about 11.3 and 11.8 eV.^{9,31,32} Both ionizations exhibit considerable vibrational structure.⁹ The intensity maximum of the first ionization occurs at the fourth band of the band system,⁹ which indicates that there is a considerable change in molecular geometry upon ionization. Such a Franck-Condon profile is consistent with ionization of a strongly bonding electron. For this reason, Rabalais,⁹ Kobayashi and Nagakura,³¹ and Rao³² assigned the lowest ionization to removal of an electron from the $a_1(\sigma)$ orbital, even though all available calculations predict that its orbital energy is greater than that of the nonbonding $a_2(\pi)$ orbital. However, Murrell *et al.*¹¹ suggest that the calculated ordering is indeed correct, with the most weakly bound electrons filling an $a_2(\pi)$ nonbonding orbital. They argue that if the assignment of Rabalais and the other authors were correct, then the energy splitting between the $a_1(\sigma)$ and $b_2(n)$ orbitals would be an order of magnitude larger than their calculations indicate (see Table I). Murrell *et al.*¹¹ do not address the issue of the Franck-Condon profile of the lowest ionization, which indicates ionization from a bonding rather than a nonbonding orbital.

The maximum intensity of the second lowest ionization, which peaks near 11.8 eV, occurs at the first vibrational band of the progression,⁹ consistent with little distortion of molecular geometry on ionization. Rabalais,⁹ Kobayashi and Nagakura,³¹ and Rao³² assign this feature to ionization of the nonbonding $a_2(\pi)$ orbital, while Murrell *et al.*¹¹ suggest that this photoelectron feature actually is a composite structure of two overlapping transitions, representing removal of a_1 or b_2 electrons.

C. Optical spectroscopy

A number of workers have investigated the UV spectrum of nitromethane.^{5,6,12-21} Early investigators¹²⁻¹⁴ observed a strong continuous absorption at transition energies above ~ 5.3 eV, and a much weaker absorption at lower energies. In succeeding years, the weaker absorption system was studied extensively,^{5,15-17} found to peak near 4.5 eV, and assigned to an $n \rightarrow \pi^*$ transition.⁵ Nagakura¹⁸ was the first to observe the 6.25 eV peak of the stronger transition, which he assigned to a $\pi \rightarrow \pi^*$ transition of the nitro group. Quantitative intensity measurements¹⁸⁻²⁰ of these two transitions vary, but the 4.5 eV feature is clearly quite weak ($\epsilon_{\max} \sim 10\text{--}20$ liter/mole cm, $f \sim 10^{-4}\text{--}10^{-3}$), while the 6.26 eV transition is considerably stronger ($\epsilon_{\max} \sim 5000\text{--}10\,000$ liter/mole cm, $f \sim 0.16$).

Early workers observed little or no fine structure in either the gas phase or solution electronic spectra of nitromethane. In 1972, Bhujle and Randhawa²¹ were able to detect a number of weak broad shoulders at 4.06, 4.12, 4.24, 4.33, 4.43, and 4.54 eV in the gas phase nitromethane spectrum. It was felt that the pro-

gression is most likely associated with excitation of the C-N stretching mode. The electronic origin of the band system was identified as the band at 4.24 eV, with the 4.06 and 4.12 eV peaks representing hot bands.

D. Electron-impact spectroscopy

The only previous electron-impact investigation of excited states of nitromethane was performed by McAllister.²² Using an ion cyclotron resonance mass spectrometer, he obtained threshold excitation spectra by monitoring the current of scattered electrons transmitted through the ICR cell. He confirmed these results by employing the CCl_4 electron scavenging method. The two lowest energy transitions which were observed peaked at 4.3 and 6.1 eV, and were correlated with the features at similar transition energies in the optical spectrum. McAllister did not detect low-lying singlet-triplet transitions, although he suggested that a peak at 8.2 eV might be due to an $\tilde{X}^1A_1 - \tilde{3}A_1$ transition. Vague features near 9.3 and 10.5 eV were also noted in the threshold excitation spectrum.

III. EXPERIMENTAL METHODS

The electron-impact spectrometer used in the present study is a modified version^{25,33} of the one described in detail by Kuppermann and co-workers.^{23,24} It consists of a multistage electron gun, a hemispherical electrostatic energy monochromator, a flexible metal bellows collision chamber containing the sample gas, an energy-loss analyzer identical to the monochromator, and a continuous dynode electron multiplier, which serves as a detector. Output pulses are amplified, shaped, and then counted with a 1024-channel scaler. An energy-loss spectrum, at a fixed incident electron energy (E_0) and scattering angle of detection (θ), is obtained by sweeping the potentials of the postscattering chamber electron optical lens elements with a ramp voltage generated by the multichannel scaler. Typically, an energy-loss region 5 or 10 eV wide is scanned in any given spectrum, with total data accumulation times of 4-6 h per spectrum.

The data are transferred to magnetic tape and processed by computer. The processing³⁴ consists of subtraction of background, averaging over a variable number of neighboring channels for purposes of data smoothing, band system deconvolution when desirable and feasible, and calculation of the areas, area ratios, and relative differential cross section (DCS) of each feature. We employ a relatively simple deconvolution procedure^{26,34,35} to separate closely spaced spin-allowed and spin-forbidden transitions. The Franck-Condon profile of a given transition is assumed to be independent of E_0 and θ , an assumption which has been shown to be valid for the operating conditions employed in the present investigation.^{24,36,37} The profile of the spin-allowed transition is determined from a suitable low-angle reference spectrum, for which the relative contribution of the spin-forbidden process is small. An appropriately scaled version of the reference is then subtracted from a higher angle spectrum, thereby furnishing the deconvoluted spin-forbidden transition.

This procedure was used in this study to separate the spin-allowed feature which peaks at 4.45 eV from the spin-forbidden feature which peaks near 3.8 eV. While relative DCS values obtained by this method are clearly subject to larger uncertainty than those obtained for isolated transitions, we feel confident that this method is a substantial improvement over those based upon measurements of peak heights.²⁶

By measuring the variation of the intensity of an unknown transition with E_0 and θ , it is possible to identify the transition as spin-forbidden, e.g., singlet \rightarrow triplet, or spin-allowed, e.g., singlet \rightarrow singlet.²³⁻³⁰ It is also often possible to subdivide the spin-allowed features into those which are fully allowed by electric dipole selection rules and those which are symmetry-forbidden.^{25,33,34,38,39} Typically, the DCS for a spin-forbidden transition is nearly isotropic in the range $\theta = 10^\circ - 80^\circ$, for E_0 values 15–50 eV above excitation threshold.²³⁻²⁵ Optically allowed transitions have strongly forward-peaked DCS curves, frequently decreasing by $1\frac{1}{2}$ –2 orders of magnitude as θ increases from 10° to 80° .²³⁻²⁵ Symmetry-forbidden, spin-allowed transitions have DCS curves that are usually forward peaked, but often appreciably less so than those of optically allowed features in the same molecule.^{25,33,38} In addition, transitions which are forbidden by either spin and/or symmetry selection rules are usually more intense at low impact energies than at high ones.²³⁻²⁵ The angular and energy dependences just described have led to a set of empirical rules obeyed by the ratio of the intensity of an unknown transition to that of an optically allowed one.³⁹

In the present study, the electron-impact energy-loss spectra of nitromethane were obtained at $E_0 = 25, 55$, and 90 eV, for θ in the range 6° to 80° . The incident electron beam intensity was approximately 50 nA, and the energy resolution was 0.13–0.16 eV, as measured by the full width at half maximum (FWHM) of the elastically scattered peak. One spectrum was obtained at a higher resolution, 0.08 eV FWHM. The nitromethane used in this investigation was obtained from Matheson,

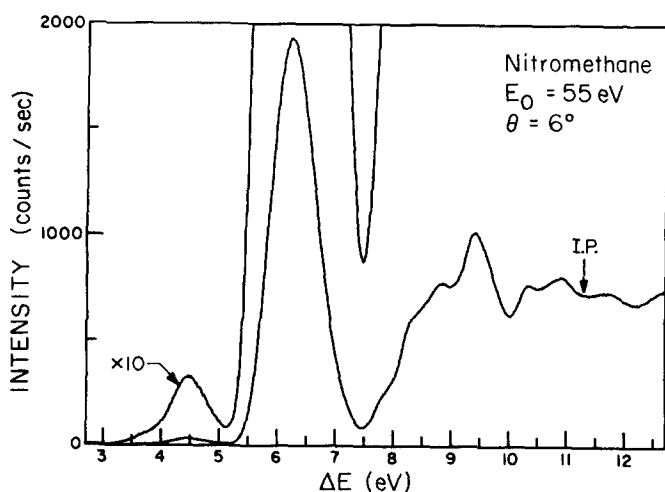


FIG. 1. Electron energy-loss spectrum of nitromethane, obtained at an incident electron energy (E_0) of 55 eV and scattering angle (θ) of 6° . The approximate position of the lowest molecular ionization potential (I. P.) is indicated.

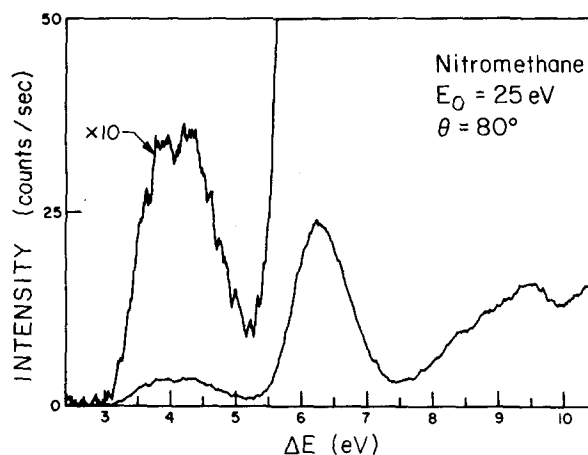


FIG. 2. Electron energy-loss spectrum of nitromethane at $E_0 = 25$ eV and $\theta = 80^\circ$.

Coleman, and Bell, and had a stated boiling point range of 100 – 102°C . The sample was degassed repeatedly under vacuum by liquid nitrogen freeze–pump–thaw cycles, and no evidence of impurity absorption was found. Measured transition energies are estimated to have an uncertainty of 0.05 eV, unless otherwise indicated.

IV. RESULTS AND DISCUSSION

A preliminary account of some of our results was published previously.⁴⁰ In Table II, we give a full summary of the present results as well as those of the more pertinent previous experimental and theoretical studies. Figure 1 shows the 2.7–12.7 eV energy-loss spectrum of nitromethane obtained at $E_0 = 55$ eV and $\theta = 6^\circ$. Figure 2 displays a spectrum obtained under a contrasting set of conditions, $E_0 = 25$ eV, $\theta = 80^\circ$, while an example of the results of the deconvolution procedure performed in this study is shown in Fig. 3. The rela-

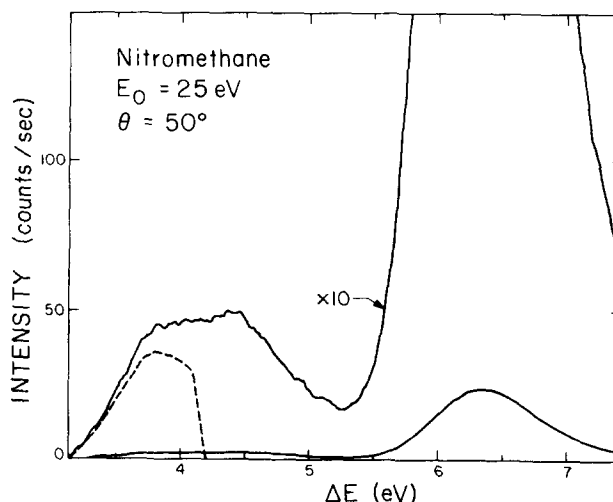


FIG. 3. Electron energy-loss spectrum of nitromethane, showing the estimated Franck–Condon envelope of the singlet \rightarrow triplet feature which peaks at 3.8 eV (dashed lines). The spectrum was obtained at $E_0 = 25$ eV and $\theta = 50^\circ$, and the deconvolution was performed using an $E_0 = 55$ eV, $\theta = 6^\circ$ reference spectrum.

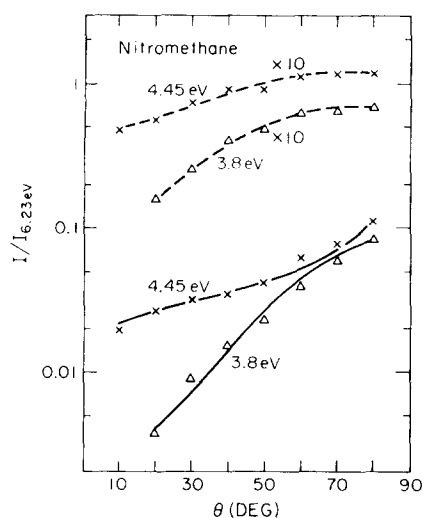


FIG. 4. Ratios of the intensities of two inelastic features in nitromethane to that of the optically allowed 6.23 eV excitation at $E_0 = 25$ eV (dashed lines) and 55 eV (solid lines). Both 25 eV curves have been multiplied by a factor of 10. The transitions shown are the 3.8 eV feature (Δ) and the 4.45 eV feature (x).

tive intensities of various features with respect to the strong transition at 6.23 eV are depicted in Fig. 4, and the variation of the relative DCS values with scattering angle at $E_0 = 25$ eV and $E_0 = 55$ eV are shown in Figs. 5 and 6, respectively.

A. The 3.8 eV feature

The lowest energy-loss feature detected in this investigation has an onset at 3.1 eV and a maximum intensity at 3.8 ± 0.1 eV (Figs. 2 and 3). The ratio of the inten-

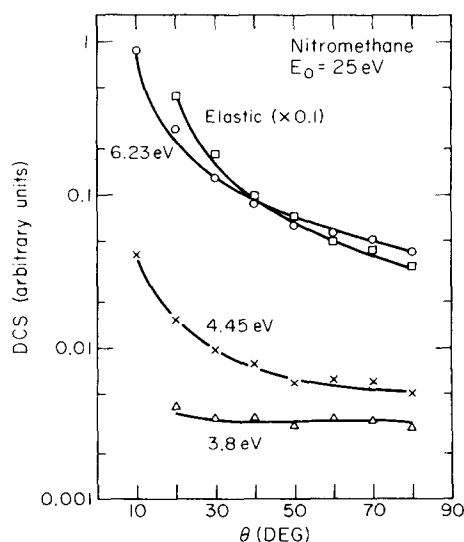


FIG. 5. Relative differential cross sections (DCS) for elastic and inelastic scattering in nitromethane at $E_0 = 25$ eV. The processes shown are elastic scattering (\square), and transitions at 3.8 eV (Δ), 4.45 eV (x), and 6.23 eV (\circ). The elastic curve has been multiplied by 0.1. The arbitrary units of the ordinate were determined by setting the value of the elastic DCS at $\theta = 40^\circ$ equal to 1.0.

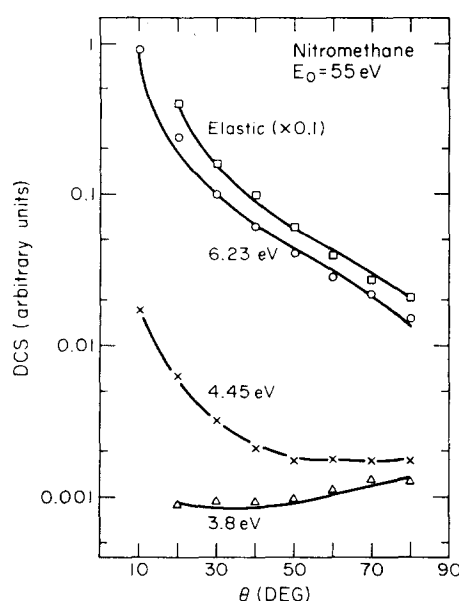


FIG. 6. Same as Fig. 5 for $E_0 = 55$ eV. The arbitrary units of the ordinate were determined as in Fig. 5, but the two sets of units cannot be compared.

sity of this feature to that of the optically allowed 6.23 eV transition increases rapidly with increasing θ (Fig. 4), while its DCS is relatively independent of θ (Figs. 5 and 6). Furthermore, at most scattering angles measured, the relative intensity of the 3.8 eV feature is greater at $E_0 = 25$ eV than at $E_0 = 55$ eV. Such DCS and intensity ratio behavior is highly characteristic of spin-forbidden transitions,²³⁻²⁵ and we are therefore confident in assigning the 3.8 eV feature to a singlet-triplet transition, or possibly several closely spaced transitions of this kind.

As discussed in Sec. II. A, there are at least three candidates for an excited triplet state at 3.8 eV, i.e., $1^3B_2(\pi, \pi^*)$, $1^3A_2(n, \pi^*)$, and $1^3B_1(\sigma, \pi^*)$. On the basis of our observations and the limited number of theoretical calculations, we are unable to choose among these possibilities. We conclude that the 3.8 eV feature may represent transitions to any one or more of these states.

B. The 4.45 eV feature

In the deconvolution procedure we employed, it was assumed that there are two distinguishable spectral features which overlap in the 3-5 eV energy-loss range. In addition to the singlet-triplet feature near 3.8 eV, a second feature peaking near 4.45 eV and extending to 5.3 eV (Figs. 1-3) was assumed to consist of one or more singlet-singlet transitions. The shape of this feature's intensity ratios (Fig. 4) and DCS curves (Figs. 5 and 6) is intermediate between those of spin-forbidden excitations and those of optically allowed ones.

One possible explanation for the angular dependence of the 4.45 eV peak intensity is that there may be an additional singlet-triplet transition which underlies the singlet-singlet transitions in the vicinity of 4.45 eV. However, given the magnitude of the singlet-triplet splittings (~ 0.5 eV) calculated for the transitions in

this region,^{7,10} we feel that it is more likely that the angular dependence in question can be explained by the presence of the spin-allowed, electric dipole-forbidden $\tilde{X}^1A_1 - 1^1A_2 (n - \pi^*)$ excitation in this portion of the electron-impact spectrum. Furthermore, it is probable that part of the intensity of the 4.45 eV peak which we observe is due to the electric dipole-allowed $\tilde{X}^1A_1 - 1^1B_1 (\sigma - \pi^*)$ transition, which undoubtedly accounts for almost all of the intensity of the 4.5 eV peak in the optical spectrum.

C. The 6.23 eV transition

The strongest feature in the nitromethane electron-impact spectrum peaks at 6.23 eV, and has a Franck-Condon envelope which extends from 5.2 to 7.4 eV (Figs. 1-3). Its DCS curves are quite forward peaked (Figs. 5 and 6), in agreement with its assignment as the optically allowed $\tilde{X}^1A_1 - 1^1B_2 (\pi - \pi^*)$ transition.¹⁸

D. Higher transitions

We also observe in our spectra transitions at 8.3, 9.43, and 10.35 eV (Figs. 1 and 2), which probably correspond to the transitions detected by McAllister²² at 8.2, 9.3, and 10.5 eV, respectively, in threshold electron-impact spectra. Since the 8.3 eV shoulder which we observe appeared clearly at both low and high scattering angles with approximately equal relative intensity with respect to the optically allowed transition at 6.23 eV, we do not think that it corresponds to the $\tilde{X}^1A_1 - 1^3A_1 (\pi_{CH_3} - \pi^*)$ transition, an assignment suggested by McAllister.²² On the basis of the term value of this transition (~ 3.0 eV) with respect to the lowest ionization potential, Robin⁴¹ has suggested that this feature represents a spin-allowed excitation of the most weakly bound electron into a 3s Rydberg orbital. The 9.43 eV peak may correspond to an $\tilde{X}^1A_1 - 1^1A_1 (\sigma - \sigma^*)$ transition, which Harris¹⁰ calculates to have an appreciable optical oscillator strength, $f = 0.07$.

We also observe other transitions at about 7.8, 8.85, 10.91, and 11.73 eV (Fig. 1). None of these features appears to have been reported previously. If we use the term value (TV) method,⁴²⁻⁴⁴ and assume that Robin's estimate of 3.0 eV for the 3s TV is accurate, then we can tentatively assign both the 8.85 and the 11.73 eV transitions to Rydberg excitations to 3s orbitals. The 8.85 eV feature has a TV of 3.0 eV with respect to the second ionization potential at 11.85 eV,³² while the 11.73 eV transition has an identical TV with respect to the third ionization potential at 14.73 eV.⁹

If the preceding assignment of 3s Rydberg states is correct, then the 7.8 eV feature is an intravalence excitation, possibly the $\tilde{X}^1A_1 - 2^1A_1 (\pi_{CH_3} - \pi^*)$ transition. Although we favor this assignment, we cannot preclude the possibility that the appropriate 3s TV is ~ 3.5 eV, in which case the 7.8 eV shoulder would correspond to the lowest 3s Rydberg state. In this alternative analysis, the 8.3 eV feature would then correspond to the second 3s Rydberg state and/or the 2^1A_1 valence state.

E. Photochemistry of nitromethane

The 313 nm (3.96 eV) photolysis of nitromethane in the gas phase has been studied by Honda, Mikuni, and Takahasi.² From their analysis of their experiments, they conclude that there are two important primary processes in the photolysis of nitromethane:



The first reaction is believed to proceed via a triplet state, whereas the second proceeds via the lowest energy excited singlet state. The quantum yield of triplet nitromethane was found to be large (~ 0.6) both by the Cundall method,⁴⁵ involving isomerization of the 2-butenes, and by product analysis.

Although the location of the triplet state was unknown to Honda *et al.*,² they suggested that it must be above 3.4 eV (their estimate of the onset of singlet-triplet absorption in ethylene), since it is capable of sensitizing the isomerization of ethylene. Employing Dexter's theory of triplet-triplet energy transfer,⁴⁶ in combination with singlet-triplet spectra obtained in these electron-impact studies of nitromethane, we can learn additional information about this transition. First we note that the onset of the singlet-triplet transition is 3.1 eV. Secondly, since triplet nitromethane can excite ethylene into its lowest triplet state by means of an electronic energy transfer process, the Dexter theory implies that the 0-0 band of the nitromethane transition must be greater than 3.5 eV, which is the most recent estimate of the onset of singlet-triplet absorption in ethylene.⁴⁷ As a result, we conclude that the region in the nitromethane electron-impact spectrum between 3.1 and at least 3.5 eV must represent excitation of hot bands. As mentioned earlier, a similar situation apparently obtains in the UV absorption spectrum of the lowest singlet-singlet transition in this molecule.

V. SUMMARY AND CONCLUSIONS

We have used the method of variable angle electron-impact spectroscopy to investigate electronically excited states of nitromethane. A feature with singlet-triplet character has been detected at 3.8 eV vertical excitation energy. This feature may be a composite structure, involving one or more closely spaced transitions to the $1^3B_2 (\pi, \pi^*)$, $1^3A_2 (n, \pi^*)$, or $1^3B_1 (\sigma, \pi^*)$ states. The peak at 4.45 eV may also be a composite structure, involving transitions to the $1^1A_2 (n, \pi^*)$ and $1^1B_1 (\sigma, \pi^*)$ states. This feature has symmetry-forbidden properties, consistent with the presence of the $\tilde{X}^1A_1 - 1^1A_2 (n - \pi^*)$ transition. Both the 3.8 and the 4.45 eV states play central roles in the gas phase photolysis of nitromethane.

A number of higher transitions are observed in the 6-12 eV energy-loss range. A feature at 7.8 eV is probably a valence shell transition, while the 8.3, 8.85, and 11.73 eV features are tentatively assigned to Rydberg transitions of increasingly tightly bound electrons into a 3s Rydberg orbital.

Note added in proof: A semiempirical calculation⁴⁸ on the electronic states of nitromethane with the HAM/3-CI method^{49,50} has recently been brought to our attention. The calculated electron affinity and lowest twelve ionization energies agree well with the corresponding experimental values. The vertical excitation energies of the first four valence singlet states are calculated to be 4.81, 4.88, 6.63, and 8.06 eV; with oscillator strengths of 1×10^{-5} , 1×10^{-4} , 0.63, and 0.15, respectively. The good agreement between these theoretical values and the experimental measurements supports our assignment of the 7.8 eV feature to the valence transition, $\bar{X}^1A_1 - 2^1A_1$.

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