

ABOUT THE KINETIC ENERGY SPECTRA OF FRAGMENT IONS. A COMPARISON BETWEEN ELECTROIONIZATION AND FIXED-WAVELENGTH PHOTOIONIZATION

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ABSTRACT

The HeI and NeI translational energy spectra have been recorded for $\text{NO}^+/\text{N}_2\text{O}$ and $\text{CH}_3^+/\text{CH}_3\text{F}$. The marked difference between the two spectra for NO^+ is related to the NeI- $\tilde{\text{A}}^2\Sigma^+$ photoelectron spectrum. Both spectra of CH_3^+ show two components, i.e. a thermal peak and a high energy distribution. As the energetic ions are ascribed to the decomposition of the CH_3F^+ (${}^2\text{E} + {}^2\text{A}_1$) states, the thermal ions could be interpreted by the dissociation of the CH_3F^+ ($\tilde{\text{X}}^2\text{E}$) state.

INTRODUCTION

Since several years, the dissociative electroionization of a number of diatomic and polyatomic molecules has been investigated using kinetic energy and mass analysis. On the other hand, ion kinetic energy data by photoionization are scarce. By photoion-photoelectron coincidence spectroscopy the average kinetic energy is inferred from time-of-flight distributions [1]. Gardner and Samson [2] obtained photoion energy distribution spectra without mass analysis, using a cylindrical mirror analyser. Doolittle et al. [3] and Chupka and Berkowitz [4] measured kinetic energy spectra by a retarding potential device.

In the present contribution, the kinetic energy spectra obtained for fragment ions produced by the electroionization and fixed-wavelength photoionization of N_2O and CH_3F will be discussed.

EXPERIMENTAL

The experimental set-up used in the present photoionization work will be described in detail elsewhere [5], whereas the electron impact experiment has been extensively laid out earlier [6].

In the former experiment, the light produced by a discharge in a rare gas, is led into an ion chamber via a capillary. The photoions are extracted by a 0-300 mV. cm^{-1} drawout field. After leaving the ion source and entering a quadrupole mass filter, the ions are energy analyzed by means of a retarding lens [6]. The retarding potential V_R is scanned by applying a voltage ramp to the retarding lens.

The ejected photoelectrons are analyzed in a retarding potential-type analyzer with a differential output [7]. The resolution, as measured on the photoelectron spectrum of Ar, has been limited to 40-50 meV.

Both ions and electrons are detected by means of conventional Cu-Be electron multipliers followed by a counting electronics. Both signals are collected and stored into a minicomputer for further handling and recording.

The photoions kinetic energy distributions are obtained by derivating the retarding potential curve. The origin of the kinetic energy scale is fixed by the maximum of the first derivative of a rare gas or molecular ions retarding potential curve.

RESULTS AND DISCUSSION

The NO⁺/N₂O

The dissociative electroionization of N₂O has been extensively discussed in a previous work [8,9]. In the present experiment, the NO⁺, N₂⁺ N⁺ and O⁺ photoions kinetic energy distributions have been recorded with both the HeI (58.43 nm) and NeI (73.58-74.37 nm) resonance lines. The N₂⁺, N⁺ and O⁺ ions essentially show the same distributions as observed by electron impact at comparable energies [8,9]. The NO photoion distributions obtained with HeI and NeI are shown in fig. 1. As the distribution observed at 58.4 nm is identical to that observed with about 20 eV electrons [8], the NeI kinetic energy spectrum of NO⁺ markedly differs from the HeI and the electroionization distributions obtained with 16 eV and 17 eV electrons [8]. Two distinct components are observed, one at thermal or nearly thermal energy and the second shows a maximum at 200 meV and spreads up to 700 meV.

As it has been shown by both photoionization [10-12] and electroionization [8,9], the distributions observed at 58.43 nm result from the added contributions of the predissociation of the $\tilde{A}^2\Sigma^+$, $\tilde{B}^2\Pi$ and/or $\tilde{C}^2\Sigma^+$ states of N₂O⁺. The predissociation of the higher vibrational levels of the N₂O⁺ ($\tilde{X}^2\Pi$) state, observed by electron impact and resonant photo-ionization is ruled out in fixed wavelength HeI-photoionization [10]. These vibrational levels are experimentally known to be populated by autoionization only [12].

Using the NeI resonance line, only the $\tilde{X}^2\Pi$ and partially the $\tilde{A}^2\Sigma^+$ states of N₂O⁺ are excited. These states have been shown to produce O⁺ and NO⁺ fragment ions only [8-12]. However it has to be kept in mind that changes could occur in the photoelectron spectrum which could account for the differences in the ion energy distributions. It has to be noticed that the 74.372 nm line produced in the Ne discharge is nearly resonant with the autoionization peak observed at 74.293 nm in the photoionization efficiency curves of O⁺, NO⁺ and N₂O⁺ with less intensity [11,13]. Autoionization could induce drastic changes in the photoelectron spectra [14].

The HeI-and NeI-photoelectron spectra of the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Sigma^+$ states of N₂O⁺ have been recorded. The deconvoluted [15] NeI-photoelectron spectrum of the N₂O⁺ ($\tilde{A}^2\Sigma^+$) state is shown in fig. 2. Table 1 displays the relative intensities, corrected for the electron analyzers transmission for both the HeI-and NeI- spectra. For comparison the values measured by Dehmer et al [13] and Frey et al [16] are reproduced. The ionization energies deduced from these spectra are listed in the last column of table 1.

TABLE 1. Comparison of the relative intensities for the N₂O A²Σ⁺ (ν₁, ν₂, ν₃) transitions obtained with NeI and HeI

ν ₁ , ν ₂ , ν ₃ [13]	He I		TPES [16]	NeI this work	Ratio NeI/[13]	I.P. (eV)
	[13]	this work				
0, 0, 0	100	100	100	100	1	16.387
0, 1, 0	~2.1	< 5	-	30	~ 15	16.472
1, 0, 0	21.7	<28	39,5	23	~ 1	16.563
1, 1, 0 (?)	(1.1)	-	-	30	~ 30	16.636
0, 0, 1	8.5	<10	10.8	17	~ 2	16.665
2, 0, 0	0.5	< 2	7.3	7.6	~15	16.722
0, 1, 1	0.1	-	-	15	~150	16,764

FIG. 1 . First differentiated retarding potential curves of $\text{NO}^+/\text{N}_2\text{O}$ observed with the HeI and NeI resonance lines.

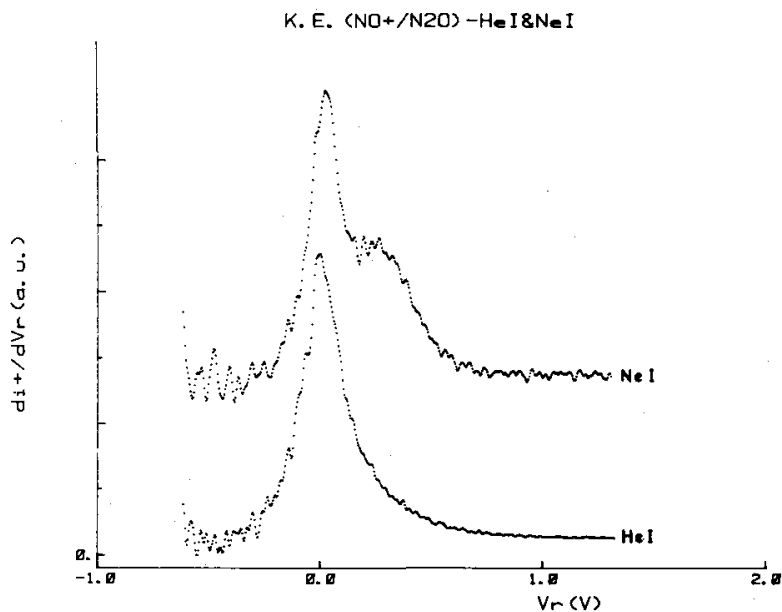
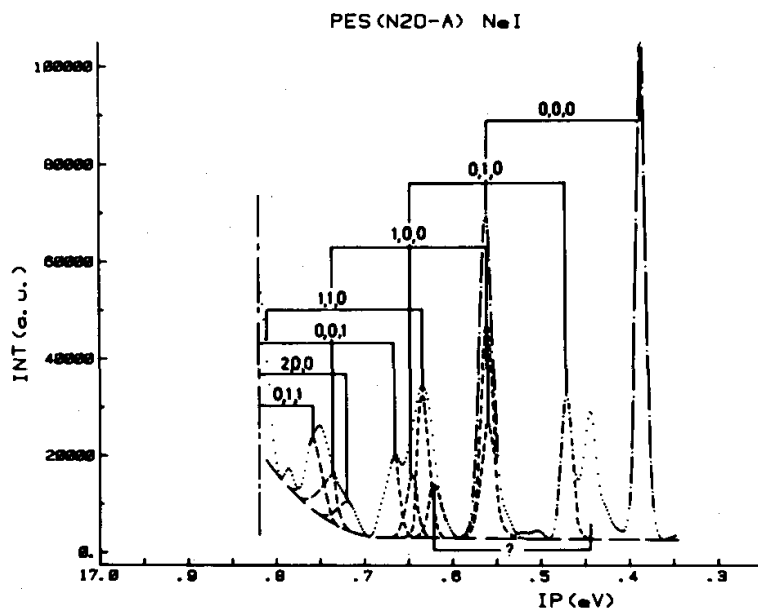
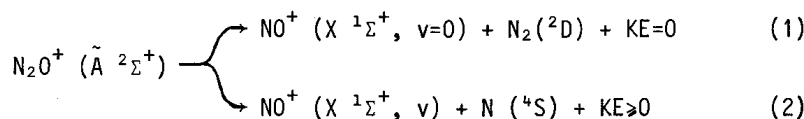


FIG. 2 . Deconvoluted NeI-photoelectron spectrum of the N_2O^+ ($A^2\Sigma^+$) state.



With the NeI resonance lines, the NO^+ ions can be produced through the predissociation of N_2O ($\tilde{A}^2\Sigma^+$) vibrational levels, lying above $v = 0, 0, 0$ [10] and leading to :



for which the thermochemical onset is 16.577 eV and 14.194 eV respectively. As noticed earlier [8], the former process could not unambiguously be deduced from the kinetic energy-versus-appearance energy diagram. This reaction is produced by photodissociation of the N_2O^+ beams [17] and proposed by Brehm et al. [10] on the basis of photoion-photoelectron coincidence experiments.

The dissociation path (1) with the onset at 16.577 eV is opened at the $\tilde{\text{A}}^2\Sigma^+$ (1,1,0) level measured at 16.636 eV producing NO^+ ions carrying 19 meV kinetic energy. Brehm et al. [10] assigned the low energetic NO ions in coincidence with 16.61 eV electrons to this process and state that "this new channel makes a small but detectable contribution". It has to be pointed out that in the NeI spectrum the relative intensity of the $\tilde{\text{A}}^2\Sigma^+$ (1,1,0) level is increased by 30. This could at least partially account for the fairly intense low energy peak in fig. 1. Another dissociation channel would at least formally be allowed at 16.636 eV and produce NO^+ ions, i.e. NO^+ ($X^1\Sigma^+$, $v=9$) + (^4S) whose onset is calculated at 16.657 eV, using the excess energy of 2.463 eV to populate the $v=9$ vibrational level [18].

The high energy part of the NO^+ ion energy distribution, as observed with NeI, has been interpreted by Brehm et al. [10] by the partition of the excess energy with respect to 14.194 eV between internal energy of NO^+ ($X^1\Sigma^+$) and the kinetic energy of the fragments. NO^+ ($X^1\Sigma^+$) is vibrationally distributed between $v=8-3$. By electroionization in the energy range of 16.0-17.0 eV [8], the kinetic energy-versus-appearance energy diagram only showed $\text{NO} (X^1\Sigma^+, v=2) + \text{N}(^4\text{S})$ fragments with an increasing amount of kinetic energy. This discrepancy has been pointed out earlier [8]. As mentioned above, the NO^+ ion energy distributions observed by electroionization and with HeI- on one hand and NeI-photoionization on the other hand are rather different.

The high energy distribution peaks at (200 ± 50) meV and corresponds to about (630 ± 150) meV total kinetic energy carried by both NO^+ and N fragments. The NO ions being produced by the predissociation of the $\tilde{\text{A}}^2\Sigma^+$ state, the intensity enhancement giving rise to the observed ion energy distribution could be accounted for by the increase of the relative intensity of a number of transitions as measured in the NeI spectrum. The $\tilde{\text{A}}^2\Sigma^+$ (2,0,0) with an enhancement ratio of 15:1 with respect to the HeI spectrum, would produce NO^+ ($X^1\Sigma^+$, $v=7$) carrying 200 meV translational energy. At higher ion energies, NO^+ ($X^1\Sigma^+$) is produced in lower vibrational levels with increasing kinetic energy. For 700 meV kinetic energy, NO^+ would be in the $X^1\Sigma^+$, $v=1$ state.

The $\text{CH}_3^+/\text{CH}_3\text{F}$

Dibeler and Reese [19] and Krauss et al. [20] studied the ionization and dissociation of CH_3F by electroionization and photoionization. The CH_3^+ ion produced by electroionization showed two components, i.e. (i) a thermal contribution corresponding to an ion-pair process at 12.5 eV and to a dissociative ionization process at (14.7 ± 0.3) eV, and (ii) a high energy contribution corresponding to a dissociative ionization process with an appearance energy at 16.5 eV. By resonant photoionization the dissociative ionization process at 14.7 eV is surprisingly absent, whereas the ion-pair process and an onset at 16.25 eV are observed.

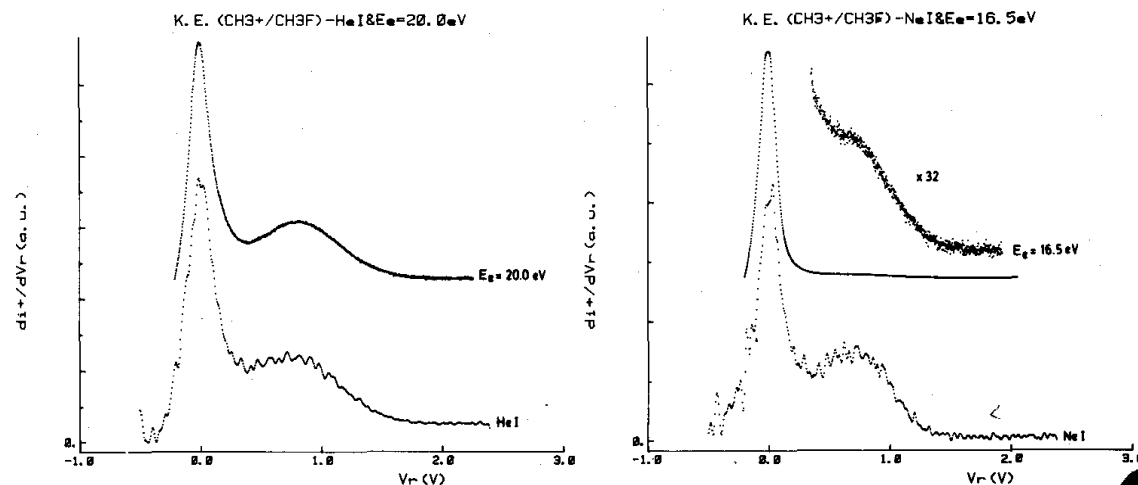
Several photoion-photoelectron coincidence experiments applied to CH_3F^+ have been reported. Eland et al. [21] measure only energetic CH_3 ions in coincidence with the CH_3F^+ ($^2\text{A}_1 + ^2\text{E}$) states. These observations apparently agree with the former photoionization experiments. The ion-pair process being not observable in coincidence and by HeI-photoionization, only the dissociative ionization at 16.5 eV is observed, i.e. CH_3^+ production with a large amount of translational energy.

The electroionization efficiency curves as well as the translational energy distribution of CH_3^+ produced by electroionization have been recorded from onset up to 70 eV [22]. Below 16.5 eV only one thermal energy distribution is observed whose intensity increases between 12.0 and 15.5 eV resulting from the added contribution of the ion-pair production $\text{CH}_3^+ + \text{F}^-$ and the dissociative ionization process $\text{CH}_3^+ + \text{F}$ with the onset at 14.7 eV. For 16.5 eV and higher electron energies, a broad kinetic energy distribution appears. Its maximum slightly shifts and weakly broadens toward higher kinetic energy.

Figs. 3 and 4 show translational energy distributions of CH_3^+ photoions recorded with the HeI and NeI resonance lines. For comparison, the distributions obtained for CH_3^+ ions at nearly equivalent electron energies are drawn in the same figures.

The most important feature is the close similarity of the kinetic energy distributions observed by electroionization and fixed wavelength photoionization. The existence of a thermal peak in the distribution of the CH_3^+ ions is unambiguously evidenced at both 21.21 eV (HeI) and 16.85-16.67 eV (NeI). These ions have not been detected in coincidence experiments [21].

FIGS. 3 and 4. First derivative of the HeI (fig. 3) and NeI (fig. 4) retarding potential curves of $\text{CH}_3^+/\text{CH}_3\text{F}$ compared to those observed with 20 eV and 16.5 eV electrons respectively.



The occurrence of thermal CH_3^+ ions at 21.21 eV excludes its formation through autoionization or ion-pair. The broad distribution has its maximum at 0.81 eV and extends to about 1.85 eV. For 20 eV electrons the same distribution peaks at 0.92 eV and extends to about 2.09 eV.

The same two translational energy components are observed with NeI: a thermal peak and a distribution with a maximum at 0.68 eV and spreading out to 1.33 eV. For 16.5 eV electrons the high energy distribution peaks at 0.74 eV and extends to 1.6 eV. The use of the NeI resonance line rules out the ion-pair process, whereas autoionization could be considered. However, the photoionization efficiency curve [20] of CH_3^+ looks fairly flat in the NeI-energy range, and autoionization would therefore be excluded. The absence of any change in the photoelectron spectra with HeI and NeI would confirm the lack of resonant autoionization at 16.85 or 16.67 eV.

Consequently, the thermal CH_3^+ ions have to be produced by direct ionization. Two mechanisms would be available to produce thermal CH_3^+ ions, (i) Through predissociation of the first excited CH_3F^+ (\tilde{A}^2A_1) state. This state would dissociate into $\text{CH}_3^+ + \text{F}$ and the total excess energy - with respect to the 14.5 eV dissociation limit - is entirely converted into vibrational energy of the CH_3^+ ion. (ii) The \tilde{X}^2E state is populated at its dissociation limit and both CH_3^+ and F are formed in their ground vibrational and/or electronic states.

Considering the photoelectron-photoion coincidence data where no thermal CH_3^+ ions are detected in coincidence with the 2A_1 electrons, the second mechanism looks likely. The CH_3F^+ (2E) photoelectron band extends to 14.5 eV. At this energy, the electrons intensity could be too weak to observe coincidences. Furthermore this mechanism would be a straightforward interpretation of the 14.7 eV threshold [19,22] measured by electroionization. The only remaining question is: why is this process not observed in the CH_3^+ photoionization efficiency curve?

The broad translational energy distribution observed in all experiments has clearly to be ascribed to the decomposition of the CH_3F^+ ($^2A_1 + ^2E$) states involving the excess energy partitioning, with respect to the 14.5 eV dissociation limit, between internal energy of CH_3^+ and translational energy of CH_3^+ and F.

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