# SUPERSONIC MOLECULAR BEAM, RESONANCE ENHANCED MULTIPHOTON IONIZATION, TIME-OF-FLIGHT MASS SPECTROSCOPY 3. REACTION DYNAMICS FROM HIGHER EXCITED STATES OF CWA SIMULANTS

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## Abstract

The dynamics of state-selective and/or energy-selective, collisionless dissociation and rearrangement reactions from higher excited states were investigated for various chemical warfare agent (CWA) simulants using supersonic molecular beam, multiphoton ionization (MPI), mass spectroscopy. The properties of the reaction including product identification and internal energy content were determined using various excitation schemes based on one and two-color MPI and electron impact (EI) ionization.

## 1. Introduction

Ultratrace detection of molecules by laser excitation requires detailed understanding of the spectroscopic and photophysical properties of the molecule of interest in order to determine the best excitation schemes for achieving optimum detection limits. Unfortunately, high quality spectral and photophysical data are woefully insufficient for the more sophisticated laser based detection techniques involving toxic compounds and CWA simulants. In the previous paper, we reported on the high resolution UV and VUV spectroscopy of a number of CWA simulants. In this paper, we present our studies of the photophysical and photochemical properties (i.e. photodissociation, ion fragmentation) of CWA simulants, not only to establish the most appropriate excitation/detection schemes, but to understand the manner in which these compounds are photolytically decomposed in the atmosphere. For instance, our studies have revealed that the excited electronic states of the CWA simulants are very dissociative. Further studies of photophysics could be relevant to the development of decontamination schemes and to understanding the natural processes that degrade the CWAs in the atmosphere.

## 2. Electron Impact Ionization Studies

### *2.1 Rovibrationally Cold Ion Mass Spectroscopy*

The use of electron impact (EI) ionization in a time-of-flight mass spectrometer has promising applications when used in conjunction with a supersonic molecular beam apparatus[1]. EI ionization, to a large extent, approximates single-photon photoionization selection rules. Hence, this method of ionization in a supersonic molecular beam has the capability for forming rotationally and vibrationally cold ions. Rotational excitation is minimal and vibrational excitation, aside from cascading from higher electronic states of the ion, is limited to Franck-Condon excitation. The drawback to EI versus single photon excitation is that EI nonselectively excites higher excited electronic states of ions. In spite of this effect, EI ionization in a supersonic beam leads to substantially less fragmentation than in a room temperature (RT) sample. This is demonstrated in Figs. 1 and 2 for DIMP and DMMP, respectively. The RT spectra were reconstructed from published data[2] and clearly show the absence of parent ion. Parent ion is present

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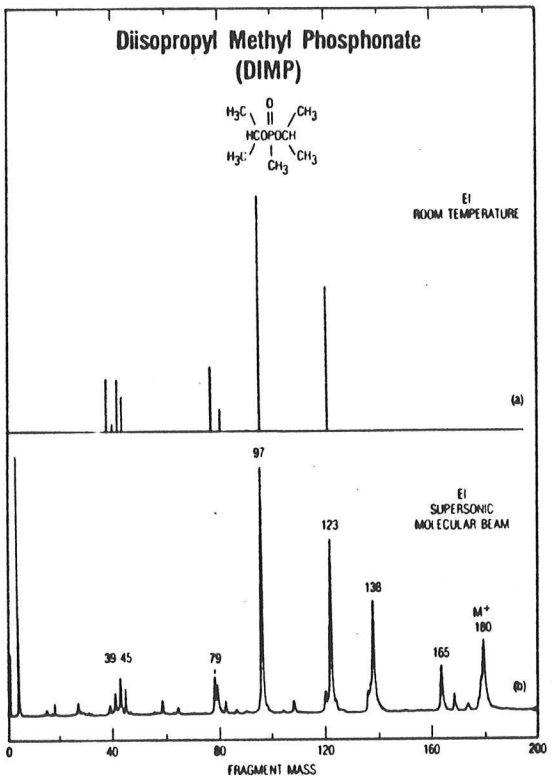


**FIG. 1.** EI ionization mass spectra of diisopropyl methyl phosphonate (DIMP). (a) Reconstructed spectrum from tabulated mass and intensity values for a room temperature sample of DIMP using 70 eV $e^-$ source (Ref. 1); (b) EI TOFMS recorded in a collimated supersonic molecular beam (0.1% DIMP in 35 psig He).

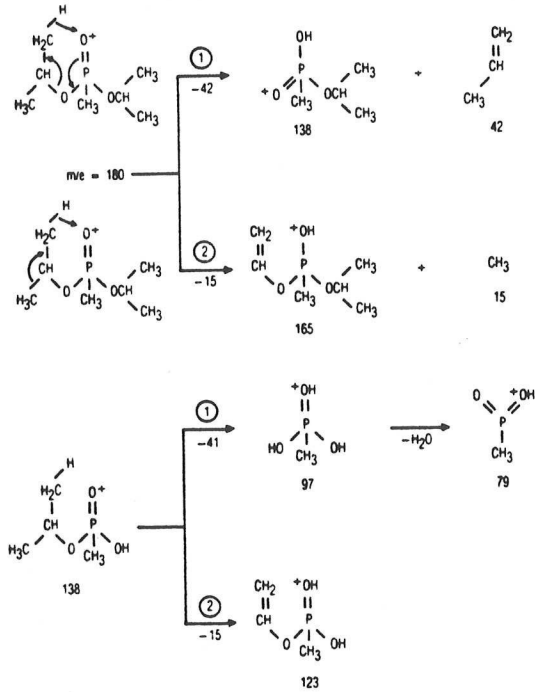


**FIG. 3.** Proposed ion fragmentation pathways for DIMP. Location of positive charge is not rigorous.

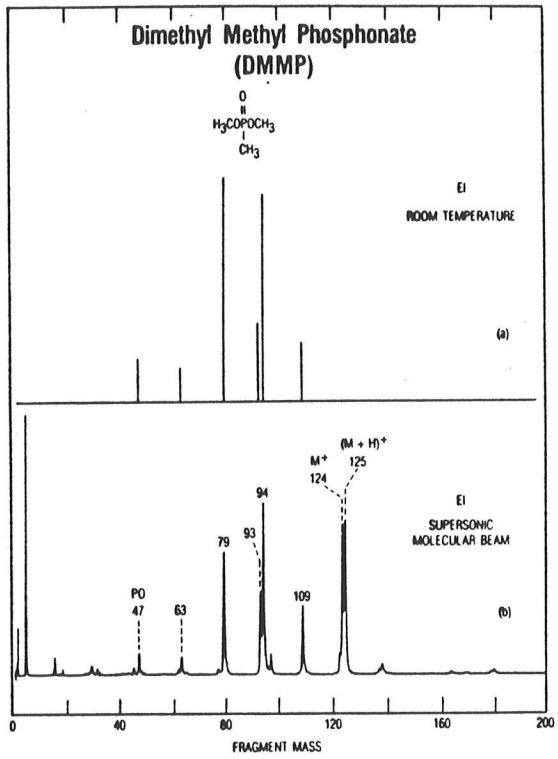


**FIG. 2.** Same as Fig. 39 except for dimethyl methyl phosphonate (DMMP).

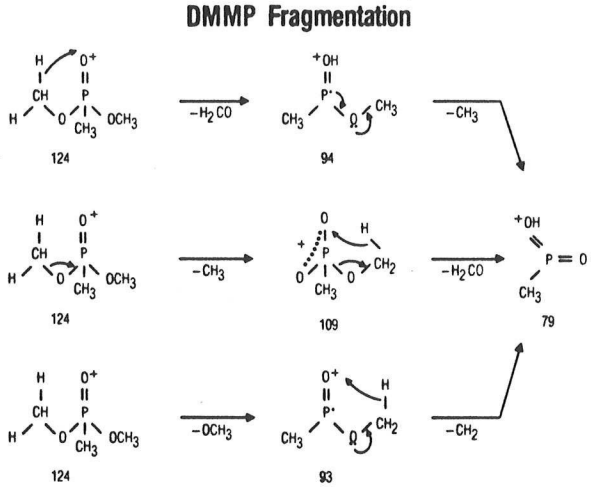


**FIG. 4.** Proposed ion fragmentation mechanism for DMMP. Location of positive charge is not rigorous.

in the supersonically cooled sample, otherwise the fragmentation patterns involving lighter masses in both cases are similar.

### *2.2. Ion Fragmentation Pathways*

DIMP and especially DMMP exhibit extensive fragmentation by either MPI or EI ionization (c.f. Figs. 1,2,6,8). Some of the fragmentation observed in MPI can be attributed to excited state molecules that rapidly dissociate to give neutral fragments that then undergo MPI. The competition between neutral dissociation versus ionization as well as the identification of neutral versus ion fragmentation pathways can be examined by comparison of MPI and EI ionization mass spectra in a supersonic molecular beam. The neutral dissociation channels of the CWA simulant molecules are the subject of Sec. 3. We present proposed ion fragmentation pathways for DIMP and DMMP in Figs. 3 and 4, respectively. From these mechanisms along with the RT and supersonic molecular beam mass spectra, we can draw the following conclusions;

(1) The absence of $M^+$ for RT excitation indicates a low barrier to fragmentation that is exceeded by the thermal vibrational energy content (approx. 16000 $cm^{-1}$ for DIMP and 8500 $cm^{-1}$ for DMMP);

(2) The presence of $M^+$ for supersonic excitation is indicative of vibrationally cold ion formation;

(3) The similarity of the fragmentation patterns in both cases probably arises from ion electronic state excitation and radiationless decay to vibrationally hot ions.

## 3. Multiphoton Dissociation and Ionization

### *3.1. DIMP*

A study of the photodissociative properties from higher excited electronic states was undertaken using the molecules DIMP and DMMP. Although, structurally similar, their UV and VUV absorption spectra are quite different (c.f. paper II). DIMP exhibits strong and structured absorption for several electronic states in the far and vacuum UV, whereas DMMP shows only weak and diffuse absorption up to energies just below the ionization potential. We decided to investigate whether this was due to photophysics and photochemistry.

Four different excitation schemes were carried out for DIMP in order to access different excited electronic states and to deposit various amounts of energy into the parent and fragment ions (see en-

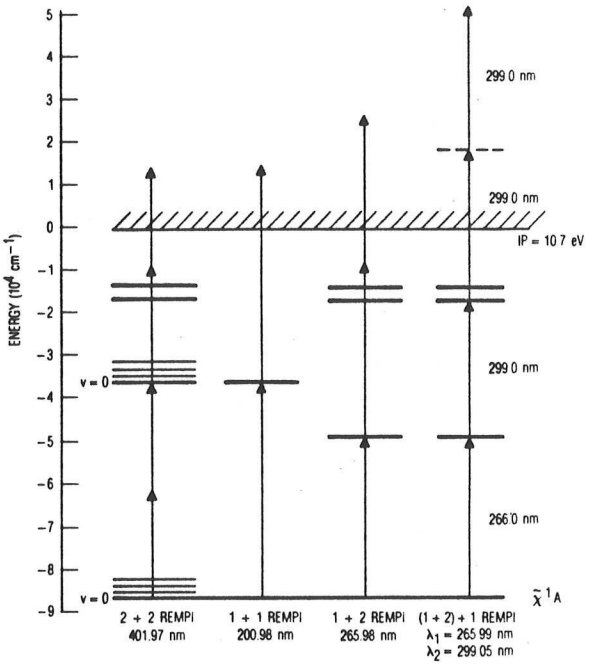


**FIG. 5.** REMPI excitation schemes used in the study of DIMP.

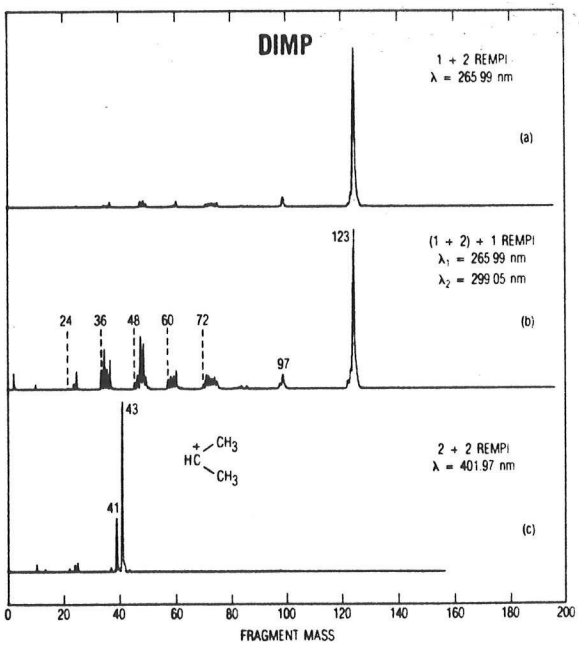


**FIG. 6.** REMPI/TOF mass spectra of DIMP in a supersonic beam, (a) 1+2 REMPI using 265.99 nm (0.4 mJ); (b) 1+2 REMPI using resonant 265.99 nm (0.4 mJ, 1st antistokes Raman) and 299.05 nm (2.5 mJ, UV fundamental) to ionize. Further absorption of 299.05 nm by ions occurs leading to fragmentation; (c) 2+2 REMPI at 401.97 nm (2 mJ/ pulse).

ergy level diagram, Fig. 5). The TOF mass spectra are given in Fig. 6. In no instance was parent ion observed, even though ions were formed with as little as 13000 $cm^{-1}$ of energy. This is consistent with the EI results at RT (Fig. 1) which show that $M^+$ is unstable at thermalized vibrational energies. The fragment ions at m/e = 97 and 123 which are prevalent in the EI mass spectra (Fig. 1) are also formed when exciting through the weak and structureless neutral electronic state at 266.0 nm (Fig. 6a). Using a high power second color for ionization and ion absorption leads to further fragmentation (Fig. 6b), but again the stable m/e = 97 and 123 ion fragment signals remain strong.

Ionization through the resonant higher excited electronic state at 200.98 nm gives entirely different behavior (Fig. 6c). As expected, no $M^+$ ion is observed in view of the excitation to 13000 $cm^{-1}$ above the IP. However, there is also no evidence for the stable m/e = 97 and 123 ion fragments that are formed in high yield by EI ionization and REMPI via the 266.0 nm neutral state. Instead, for 2+2 REMPI via the $0_0^0$ transition at 200.98 nm, a prominent m/e = 43 ion fragment, attributable to the isopropyl group occurs. Furthermore, attempts to observe 1+1 REMPI using low laser power (.03 mJ) gave negligible ion signal.

These results are consistent with the following scenario:

(1) The lower excited electronic state reached by 266.0 nm excitation is nondissociative and is further ionized to form vibationally excited $M^+$ parent ion. $M^+$ then undergoes rapid fragmentation via a Norrish type II mechanism (see Fig. 3) to form stable m/e = 97 and 123 fragment ions.

(2) The higher excited state reached by 1 or 2 photon resonance is dissociative, even from the vibrationless level (predissociation). The rate of predissociation is much faster than the rate of photoionization such that no $M^+$ is produced from which to form the m/e = 97 and 123 fragment ions.

### *3.2. DMMP*

DMMP photochemistry is apparently rather different from that of DIMP. The VUV absorption spectrum of DMMP (paper II) indicates that the opportunities for resonance enhanced ionization are rather limited. However, there are reports in the literature for efficient production of PO radicals by ArF and KrF excimer laser excitation[3], by $CO_2$ laser excitation [4] and by microwave discharge[5,6]. In these published studies, the sample pressures were

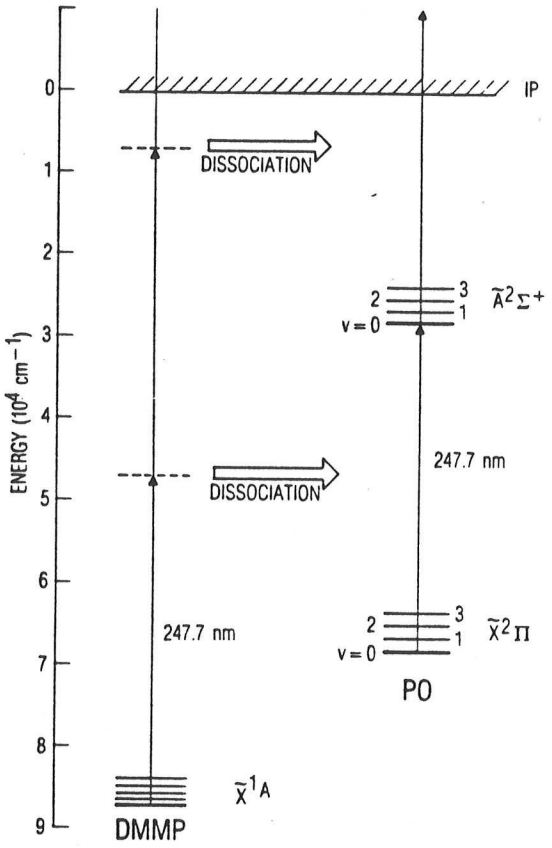


**FIG. 7.** REMPI pump-probe excitation scheme used to study the neutral photodissociation of DMMP. The detection of DMMP is accomplished via the ionization of the dissociative product PO.

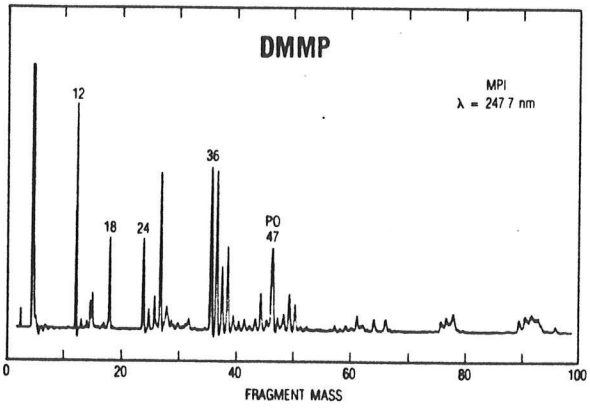


**FIG. 8.** MPI/TOF mass spectrum of DMMP in a supersonic molecular beam. Ionization is either by non-resonant three photon absorption or 2+1 involving a higher excited electronic state. 244.7 nm wavelength was chosen to probe for dissociative neutral PO fragments by 1+1 REMPI.

on the order of 1 Torr and therefore far from collisionless. The IR $CO_2$ multiphoton dissociation (MPD) results, however, were under collisionless conditions. We decided to explore the possibility for efficient production of PO by energy selective excitation in a cold supersonic molecular beam under collisionless conditions. PO detection was achieved by RE2PI at 244.7 nm; this wavelength being scanned to assure resonance. Since DMMP has been reported to decompose by KrF excimer laser excitation (248 nm), we used the probe light as a pump source as well. We outline the excitation scheme in Fig. 7. One-photon dissociation does not appear likely in view of the VUV absorption spectrum, however, a strong absorption does occur at twice the photon excitation energy (paper II).

The REMPI TOF mass spectrum, shown in Fig. 8, indicates a small yield of PO. Most of the ion signal though can be attributed to ion fragmentation following ionization of DMMP. These results along with previous results suggest that the decomposition of DMMP to form PO is a thermal reaction and not a photolytic reaction. IR MPD under collisionless conditions[4] results in vibrationally hot molecules that dissociate. The decomposition under excimer excitation[3] can be explained by excited electronic state excitation, followed by rapid collisionally induced relaxation to vibrationally hot ground electronic levels which in turn dissociate. The microwave experiments, which result in nonselective electronic state excitation are likewise explained by collisional decomposition.

### *3.3. Sulfides*

Dimethyl sulfide (DMS) is known to have a number of Rydberg-like electronic states of moderate energy[7–9] (c.f. paper II). The VUV absorption spectrum at RT shows a strong and structured state with an origin at 195.3 nm attributed to excitation to the first member of the p-series (3p), a weak and structured state at 227.9 nm assigned to the first member of the s-series (3s) and a strong but broad valence (i.e. non-Rydberg) state at about 203.7 nm. We recorded the 2+1 REMPI excitation spectrum of the 3p state and observed rather broad lines. (A brief discussion of the spectral linewidths was given in paper II). This property is not unusual for transitions to higher excited vibronic levels due to greater density of states as well as interactions with many near lying electronic states. However, the possibility for predissociation also seemed possible. It has been reported, for instance, that DMS undergoes dissociation to form $CH_3S$ radicals following 193 nm

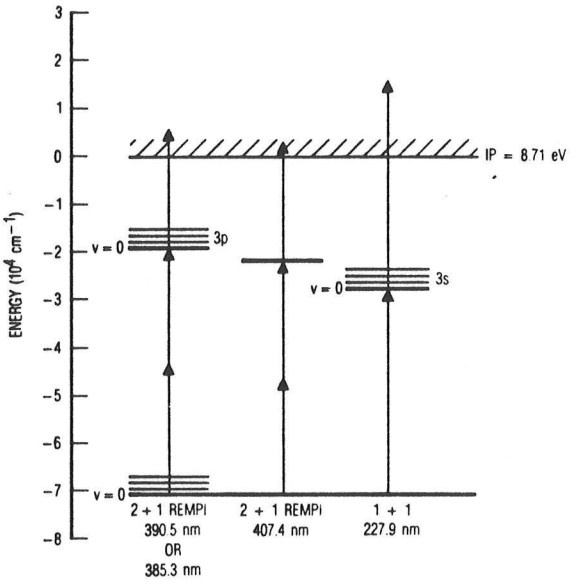


**FIG. 9.** REMPI excitation schemes employed in the study of dimethyl sulfide.

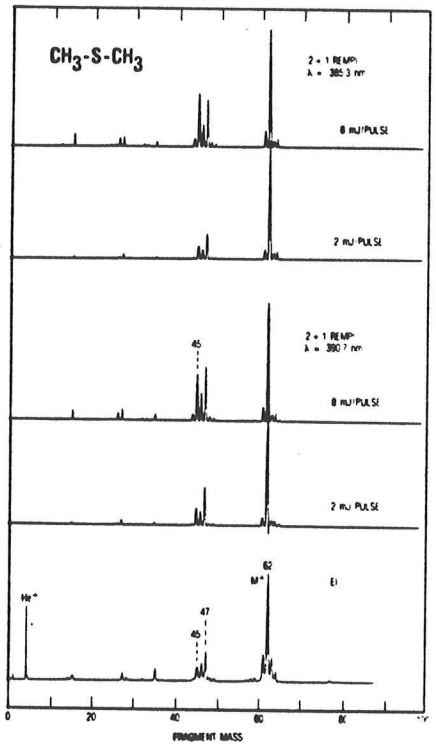


**FIG. 10.** 2+1 REMPI TOF mass spectra recorded via the vibrationless (390.7 nm) and the 704 cm$^{-1}$ vibrational level (385.3 nm) of the 3p Rydberg state. Electron impact (EI) ionization TOF mass spectrum is shown to give very similar results.

excitation[10]. However, this work was performed on a room temperature vapor in a collisional regime.

We investigated the possibility of photoreactions from Rydberg versus valence states using the excitation schemes outlined in Fig. 9. TOF mass spectra following REMPI excitation via the structured 3p state are presented in Fig. 10. The results by REMPI are essentially the same as those obtained by EI (Fig. 10) whether the vibrationless level (390.6 nm) or the C–S stretch vibration (704 $cm^{-1}$, 385.3 nm) was excited. Parent ion, $M^+$, predominates, indicating a stable neutral excited state molecule, at least over the time span of the 5 ns laser pulse. A similar result was obtained when exciting into the weak 3s state at 227.9 nm using 1+1 REMPI (Fig. 11a). The mass spectrum consists almost entirely of $M^+$, indicating not only a stable electronically excited neutral molecule, but a stable ion with about 16000 $cm^{-1}$ of vibrational energy (Fig. 9).

Excitation of the structureless valence state at 203.7 nm by 2+1 REMPI gives a somewhat different result. The mass spectrum in Fig. 11b reveals a strong $[M-1]^+$ fragment at m/e = 61 that is not as prominent in the REMPI excitation via the Rydberg states. The additional fragmentation for m/e = 45-47 is similar to that observed by EI and by 3p REMPI (Fig. 10) and is therefore probably attributable to parent ion absorption and fragmentation. Unfortunately, we cannot at this time rule out this explanation for the m/e = 61 fragment.

Chloro-dimethyl sulfide is of interest due to the low dissociation energies that often characterize carbon-halogen bonds. The VUV absorption spectrum shows a very long Franck-Condon progression in a 405 $cm^{-1}$ vibration which is consistent with a C–Cl bend (assignment discussed in paper II). The apparently large geometry change that the molecule undergoes upon excitation may be interpreted as being the onset of dissociation. To explore this possibility, we recorded TOF mass spectra by EI and 2+1 REMPI via the v=4 overtone at 199.6 nm (Fig. 12). Excitation into this level was necessary to exceed the 3-photon ionization threshold. EI excitation led to efficient ionization with significant $M^+$ formation. The REMPI excitation, on the other hand, gave extremely weak ionization and the absence of $M^+$. Instead, the prominent ion mass was the m/e = 61 fragment resulting from loss of Cl. These results are suggestive of a rapid C–Cl dissociation in the neutral excited state followed by nonresonant MPI of the neutral m/e = 61 fragment.

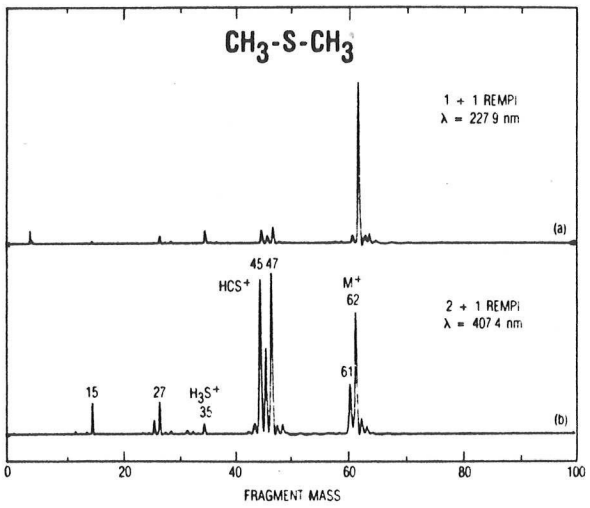


**FIG. 11.** REMPI TOF mass spectra of dimethyl sulfide in a supersonic molecular beam; (a) 1+1 REMPI via the 3s Rydberg state at 227.9 nm; (b) 2+1 REMPI via the featureless valence state at 203.7 nm (c.f. Fig. 10).

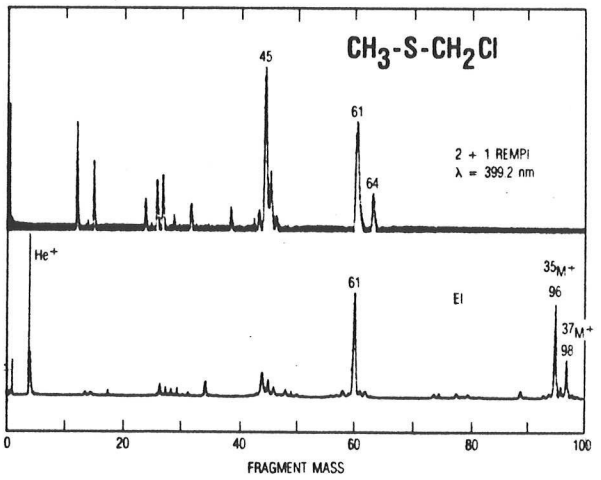


**FIG. 12.** TOF mass spectra of chlorodimethyl sulfide in a supersonic molecular beam; (a) 2+1 REMPI (399.2 nm) showing very weak ionization and lack of parent ion signal; (b) EI TOF mass spectrum showing strong ionization and presence of parent ion.

## 4. Conclusions

The dynamics of state-selective and/or energy-selective, collisionless dissociation and rearrangement reactions from higher excited states were investigated for various CWA simulants using the supersonic MB/REMPI/TOFMS technique. The photodissociation of DIMP via the strong 200.98 nm electronic state was studied by 1+1 and 2+2 REMPI. The excited state is very dissociative and occurs from the vibrationless level (i.e. $0_0^0$ transition) suggesting predissociation. Studies of DMMP showed no vibrational structure at similar energies. Detection of the neutral PO fragment from DMMP was attempted using a pump-probe scheme to excite and ionize PO. Energy and mass resolved MPI studies for various electronic states of DMS gave no evidence for dissociation. On the other hand, photodissociation was found to be very rapid for CDMS.

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