HeI and HeII Photoelectron Study of N_2O_4

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(Received December 11, 1978)

A 304 Å HeII photoelectron spectrum of N_2O_4 in the gaseous phase has been deduced in the region up to 29 eV from a HeII spectrum of NO_2–N_2O_4 mixture obtained with a nozzle beam technique, indicating three new maxima in the region between 20 and 29 eV. A 584 Å HeI spectrum of N_2O_4 was also obtained here. From a comparison of the HeI and HeII spectra of N_2O_4 below 20 eV, it was confirmed that two ionization bands exist at 16.5 and 18.2 eV which appear as shoulders in the HeII spectrum. At least fourteen ionization bands have been identified from the HeII spectrum in the region studied. The thirteen bands below 24 eV have been assigned on the basis of a recent Green's function study of von Niessen *et al.*

It is well known that there exists a monomer-dimer equilibrium between NO_2 and N_2O_4 ($N_2O_4 \rightleftharpoons 2NO_2$) in the gaseous phase. Its thermodynamic properties have been studied extensively by Hisatsune.[1] Anomalous geometric features such as an unusually long N–N distance (1.78 Å) and planar structure for N_2O_4 have been found from a gas-phase electron diffraction study by Hedberg *et al.*[2] Furthermore a relatively high barrier to internal rotation (2.9 kcal mol^{-1}) and a relatively small heat of dissociation (12.7 kcal mol^{-1}) have been reported for N_2O_4 by Snyder and Hisatsune.[3] Because of such anomalous features, N_2O_4 has been received much attention in molecular structure and electronic structure from both experimental and theoretical points of views.

Vacuum UV photoelectron (PE) spectroscopy provides ionization energy data useful for studying valence electron orbitals.[4] HeI and HeII PE spectra of the NO_2 monomer have well been studied by Edqvist *et al.*[5] and Brundle *et al.*[6] For its bonded dimer (N_2O_4), however, there is some difficulty in obtaining PE spectra for N_2O_4 with a conventional PE spectrometer, because of its rapid dissociation in the ionization chamber in which the sample pressure is normally the order of 10^{-3} Torr. In order to overcome this difficulty, special gas inlet systems have recently been used to measure HeI PE spectra for mixtures of NO_2 and N_2O_4 by Ames and Turner,[7] Yamazaki and Kimura,[8] Frost *et al.*,[9] and Gan *et al.*[10] Ames and Turner[7] have used a nozzle inlet system in which rapid expansion of gas takes place by a large pressure difference through a pinhole with a nozzle pressure of about 1 atm. In a previous work in our laboratory, Yamazaki and Kimura[8] have used a long-path cooling inlet system in which the gas sample is cooled to −60 °C. Frost *et al.*[9] have used two kinds of gas samples one of which is a vapor from a frozen N_2O_4 sample condensed in the inlet system and the other is a continuous rapid flow of a cold NO_2 gas (−30—−50 °C). In those works of Ames and Turner[7] and Frost *et al.*,[9] the effused gas in the ionization chamber has been pumped out by an additional pumping system to increase the mole fraction of N_2O_4 up to 60—70%. Gan *et al.*[10] have also used a nozzle inlet system with a pressure near 1 atm.

In each of those PE studies,[7–10] the HeI spectrum of N_2O_4 has been deduced from that of the NO_2–N_2O_4 mixture by subtracting the NO_2 component in an appropriate manner. Spectral assignments already reported on the HeI spectra however differ largely from one another, although they are based on *ab initio* MO calculations. A number of theoretical studies on molecular orbitals of N_2O_4 have been published, employing *ab initio* methods[11–14] and many kinds of semiempirical methods.[15] Very recently, von Niessen *et al.*[16] have carried out *ab initio* many-body Green's function calculations on the photoionization of N_2O_4.

In order to obtain a further information about the photoionization of N_2O_4, in the present work we considered it important to compare HeI and HeII PE spectra with each other in spectral shape and intensity, as well as to find new PE bands in the region above 21 eV.

Experimental

PE measurement by HeI (584 Å) and HeII (304 Å) resonance radiations were carried out with our PE spectrometer with some improvements in the gas inlet system and a data accumulation system. The spectrometer is essentially the same as used previously,[17,18] containing a hemispherical electrostatic analyzer of 10 cm in diameter. The resolution is about 25—30 meV as measured for Ar using 584 Å radiation. The improvements of the gas inlet system and the data accumulation system are the following.

The gas inlet system used here is shown schematically in Fig. 1. Gas sample was introduced into the ionization chamber through a pinhole of a glass tube connected to a 2-litre gas reservoir in which the sample was contained at about 600

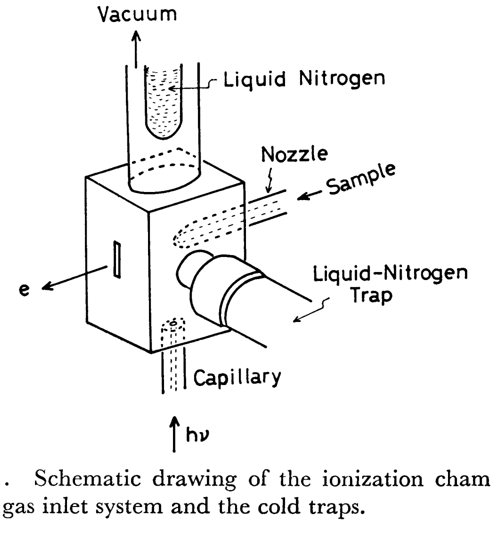

Fig. 1. Schematic drawing of the ionization chamber, the gas inlet system and the cold traps.

Torr. The nozzle pinhole was formed by discharge with a Tesla coil and then appropriately expanded by slowly dissolving in an aqueous HF solution so as to keep the pressure of the ionization chamber in the order of 1×10^{-3} Torr. (The diameter of the pinhole is approximately 50—60 μm.) In order to prevent accumulation of a static charge, the glass nozzle was covered with a brass cap coated by Aquaduck. The effused gas in the ionization chamber was pumped out with two additional diffusion pumps (2″ and 6″) as well as a liquid nitrogen trap, since N_2O_4 rapidly decomposes upon wall collision.

The data accumulating and processing system used consists of a multichannel analyzer (16 bit, 4 K memory) and a computer (YHP 2105-A). The PE spectrum was repeatedly measured, stored in the multichannel analyzer. After improved in signal-to-noise ratio by numerous numbers of repetitions, the data were transferred from the multichannel analyzer to the computer for data analysis. HeI and HeII spectra of pure NO_2 monomer were also measured in order to subtract them from those of the mixture. The procedure of extracting the dimer component is the following. (1) The spectra of both the monomer and the mixture were corrected in intensity for electron collecting efficiency on the basis of the intensity data of N_2, O_2 and CO_2 reported by Gardner and Samson.[19] (2) All the HeI and HeII spectra were smoothed by a moving average method[20] with which five successive points were averaged making each point. The number of points to be averaged was selected as it does not affect spectral resolution seriously. (3) Finally, HeI and HeII spectra of N_2O_4 were obtained from those of NO_2–N_2O_4 mixture by substracting the NO_2 component. Before each substraction, a slight correction for PE kinetic energy was also carried out for the NO_2 spectrum, since the abscissa of the spectrum depends slightly on the sample pressure.[21] (The spectra of NO_2–N_2O_4 mixture and pure NO_2 were observed under different pressure conditions.)

A relatively intense DC-discharge lamp which has recently been designed and constructed in our laboratory[22] was used for measurements of HeII spectra. With this HeII lamp, the PE count rate obtained as a test for the first ionization peak of N_2 was 400 cps under discharge conditions of 500 V, 100 mA and 0.7 Torr He pressure. Under such conditions, count rates of about 70 and 50 cps were obtained at highest peaks for the pure NO_2 and NO_2–N_2O_4 mixed samples.

Results

The HeI PE spectra obtained here for pure NO_2 and a mixture of NO_2 and N_2O_4 are shown in Fig. 2 (a and b, respectively) already corrected for analyzer transmission. The spectrum of pure NO_2 in Fig. 2a was obtained with an ordinary gas inlet system, while the spectrum of NO_2–N_2O_4 mixture in Fig. 2b was obtained with the pinhole nozzle. The spectrum of N_2O_4 in Fig. 2c

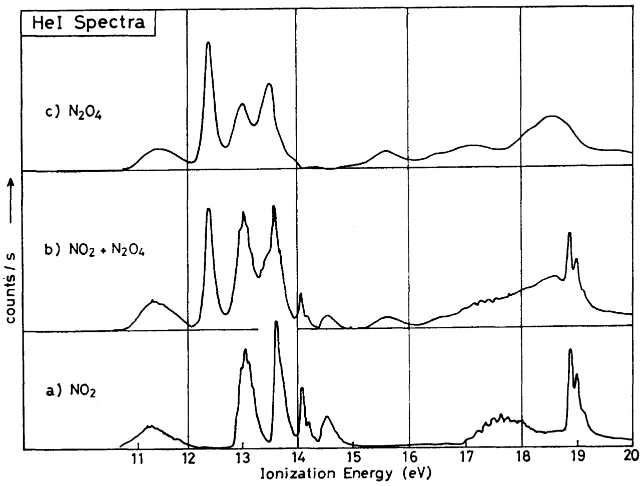

Fig. 2. HeI PE spectra corrected for analyzer transmission. (a) Spectrum of pure NO_2, obtained with a normal inlet system. (b) Spectrum of NO_2–N_2O_4 mixture, obtained with a nozzle inlet system at a total pressure of 600 Torr. (c) Spectrum of N_2O_4, deduced by subtraction of Spectrum a from Spectrum b. Spectra a and b are those already smoothed by a moving averaged method.

TABLE 1. VERTICAL IONIZATION ENERGIES (eV) OBTAINED HERE FOR N_2O_4 AND THOSE REPORTED BY OTHER WORKERS

This work		Ames, Turner[b)]		Frost *et al.*[d)]		Gan *et al.*[e)]	
HeI, HeII	(Tentative assignment)[a)]	HeI		HeI		HeI	
$11.4_5 \pm 0.1$	$(6a_g)$	11.6	$(6a_g)$	11.4 ± 0.1	$(6a_g)$	11.4	$(6a_g)$
12.39 ± 0.03	$(4b_{2g})$	12.4[c)]	$(1a_u)$	12.35 ± 0.03	$(1a_u)$	12.4	$(4b_{2g})$
$13.0_5 \pm 0.1$	$(1a_u)$	12.4[c)]	$(1b_{1g})$	13.0 ± 0.1	$(1b_{1g})$	13.0	$(1a_u)$
$13.5_5 \pm 0.1$	$(1b_{1g})$	13.0[c)]	$(4b_{2g})$	13.5 ± 0.1	$(4b_{2g})$	13.4	$(1b_{1g})$
	$(4b_{3u})$	13.5[c)]	$(4b_{3u})$	15.6 ± 0.1	$(4b_{3u})$	13.5	$(4b_{3u})$
15.6 ± 0.1	$(5b_{1u})$	15.5	$(5b_{1u})$	17.1 ± 0.2	$(5b_{1u})$	15.6	$(5b_{1u})$
16.5 ± 0.3	$(1b_{3g})$	16.9	$(3b_{2g})$	18.0 ± 0.3	$(1b_{3g})$	17.1	$(1b_{3g})$
17.2 ± 0.3	$(3b_{2g})$	18.6[c)]	$(1b_{3g})$	18.6 ± 0.3	$(3b_{2g})$	18.1	$(3b_{2g})$
18.2 ± 0.3	$(3b_{3u})$		$(3b_{3u})$			18.6	$(3b_{3u})$
18.6 ± 0.3	$(1b_{2u})$					19.0	$(1b_{2u})$
(19.5)	$(5a_g)$					19.7	$(5a_g)$
20.7	$(4b_{1u})$						
22.5	$(4a_g)$						
25.9							

a) Based on the Green's function study of von Niessen *et al.* (Ref. 16). Throughout this paper, the z axis is put on the N–N bond and the y axis is perpendicular to the molecular plane. b) Ref. 7. c) Read from the positions of band maxima. d) Ref. 9. e) Ref. 10.

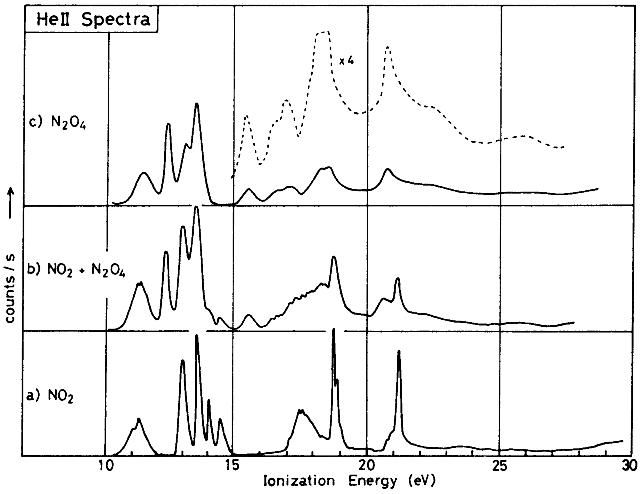

Fig. 3. HeII PE spectra corrected for analyzer transmission. (a) Spectrum of pure NO_2, obtained with a normal inlet system. (b) Spectrum of NO_2–N_2O_4 mixture, obtained with a nozzle inlet system at a total pressure of 450 Torr. (c) Spectrum of N_2O_4, deduced by subtraction of Spectrum a from Spectrum b. Spectra a and b are those already smoothed by a moving averaged method.

was obtained by subtracting a from b. Essentially no NO_2 peaks remain in the subtracted spectrum shown in Fig. 2c.

Similarly, HeII PE spectra obtained here for the monomer and dimer of NO_2 and their mixture are shown in Fig. 3 (a, c, and b, respectively). In the HeII spectrum of N_2O_4 in Fig. 3c, there appear three new maxima at 20.7, 22.5, and 25.9 eV. Results on ionization energies obtained here for N_2O_4 are summarized in Table 1, together with literature data for comparison. Relative intensities of the first five PE bands obtained from the HeI and HeII spectra of N_2O_4 are summarized in Table 2.

Table 2. Experimental relative intensities (band areas) in the transmission-corrected HeI and HeII spectra of N_2O_4

Band maximum (eV)	Relative band area HeI	HeII
11.4_5	0.71	1.13
12.39	1.00	1.00
13.0_5	0.8	2.4
13.5_5	1.2	
15.6	0.36	0.49

Discussion

The mole fraction of N_2O_4 in the reservoir behind the nozzle was 65% in the HeI PE measurements, while it was 58% in the HeII measurements. However, the mole fraction in the ionization chamber is not the same as that in the reservoir. The HeI spectrum of the mixture (Fig. 2b) indicates that the N_2O_4 mole fraction in our HeI measurements is very close to that in the work of Gan *et al.*,[10] and considerably higher than those in the works of Ames and Turner[7] and Frost *et al.*[9] The peak height ratio of the 12.39 eV band to the 13.0_5 eV band is about 1: 1 in our intensity-corrected HeI spectrum, while it is 0.8: 1 in the spectrum of Ames and Turner[7] and 0.6: 1 in the spectrum of Frost *et al.*[9]

The reported HeI spectra of N_2O_4 more or less differ in band shape from one another, and there are some discrepancies in the number of PE bands.[7,9,10] It should be mentioned that the HeI spectrum of N_2O_4 shown in Fig. 2c is most close in spectral shape to that reported by Gan *et al.*[10] For HeII spectra of N_2O_4, no reports have been published so far. From the present HeII spectrum of N_2O_4, two interesting facts may be pointed out, one of which is the fact that three broad maxima appear in the region beyond 20 eV, and the other is that the HeI and HeII spectra below 20 eV considerably differ from each other in spectral shape and relative intensity.

Region below 14 eV. The HeI and HeII spectra below 14 eV, showing four maxima, largely differ in the relative intensity from each other. In the previous HeI studies[7–10] there have been large discrepancies in spectral interpretation in this region. Ames and Turner[7] have assigned the 12.39 eV band as a serious overlap of two ionization bands. Frost *et al.*[9] have considered that each of the maxima corresponds to a single ionization. Gan *et al.*[10] have interpreted that two ionization bands exist very closely at 13.4 and 13.5 eV to form apparently one maximum.

If Koopmans' theorem[23] is assumed, the first five ionic states are given in the order of $(6a_g)^{-1}<(1a_u)^{-1}<(1b_{1g})^{-1}<(4b_{2g})^{-1}<(4b_{3u})^{-1}$ with increasing ionization energy on the basis of *ab initio* MO calculations.[11–13] Such Koopmans' theorem assignment has been used in the previous PE studies except that of Gan *et al.*[10] who have proposed the following order on the basis of relative band intensities as well as orbital interactions between two NO_2 moieties: $(6a_g)^{-1}<(4b_{2g})^{-1}<(1a_u)^{-1}<(1b_{1g})^{-1}<(4b_{3u})^{-1}$. This PE assignment of Gan *et al.*[10] that differs from the Koopmans' theorem assignment has been supported by the recent Green's function study of von Niessen *et al.*[16]

In Fig. 4 the HeII spectrum obtained from the present work is compared with a theoretical ionization spectrum obtained by von Niessen *et al.*[16] If the Green's function calculation of von Niessen *et al.*[16] is correct, the three maxima in the 12—14 eV region should correspond to four rather than three ionized states. Considering the fact that the 13.5 eV band is highest in intensity in the HeII spectrum, there may be a large possibility that this band is due to two ionizations. Such interpretation of the 13.5_5 eV band supports the spectral assignment of Gan *et al.*[10] At the present stage, however, it is difficult to interpret unambiguously the HeI and HeII spectra in the 12—14 eV region in terms of the Green's function results. The relative intensity data given in Table 2 will give a clue to solve this question in future theoretical studies.

Region from 14 to 20 eV. In this region, the HeI and HeII spectra considerably resemble each other in spectral shape except that a bump is observed at 18.2 eV

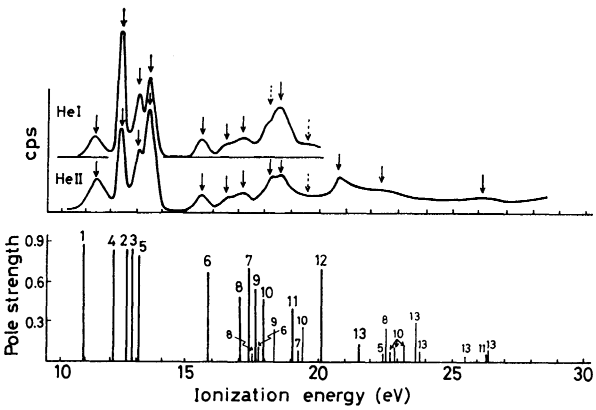

Fig. 4. Comparison of (a) the PE spectra and (b) the theoretical spectrum of von Niessen *et al.* (Ref. 16) in which lines with pole strengths larger than 0.05 are shown and the numbers indicate the following ionized states: $1=(6a_g)^{-1}$, $2=(1a_u)^{-1}$, $3=(1b_{1g})^{-1}$, $4=(4b_{2g})^{-1}$, $5=(4b_{3u})^{-1}$, $6=(5b_{1u})^{-1}$, $7=(3b_{2g})^{-1}$, $8=(1b_{3g})^{-1}$, $9=(2b_{3u})^{-1}$, $10=(1b_{2u})^{-1}$, $11=(5a_g)^{-1}$, $12=(4b_{1u})^{-1}$, $13=(4a_g)^{-1}$.

in the latter. As can be seen from Fig. 3c, two band maxima are clearly observed at 15.6 and 17.2 in the HeII spectrum.

The 15.6 eV band has previously been assigned to the $(5b_{1u})^{-1}$ ionization by Ames and Turner[7] and Gan *et al.*[10] This assignment has also been supported by the Green's function calculation of von Niessen *et al.*[16]

The shoulder appearing at 16.5 eV in the HeI spectrum has been neglected in the previous PE studies in which, for instance, Gan *et al.*[10] have assigned it to a HeI β (537 Å) band of the 18.6 eV peak. However, this 16.5 eV shoulder has been confirmed to appear also in the HeII spectrum, so that there should be at least one ionization band around here. Gan *et al.*[10] have mentioned that there are two ionization bands at 19.0 and 19.7 eV in the HeI spectrum. In the present work, however, we have not been able to identify any shoulder at 19.0 eV from the HeII as well as the HeI spectra. A slight shoulder may be seen at about 19.5 eV in the HeI spectrum, although there is no such shoulder in the HeII spectrum. From the HeI and HeII spectra, it may be considered that there is at least one ionization band in the 19—20 eV region. From their HeI spectra Gan *et al.*[10] have taken a total of six ionization energies, 15.6, 17.1, 18.1, 18.6, 19.0, 19.7 eV in the 14—20 eV region. In the present work, however, we have selected a different set of six ionization energies (15.6, 16.5, 17.2, 18.2, 18.6, 19.5 eV) in this region.

As shown in the theoretical spectrum of von Niessen *et al.*[16] in Fig. 4b, there are several main ionization lines in the 14—20 eV together with many satellite lines due to strong correlation effects. In this region, the main lines (6—11) are located in the order of the Koopmans' theorem assignment except that two lines 7 and 8 are reversed. Taking these theoretical results into account, we may point out a possibility that the six maxima or shoulders in the 14—20 eV correspond to theoretical lines 6, 8, 7, 9, 10, and 11 in this order, besides the satellite lines.

Region above 20 eV. The HeII spectrum obtained here shows three additional maxima at 20.7, 22.5, and 25.9 eV. There are no available spectra for comparison in this region. From the *ab initio* MO calculations,[11—13,16] it has been known that the first thirteen valence MO's are located between −12 and −30 eV in orbital energy and the remaining four valence MO's of oxygen 2s-type are between −40 and −50 eV. If Koopmans' theorem is assumed, thirteen PE bands would be observed below about 30 eV. However, according to the Green's function study of von Niessen *et al.*,[16] thirteen main ionizations occur below about 22 eV and the last two main lines (12 and 13) appear with a separation of about 1.5 eV in the region 20—22 eV, as shown in Fig. 4b. Therefore, it may be possible to correspond the two main theoretical lines (12 and 13) to the two PE maxima observed at 20.7 and 22.5 eV with a separation of 1.8 eV. The remaining broad maximum appearing at 25.9 eV may be due to a contour of many satellite lines.

Finally it may also be pointed out that the minima of the HeII spectrum above 17 eV are considerably lifted upwards from the base line, this suggesting the existence of many satellite ionizations indicated by von Niessen *et al.*[16] According to von Niessen *et al.*,[16] there are many satellite lines with considerably strong intensities even in the higher-energy region up to 50 eV. In the present work we were unable to deduce any HeII spectrum above 29 eV for N_2O_4 owing to a serious overlap of the HeI spectrum. A further experimental study on such higher-energy region is quite interesting in testing a validity of the Green's function calculations.

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