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Characterization of ammonia phosphorus oxide H_3NPO^+ ions and their neutral counterparts by mass spectrometry and computational chemistry

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Abstract

Dissociative electron ionization of O, S-dimethyl acetylphosphoramidothioate yields $[N, H_3, P, O]^+$ ions at *m/z* 64 whose structure was investigated by tandem mass spectrometry in combination with electronic structure calculations. Collisional activation mass spectra of source generated and low energy (MS/MS/MS) *m/z* 64 ions suggest that the majority of the *m/z* 64 ions possess the connectivity NH_3PO^+ (**1**). Neutralization-reionisation experiment on *m/z* 64 ions indicates that $NH_3PO^{\cdot}$ is a viable species in the gas phase. The relative energies of the ions and neutrals of the two isomeric species, $NH_3PO^{+/\cdot}$ (**1**) and $NH_2POH^{+/\cdot}$ (**2**) corresponding to the $[N, H_3, P, O]^{+/\cdot}$ potential energy surface and the fragmentation energies calculated at B3LYP/6-31G** level is used to support the interpretation of experimental results. (Int J Mass Spectrom 208 (2001) 59–65) © 2001 Elsevier Science B.V.

Keywords: Ammonia phosphorus oxide; Collisional activation; Neutralization-reionization; Computational chemistry

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1. Introduction

Over the years a great deal of attention has focused on the chemistry of low coordinated phosphorus compounds. They are believed to play an important role in the chemistry and biochemistry of phosphorus containing compounds and have been extensively studied by experiment and theory [1–5]. Low coordinated organodithiophosphanes are also known to be reactive intermediates and some of them have been isolated as stable ligands in complexes [6,7]. Unfortunately direct evidence for the existence of these species as stable monomeric entities is scarce due to facile intermolecular reactions. The neutralization-reionization mass spectrometry (NRMS) technique [8–20] has been established over the years as a powerful tool for investigating the stabilities and structures of highly reactive and elusive transient species in the isolated gas phase and it has been successfully used to generate and characterize some of the low coordinated phosphorus species. Keck and Terlouw and their co-workers have provided NRMS experimental evidence for the gas-phase existence of (methylthio) thioxophosphane ($CH_3S{-}P{=}S$) [21], phosphenethiol ($H_2P{-}SH$) [22], phosphenedithiol $HP(SH)_2$ [23], and thioxophosphane HPS and its tau-

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Table 1
Calculated total energies and zero-point vibrational energies (ZPVE) (in Hartrees), relative energies (kcal/mol) of ions, neutrals and transition states of $[N, H_3, P, O]^{+/\cdot}$ isomers at B3LYP/6-31G** level

Species	Total energy	ZPVE	Relative energy
H_3NPO ($^11^+$)	−472.871 794	0.042 309	158
H_3NPO (^{21})	−473.111 185	0.040 607	7
H_2NPOH ($^12^+$)	−472.886 895	0.042 036	149
H_2NPOH(^{22})	−473.121 500	0.039 639	0
$H_2NP(O)H$ ($^13^+$)	−472.835 036	0.040 070	180
$H_2NP(O)H$ (^{23})	−473.109 877	0.038 372	7
HNP(H)OH ($^14^+$)	−472.812 864	0.038 447	193
HNP(H)OH (^{24})	−473.088 113	0.036 709	19
TS(^{21}–^{22})	−473.082 823	0.037 005	23
TS($^11^+$–$^12^+$)	−472.811 191	0.037 394	193
TS(^{21}–^{23})	−473.054 590	0.033 840	38
TS($^11^+$–$^13^+$)	−472.755 563	0.035 336	227
TS(^{22}–^{23})	−473.049 082	0.033 486	42
TS($^12^+$–$^13^+$)	−472.751 990	0.035 944	230
TS(^{22}–^{24})	−473.037 402	0.032 479	48
TS($^12^+$–$^14^+$)	−472.736 678	0.034 123	238

tomer HSP [24] molecules. Gu and Turecek [25] and Turecek et al. [26] have demonstrated by NRMS that neutral $CH_3OPH^\cdot$, $CH_3OPOH^\cdot$, $CH_3OPOCH_3^\cdot$, $(CH_3O)_2PO^\cdot$ and $P(OH)_3$, and $P(OH)_4^\cdot$ are stable in the gas phase. We recently reported [27] on the generation and characterization of low coordinated phosphorus species, viz., $CH_3O–P{=}O$ and $CH_3S–P{=}O$ by using a combination of tandem mass spectrometric techniques. In continuation of our interest in low coordinated phosphorus molecules, we report on the generation and characterization of ionic and neutral $H_3N–P–O^{+/\cdot}$ in the gas phase by a combination of tandem mass spectrometric experiments and theoretical calculations at B3LYP/6-31G** level. Recently Gudat [28] has reported on the stability and electrophilicity of low coordinated phosphorus cations at MP2/6-31+G* level, which includes $H_2N\text{-}P^+–OH$ ion.

Table 2
Calculated total energies and ZPVE (in Hartrees) of fragments of $[N, H_3, P, O]^{+/\cdot}$ at B3LYP/6-31G** level

Species	Total energy	ZPVE
$^1NH_2PO$	−472.553 223	0.029 668
$^1PNH_2$	−397.248 996	0.025 741
$^2PNH^\cdot$	−396.646 288	0.012 256
^1POH	−417.091 455	0.012 910
$^2PO^\cdot$	−416.530 081	0.002 802
^1H_2O	−76.419 739	0.021 364
$^2OH^\cdot$	−75.728 685	0.008 409
^1O	−74.988 874	—
$^2H^\cdot$	−0.500 273	—
$^1NH_3$	−56.557 771	0.034 439
$^2PNH_3^\cdot$	−397.818 568	0.037 595
$^2NH_2^\cdot$	−55.879 170	0.018 986
$^2PNH_2^{\cdot+}$	−396.980 654	0.025 592
$^1PNH^+$	−396.377 157	0.014 648
$^2POH^{\cdot+}$	−416.812 806	0.012 472
$^1PO^+$	−416.221 419	0.003 254
$^1PNH_3^+$	−397.531 273	0.037 929
$^1OH^+$	−75.141 417	0.006 996
$^2NH_3^{\cdot+}$	−56.193 929	0.032 755
$^2NH_2PO^{\cdot+}$	−472.192 294	0.029 259

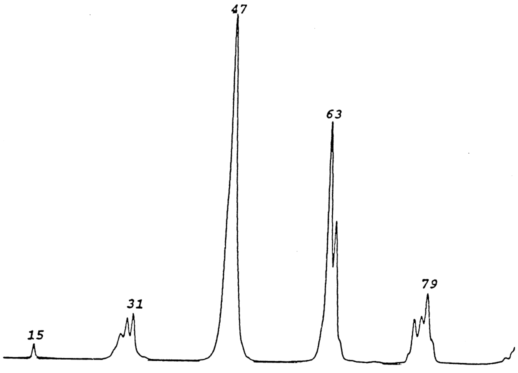


Fig. 1. Collisional activation (CA) spectrum of *m/z* 94 ions.

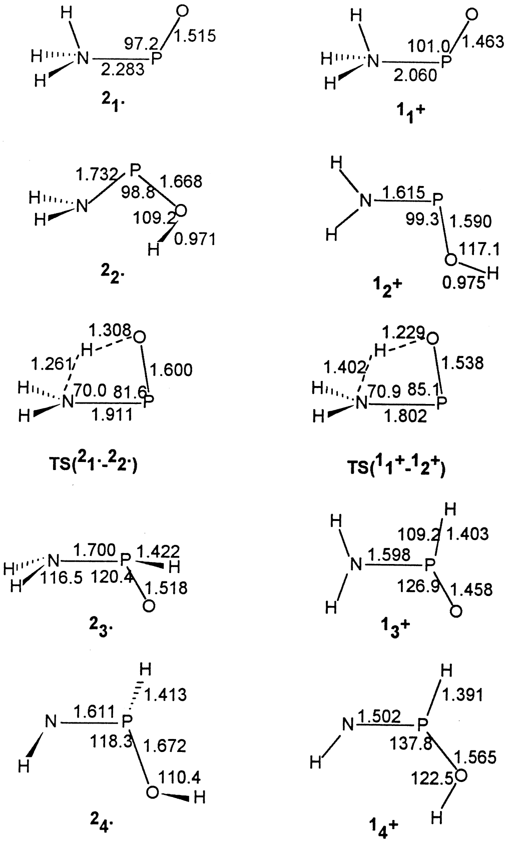


Fig. 2. Selected optimized geometries of ionic and neutral [N, H_3, P, O] isomers from B3LYP/6-31G** calculations.

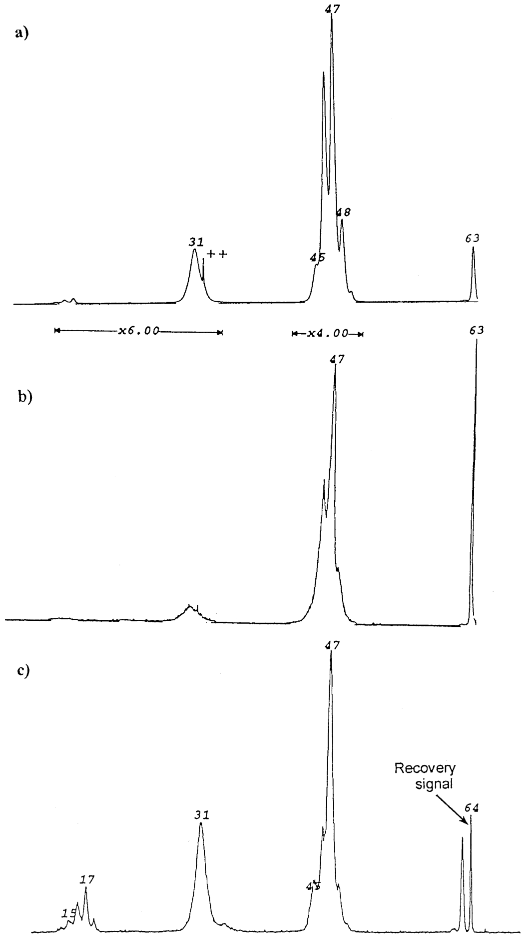


Fig. 3. CA spectrum, (a) source generated *m/z* 64 ions, (b) metastably generated *m/z* 64 ions (MS/MS/MS), and (c) NR mass spectrum of *m/z* 64 ions.

2. Experimental

All the mass spectrometric experiments were carried out using a VG Micromass Autospec M mass spectrometer of E_1BE_2 geometry [27] (E denotes an electric sector and B a magnetic sector). The instrument has two collision chambers (Cls-2 and Cls-3) and an intermediate deflector electrode, all in the third field free region (between E_1B and E_2).

O,S-dimethyl acetylphosphoramidothioate (common name, acephate) was commercially available and used without further purification. The sample was introduced into the ion source by way of the direct insertion probe under the following conditions: source temperature, 250 °C; electron energy, 70 eV; trap current, 250 μA.; acceleration potential, 8 kV. High-resolution data for the ion at *m/z* 64 from O,S-dimethyl acetylphosphoramidothioate was obtained at a resolution of $m/\Delta m = 7000$ (10% valley definition), using the data system. The collisional activation mass spectrum (CA) [29] was recorded by mass selecting the beam of *m/z* 64 ions using E_1B (MS-1), with 8 keV translational energy and allowing collisions with oxygen in the collision cell Cls-3; the resulting ions were analyzed by scanning E_2 (MS-2). The MS/MS/MS experiments were performed by allowing the precursor ions to dissociate in the FFR-1 (preceding E1) and transmitting the fragment ions formed there into the FFR-3, where a CA spectrum was obtained

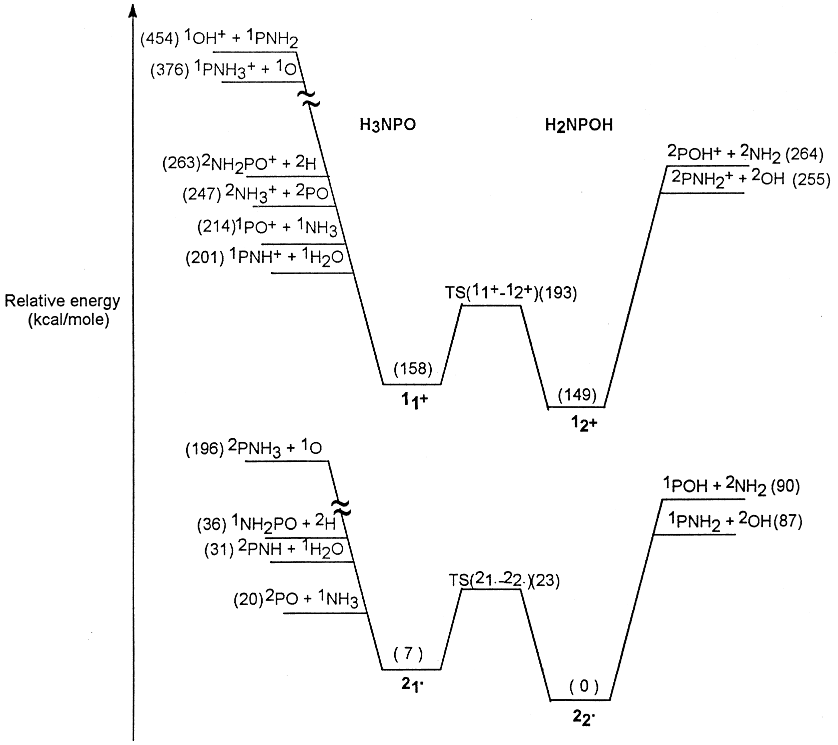


Fig. 4. Potential energy diagram with relative energies in kcal/mol in parentheses for the rearrangement and dissociation reaction of ions $^1\mathbf{1}^+/^1\mathbf{2}^+$ and their neutral counterparts.

using Cls-3. The NR experiments were conducted by mass selecting the beam of ions of *m/z* 64 with E_1B (MS-1) and neutralizing them in Cls-2 with xenon. The remaining ions were deflected away from the beam of neutrals by means of a deflector electrode (+5 kV). The neutral beam was reionized in Cls-3 with O_2 target gas and the resulting ions were recorded by scanning E_2. The spectra shown are accumulations of 25–50 scans.

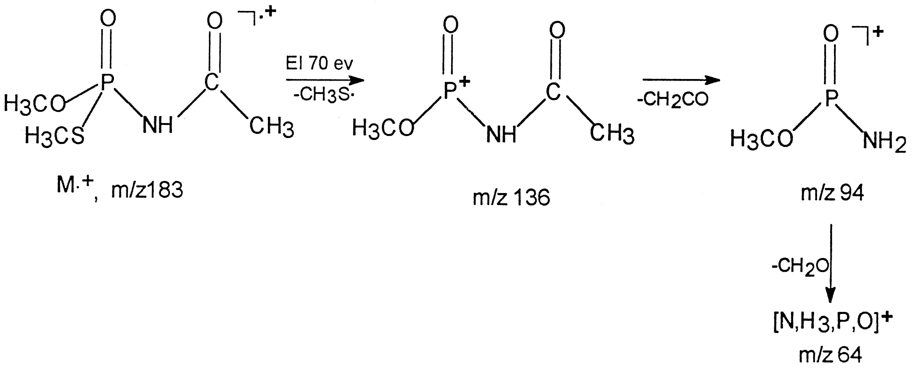
3. Computational methods

The theoretical calculations for the isomers of [N, H_3, P, O]$^{+/\cdot}$ were performed using both GAMESS-US [30,31] and the GAMESS-UK [32] software whereas only the GAMESS-UK results have been reported here. The 6-31G** basis sets were used throughout. Geometry optimizations were performed using the three-parameter hybrid density functional method of Becke (B3LYP) [33–36]. Harmonic vibrational frequencies have been determined at this level in order to characterize stationary points as minima (no imaginary frequency) or transition states (one imaginary frequency). The zero-point vibrational energy (ZPVE) of the isomers and the fragments has also been calculated. The total and relative energies of the isomeric ions, neutrals, and the transition states for $\mathbf{1}^{+/\cdot} - \mathbf{4}^{+/\cdot}$ are shown in Table 1, whereas the total energies along with the ZPVE of the fragment ions and neutrals are shown in Table 2.

4. Results and discussion

The 70 eV electron-ionization spectrum of O,S-dimethyl acetyl phosphoramidothioate affords a weakly abundant peak at *m/z* 64 (7%) corresponding to $[N, H_3, P, O]^+$ ions. The elemental composition of this ion has been confirmed by high-resolution experiment and isobaric impurities were not detected. These ions can be formed by the successive losses of $CH_3S\cdot$ and CH_2CO followed by the elimination of neutral CH_2O from the molecular ion ($M^{\cdot+}$) of O,S-dimethyl acetyl phosphoramidothioate (Scheme 1) as has been evidenced from the metastable ion spectra of the molecular ion and the ion at *m/z* 94. The CA spectrum of the ion *m/z* 94 (Fig. 1) shows *m/z* 47 (PO^+) as the base peak and fairly abundant peaks at *m/z* 79 ($-CH_3^{\cdot}$), *m/z* 78 ($\cdot NH_2$), *m/z* 64 ($-CH_2O$), and *m/z* 63($-CH_3O^{\cdot}$) and the characteristic peaks of OCH_3 group at *m/z* 28–30. All these structure indicative signals support the assigned connectivity for the *m/z* 94 ions (Scheme 1). Four plausible isomeric ion structures $^1\mathbf{1}^+$–$^1\mathbf{4}^+$ can be envisaged for the ions at *m/z* 64. The calculated relative energies at B3LYP/6-31G** level also show that all the four structures are minima on the potential energy surface (Fig. 2, Table 1) and separated by substantial energy barriers, disabling facile interconversion.

The CA mass spectrum [Fig. 3(a)] of *m/z* 64 ions shows abundant peaks at *m/z* 63 ($-H^{\cdot}$), *m/z* 47 (PO^+/$PNH_2^{\cdot+}$), and *m/z* 46 (HNP^+) and low intense ions at *m/z* 48 (PNH_3^+/$POH^{\cdot+}$), *m/z* 45 ($PN^{\cdot+}$), *m/z* 31 (P^+), and *m/z* 17 (OH^+/$NH_3^{\cdot+}$). The absence of a peak at *m/z* 32 corresponding to PH^+ ion rules out a significant contribution of ions $^1\mathbf{3}^+$ and $^1\mathbf{4}^+$ to the *m/z* 64 ion population. The calculated relative energies (Table 1) show that both these ions lie about 31 and 44 kcal/mol, respectively, higher in energy than the lowest energy isomer $^1\mathbf{2}^+$ and the energy barriers for isomerization from $^1\mathbf{2}^+ \rightarrow {}^1\mathbf{3}^+$, $^1\mathbf{4}^+$, and $^1\mathbf{1}^+ \rightarrow {}^1\mathbf{3}^+$ are 81, 89 and 70 kcal/mol, respectively. It seems therefore unlikely that $^1\mathbf{3}^+$ and $^1\mathbf{4}^+$ are co-generated. Thus the observed fragmentation in the CA spectrum clearly points to the connectivities $^1\mathbf{1}^+/^1\mathbf{2}^+$. The most abundant peak in the spectrum at *m/z* 47 can correspond to either PO^+ or $PNH_2^{\cdot+}$. The calculated dissociation energies (Fig. 4) of $^1\mathbf{1}^+/^1\mathbf{2}^+$ show that the fragmentation channel leading to $PO^+ + NH_3$ requires around 55/64 kcal/mol as compared to 96/106 kcal/mol for $PNH_2^{\cdot+} + OH^{\cdot}$. Based on this, it can be suggested that the peak at *m/z* 47 corresponds to PO^+. The relatively high-energy requirement for the previous dissociations from $^1\mathbf{2}^+$ can be ascribed to the fact that $^1\mathbf{2}^+$ has to rearrange before dissociation to give PO^+ whereas it is formed by a simple cleavage from $^1\mathbf{1}^+$. It is also known that some of phosphorous containing ions, viz., CH_3OPH^+, CH_3POH^+, and $CH_3OPOCH_3^+$ also yield *m/z* 47 (PO^+) as an abundant peak in their CA and NR spectra [25–27]. This has been attributed to relatively low ionization energy of PO (IE $=$ 8.39 eV) and high dissociation energy of PO^+ to P^+ and O (D(P–O) $=$ 191 kcal/mol). The next abundant peak in the spectrum is *m/z* 46 which can be assigned to PNH^+ ions based on the calculated lowest dissociation energies of 42 and 51 kcal/mol from $^1\mathbf{1}^+/^1\mathbf{2}^+$, respectively (Fig. 4). The computational results suggest that the formation of *m/z* 48 peak from $^1\mathbf{1}^+/^1\mathbf{2}^+$ is a high energy process which is in keeping



Scheme 1.

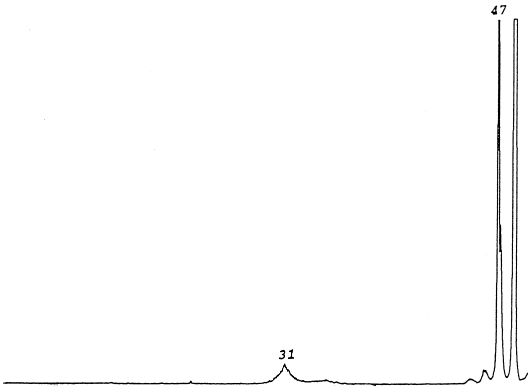


Fig. 5. MS/MS/MS spectrum of *m/z* 48 ions.

with its low abundance. In order to check the connectivity of this ion, the CA spectrum of metastably generated *m/z* 48 ions from *m/z* 64 ions in the FFR-1, was examined. The spectrum (Fig. 5) clearly shows loss of three hydrogens and a peak at *m/z* 31 (P^+), suggesting that some of the *m/z* 48 ions have the connectivity $PNH_3^{\cdot+}$. Another low intense peak at *m/z* 17 can be assigned to $NH_3^{\cdot+}$ rather than OH^+ as former requires 89 kcal/mol and the latter 296 kcal/mol. Based on all these structurally diagnostic ions in the CA spectrum combined together with the computational results, we propose that the most of the *m/z* 64 ions have the connectivity NH_3PO^+. However, a partial isomerization of $^1\mathbf{1}^+ \rightarrow {}^1\mathbf{2}^+$ is not ruled out. The spectrum also features a narrow peak at *m/z* 32 corresponding to the doubly charged $[H_3NPO]^{2+}$ ion. In order to check the purity of $[N, H_3, P, O]^+$ ions, we have examined the CA spectrum (MS^3) [Fig. 3(b)] of the low energy *m/z* 64 ions generated metastably from *m/z* 94 in the FFR-1. The spectrum indeed shows all the structure indicative signals, albeit, of low abundance which can be attributed to the low energy (4.7 kV) with which the ions are sampled. However, the decrease in the abundance of ions at *m/z* 45–48 and *m/z* 31 with respect to *m/z* 63 ($-H^{\cdot}$), indicates that $[N, H_3, P, O]^+$ ions do not correspond to a single structure and part of the NH_3PO^+ ions rearrange to the lowest energy isomer $^1\mathbf{2}^+$.

The NR mass spectrum [Fig. 3(c)] shows a fairly abundant recovery signal at *m/z* 64 (50% of the base peak at *m/z* 47) which suggest that a majority of the $[N, H_3, P, O]^+$ ions subjected to NR process have remained intact. It can be seen that the spectrum displays increased abundances of the structure indicative peaks at *m/z* 47 and *m/z* 17 which is found to be in perfect agreement with the calculated lowest energy fragmentation channel leading to $PO + NH_3$ (Fig. 4). It appears therefore, that the structural connectivity of the NH_3PO^+ ions is retained on neutralization implying that neutral $NH_3PO^{\cdot}$is a stable species in the rarefied gas phase. However, again the possibility of co-generation of $NH_2POH^{\cdot}$ is not ruled out.

In view of the vertical nature of the electron transfer processes in NR experiment, we have considered the vertical recombination energy (RE) of the cation and the vertical ionization energy (IE) of the neutral. The B3LYP/6-31G** calculated vertical transition energies and the adiabatic energy are shown in the (Table 3). The energy difference between the adiabatic transition and the vertical transition is not large. Thus, the vertical ionization of the neutral (IE = 6.75) is 0.24 eV higher than the adiabatic process and likewise vertical neutralization of the cations ground state (RE = 6.31) is only 0.20 eV lower than the adiabatic data. This shows that the vertical electron transfer between the neutral $NH_3PO^{\cdot}$ and the cation NH_3PO^+ is favorable in both directions. These effects are consistent with the very small geometry difference between the neutral and cation, which explains the substantial survivor signal in the NR experiments [Fig. 3(c)].

Table 3
Calculated adiabatic energies IE_a and vertical one-electron transition energies (in eV) of ions and neutrals of $[N, H_3, P, O]^{+/\cdot}$ isomers at B3LYP/6-31G** level: RE and IE_v represents recombination (neutralization) and ionization energies, respectively

Transitions	IE_a	RE	IE
$^1\mathbf{1}^+ \rightarrow {}^2\mathbf{1}^{\cdot}$	6.51	6.31	. . .
$^2\mathbf{1}^{\cdot} \rightarrow {}^1\mathbf{1}^+$	. . .	. . .	6.75
$^1\mathbf{2}^+ \rightarrow {}^2\mathbf{2}^{\cdot}$	6.38	5.95	. . .
$^2\mathbf{2}^{\cdot} \rightarrow {}^1\mathbf{2}^+$	. . .		7.58

5. Conclusions

The combined results of tandem mass spectrometric experiments and theoretical calculations suggest that the *m/z* 64 ions from O,S-dimethyl acetyl phosphoramidothioate predominantly have the connectivity NH_3PO^+. The partial isomerization of these ions to the lowest energy isomer NH_2POH^+ is also not ruled out. Neutralization-reionization experiments on these ions revealed that the neutral $NH_3PO^{\cdot}$ is a stable species in the gas phase.

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