SUPERSONIC MOLECULAR BEAM, RESONANCE ENHANCED MULTIPHOTON IONIZATION, TIME-OF-FLIGHT MASS SPECTROSCOPY 2. UV AND VUV SPECTROSCOPY OF CWA SIMULANTS

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Abstract

The preparation of molecules in single vibronic levels by laser excitation in supersonic molecular beams has enabled us to record high resolution spectra of higher excited electronic states showing fully resolved vibrational structure for diisopropyl methylphosphonate (DIMP) and dimethyl sulfide (DMS). VUV absorption spectra have also been recorded for several chemical warfare agent simulant (CWA) molecules at ambient temperature revealing several new electronic states extending up to the ionization threshold.

1. Introduction

Spectroscopic information on CWA and simulant molecules, aside from IR and Raman work[1,2], is very sparse. A UV spectrum of DIMP in solution has been reported showing a weak absorption at about 260 nm and the onset of a strong absorption beginning at about 220 nm[3]. We have recorded vapor phase vibrationally resolved electronic state spectra for six CWA simulant molecules using two basic techniques: UV and VUV absorption spectra in low pressure ambient vapor phase samples and tunable UV and far UV laser excitation/ionization spectra in a supersonic molecular beam.

2. VUV Spectroscopy

2.1. Apparatus

The molecular beam apparatus is described in the previous paper. The VUV spectrometer is independent of the molecular beam system. Briefly, the radiation from a broadband D_2 lamp source is dispersed in a 0.2 m vacuum monochromator equipped with a 1200 lines/mm holographic concave grating. The light source, monochromator and 15 cm length sample cell are coupled by vacuum sealed MgF_2 windows with transmission to wavelengths as short as 110 nm. The wavelength of the transmitted light

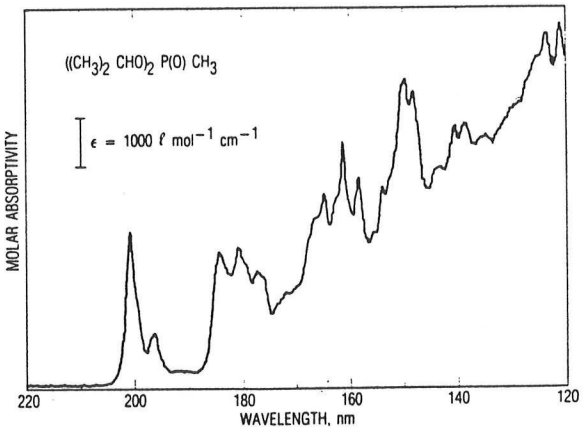

FIG. 1. VUV absorption spectra of DIMP in a room temperature vapor. Spectra were recorded by dispersing the output of a D_2 lamp in a vacuum monochromator.

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is up-converted using sodium salicylate scintillator coated on the outside of the cell exit window. The light is detected by a photomultiplier, amplified and digitized. Monochromator scans and data acquisition are controlled using an IBM AT computer. All spectra are normalized to the spectral output of the D_2 source lamp.

2.2. Organophosphonates

VUV spectra were recorded for DIMP (Figs. 1-2), DMMP (Fig. 3), chloro-dimethyl sulfide (CDMS, Fig. 5) and chloro-diethyl sulfide (i.e. CDES, Fig. 6). VUV spectra have been previously reported for DMS and diethyl sulfide (DES)[4-6]. We reproduce the published spectrum for DMS in Fig. 4 since it is relevant to the high resolution molecular beam spectra discussed below.

The VUV spectrum of DIMP in Fig. 1 shows many previously unknown strong absorptions in the 120 nm to 200 nm region. The weak absorption at about 260 nm reported previously in a solution phase UV spectrum[3] is perceptible in the longer wavelength scan in Fig. 2a. The first strong transition at 200 nm was recorded under high resolution showing underlying vibrational structure (Fig. 2b). This electronic state is the focus of the molecular beam work reported below.

The VUV spectrum of DMMP, shown in Fig. 3, shows remarkably different features than those observed for DIMP. Unlike, DIMP, there are no strong absorptions in DMMP except at very high energies near to the reported ionization potential (10.0 eV, ca. 125 nm)[7]. There is no apparent explanation for the vastly different spectral properties for these otherwise similar molecules. Since, the alkyl groups in DIMP and DMMP are not expected to exert a strong electronic interaction on the PO group where most of the oscillator strength resides, it is suggestive that the electronic states are subject to strong geometry effects. We are currently examining this possibility via molecular orbital calculations[8].

Unlike the organophosphonates, DIMP and DMMP, the VUV spectra for a series of sulfides exhibit a large degree of similarity. This is evident in a study by Clark and Simpson[4] for DMS, DES, isopropyl sulfide and t-butyl sulfide. Scott, et al[5], also recorded the VUV spectrum of DMS, which we display in Fig. 4. We remark on a few features that are the focus of the molecular beam work discussed below. Scott, et al assigned as first member Rydberg states the weak, but structured absorption at 228 nm (3s state), the strong and structured absorption at 195 nm (3p state), and the moderately strong,

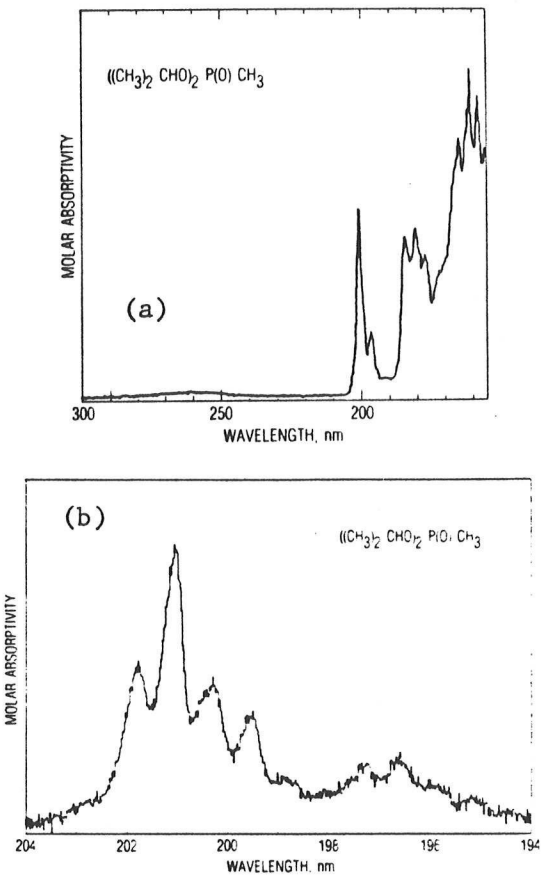

FIG. 2. UV and VUV absorption spectra of DIMP in a room temperature vapor. (a) scan showing a weak and broad absorption at 260 nm; (b) high resolution scan of 200 nm band.

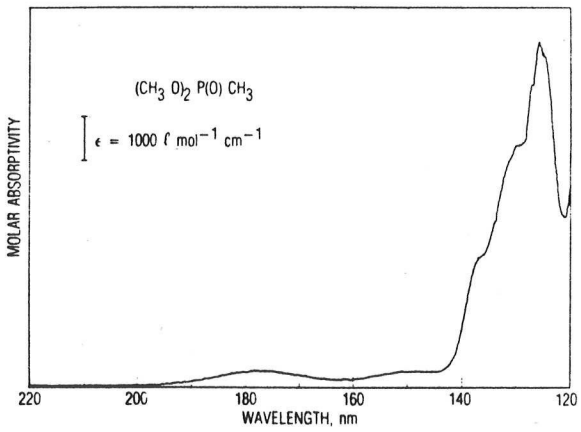

FIG. 3. VUV absorption spectrum of DMMP in a room temperature vapor. Note lack of near to far UV absorptions, in contrast to DIMP.

but featureless absorption at 180 nm (3d state). A moderately strong, but broad absorption at about 203 nm is assigned as a valence state[5].

We have studied the chloro- substituted alkyl sulfide VUV absorptions. The CDMS spectrum is presented in Fig. 5 and shows similarities to the DMS spectrum (Fig. 4) in that the 3p and 3d Rydberg states appear to correlate well in the two molecules in terms of intensity, wavelength and structure. It is not clear, however, whether the broad absorption at about 235 nm in CDMS corresponds to the 3s Rydberg state or the broad valence state in DMS, although the former assignment is favored based on wavelength. Interestingly, the 3p state exhibits a strong Franck-Condon progression with a vibrational interval of 405 cm^{-1}. We assign this vibration to a S−C−Cl deformation or bend mode in analogy with the 590 cm^{-1} mode observed in CH_2ClBr [9]. The long Franck-Condon progression indicates a large geometry change along this normal coordinate upon electronic excitation. Evidence below indicates that this geometry change is induced by a rapid C−Cl bond dissociation concommitant with a restructuring of the carbon bond order (c.f. following paper).

The VUV spectrum of CDES in Fig. 6 resembles only slightly the lower energy characteristics of CDMS. One finds weaker and broader absorptions at wavelengths longer than 160 nm and the usual onset of strong absorptions at 160 nm. The lower energy spectrum of DES reported by Clark and Simpson[4] is likewise broad, however, the absorption intensities are much greater.

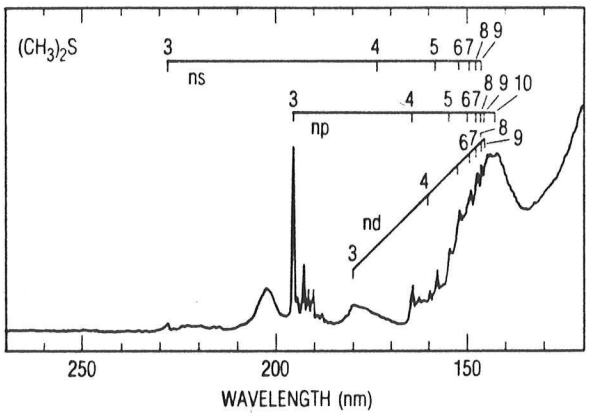

FIG. 4. VUV absorption spectrum of dimethyl sulfide in a room temperature vapor (Ref. 5). Rydberg assignments and their quantum defect values are indicated.

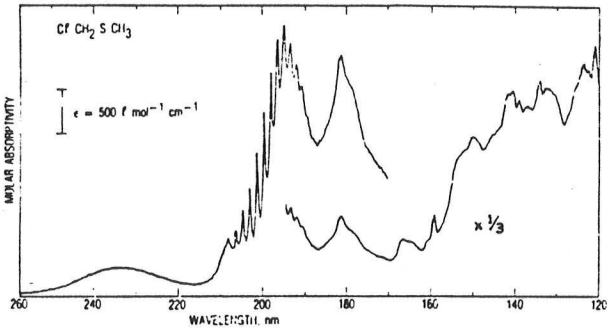

FIG. 5. VUV absorption spectrum of chloro-dimethyl sulfide (CDMS) in a room temperature vapor showing a strong absorption and long Franck-Condon progression of a 405 cm^{-1} mode.

3. Molecular Beam Spectroscopy

3.1. DIMP Excitation Spectra

The excitation wavelengths that produce detectable ion mass signals by MPI were determined by recording ionization excitation spectra. In this mode, a single ion mass signal is detected as a function of the scanning laser wavelength. The laser wavelength regions of interest for DIMP were determined from the VUV spectra recorded in our laboratory (Fig. 1-2). To determine the prominent ion mass signal in which to record wavelength resolved spectra, a complete TOF mass spectrum was recorded at a single excitation wavelength. Two spectral regions of DIMP were of interest; the weak featureless absorption at 260 nm and the strong structured absorption at 200 nm (Figs. 1-2). The REMPI excitation scheme used for the 260 nm band

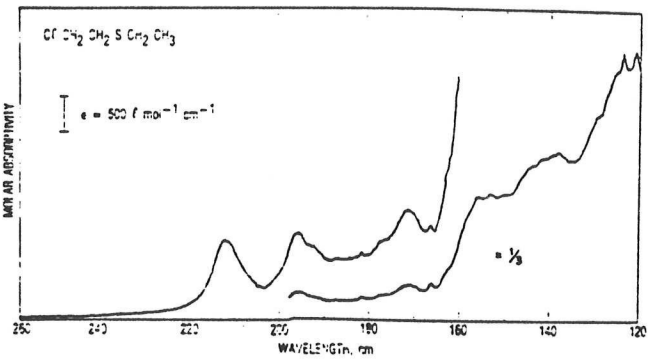

FIG. 6. VUV absorption spectrum of chloro-diethyl sulfide (CDES) in a room temperature vapor.

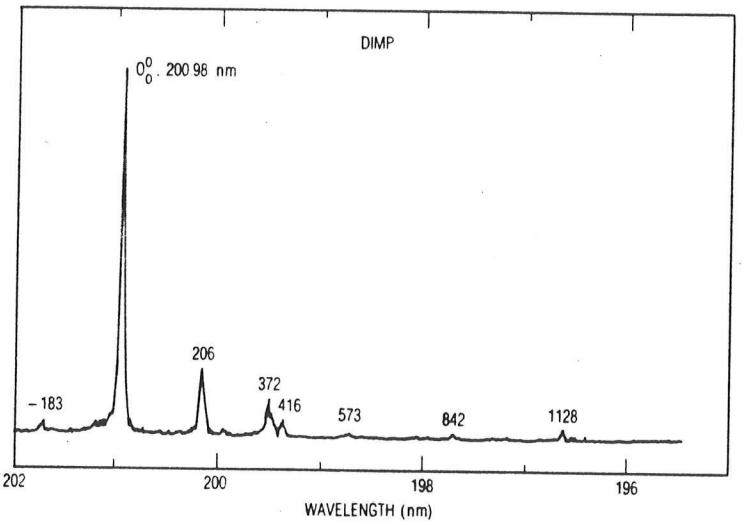

FIG. 7. 2+2 REMPI excitation spectrum of DIMP in a supersonic molecular beam (0.1% DIMP in 50 psi He). Spectrum was recorded by detecting the m/e=43 fragment. Vibrational intervals are reported in cm^{-1}.

was a one-photon absorption followed by a two photon ionization (i.e. 1+2 REMPI). Excitation into the 200 nm band was achieved using 2 photon absorption, 2 photon ionization (i.e. 2+2 REMPI) using 400 nm light. The MPI mass spectra for both electronic state excitations are presented in paper III along with a discussion of the fragmentation mechanisms. Two prominent observations can be made; (i) no molecular ion at mass m/e = 180 is observed for either excitation and (ii) very different fragmentation patterns are observed.

The 2+2 REMPI excitation spectrum of the 200 nm band was recorded for the prominent isopropyl ion at m/e = 43 and is presented in Fig. 7. Excellent supersonic cooling using 50 psi He backing pressure was achieved as evidenced by the narrow rotational bandshapes and the virtual elimination of the vibrational hot band at -183 cm^{-1} compared to the ambient vapor phase absorption spectrum in Fig. 2. By fitting the intensity of this hot band in the helium supersonic expansion to a Boltzmann distribution, one obtains a vibrational temperature for DIMP of about 50 K. The extent of cooling using atmospheric air as the carrier gas is likewise excellent (T_{vib} = 55 K). The rotational temperature is more difficult to determine since it requires knowing the principal rotational constants for the ground and excited electronic states[10]. We have recorded high resolution bandshape spectra for the 0_0^0 transition (i.e. transition between the vibrationless levels of the ground and excited electronic states). Distinct rotational contours have been resolved which are presently being analyzed to give information on the rotational constants and temperature as well as important properties of the electronic transition dipole moment (i.e. dipole axis and electronic state)[10].

The 1+2 REMPI excitation of the weak 260 nm band did not yield a m/e=43 mass fragment, but rather gave a strong mass signal at m/e=123 (see following paper) which was used to record ionization excitation spectra. The supersonic molecular beam spectra did not reveal any structure, which is consistent with the broad featureless absorption observed in the ambient vapor phase VUV absorption spectrum (Fig. 2). An apparent onset at 280 nm was observed, peaking at about 260-265 nm.

3.2. DMS Excitation Spectra

The electronic state transitions of interest for DMS are the 3s and 3p Rydberg-like states at 228 and 195 nm, respectively, and the valence state at about 203 nm (Fig. 4). REMPI excitation via any of these intermediate states gives predominantly the molecular ion at m/e = 62 (c.f. paper III) and hence this mass signal was used in recording excitation spectra.

The excitation spectrum of the 3p state at 195 nm was recorded using 2+1 REMPI and is presented in Fig. 8. Vibrational frequencies and assignments in the 3p state are reported in the Table. Considerable vibrational and rotational cooling is evident, however, the linewidths of 15-20 cm^{-1} (Fig. 8) are much greater than the 6-8 cm^{-1} observed for DIMP (Fig. 7). Lineshape studies of the 0_0^0 transition at 195.31 nm were carried out to determine the extent of rotational effects and power broadening on the observed linewidths. The relatively broad linewidths are intrinsic to the isolated molecule and most likely due to strong vibronic coupling with near lying electronic states. This is a common situation for higher excited electronic states due to

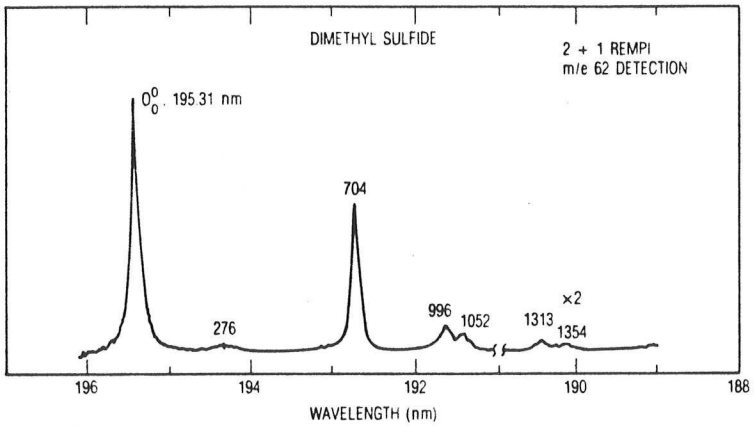

FIG. 8. 2+1 REMPI excitation spectrum of the 3p Rydberg state of dimethyl sulfide (DMS) in a supersonic molecular beam (0.1% DMS in 35 psig He). Spectrum were recorded by detecting the parent ion at m/e=62. Vibrational intervals are reported in cm^{-1}.

the increasing density of vibronic levels at increasing energies[11,12]. Recent studies on isolated molecules in supersonic molecular beams have confirmed the intrinsic broadening for higher excited electronic states[13,14].

The 1+1 REMPI excitation spectrum of the weak 3s state at 228 nm and the 2+1 REMPI spectrum of the valence state at 203 nm gave no evidence for vibrational structure. A discussion of these states in terms of their mass spectra is given in the following paper.

4. Conclusion

The preparation of molecules in single vibronic levels by laser excitation in supersonic molecular beams has enabled us to record high resolution spectra of higher excited electronic states showing fully resolved vibrational structure for diisopropyl methylphosphonate (DIMP) and dimethyl sulfide (DMS). VUV absorption spectra have also been recorded for a large number of CWA simulants at ambient temperature revealing several new electronic states extending up to the ionization threshold. DIMP and DMMP exhibited very different VUV spectral properties. Molecular orbital and normal mode calculations are in progress to understand the nature of the geometric and electronic structure as well as the vibrational motions.

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