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Fourier Transform Infrared and Raman Spectra of Dimethyl Methylphosphonate Adsorbed on Montmorillonite

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■ FTIR and Raman spectroscopic analyses were used to determine the adsorption interaction between the highly polar organophosphonate dimethyl methylphosphonate (DMMP) and a standard montmorillonite clay (SAZ-1). The polar DMMP molecule appears to interact with the interlamellar exchangeable cation in the montmorillonite clay and to displace water from the clay mineral interlamellar spaces. This was confirmed by XRD observation of a primary lattice distance expansion of about 3.3 Å during the adsorption process. Some evidence for a secondary interaction of DMMP with the natural organic matter associated with the clay mineral was obtained.

Introduction

The determination of the adsorption interactions of organic compounds and clay minerals is important in understanding the fate of organic pollutants as they pass through the soil column (1). We wish to report the direct determination of such an adsorption mechanism with the use of Raman and infrared spectroscopy (2).

It is well-known that the swelling clays such as montmorillonite can adsorb organic molecules into the interlamellar spaces (3, 4) and these substrates have often been used in the study of clay–organic complexes (3, 5, 6). Several investigators have also studied the interactions of pesticides on clays by infrared analysis (7–9).

This study describes the analysis of the interaction between a relatively nontoxic phosphonate, dimethyl methylphosphonate (DMMP) (Figure 1), which is used as an organophosphorous pesticide model compound (10, 11), and a clay mineral, calcium montmorillonite (SAZ-1), with FTIR and Raman spectroscopic analysis.

Experimental Section

Materials. The clay mineral used was calcium montmorillonite (SAZ-1) obtained from and characterized by the Clay Minerals Society's Source Clay Repository. The SAZ-1 montmorillonite contains about 72% Ca^{2+} as its interlamellar exchangeable cation, the rest being Na^+ and K^+ in approximately equal concentrations (12–14). The infrared and Raman spectra of this clay mineral and of the corresponding organo–clay complex and the conclusions derived from them reflect the majority concentration of the exchangeable calcium ions (15). For the KBr pellet studies, SAZ-1 was used without further treatment after confirming that residual adsorbed organics were in concentrations below the detection limit of FTIR spectrometry (0.05% by weight). The SAZ-1 was later saturated with potassium ions and treated with DMMP in a similar manner in order to compare the effect of a cation of differing polarizability on the spectral shift of the proposed primary interaction. DMMP, obtained from Aldrich Chemical Co. as a 97% pure compound, was used without further purification after successful comparison of its Raman and IR spectra against the literature (16).

Instrumentation. Infrared absorption spectra were obtained with an IBM IR/32 Fourier transform infrared

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spectrometer at 4-cm^{-1} resolution. Raman spectra were recorded on a ISA Ramanor U-1000 laser Raman microprobe at 4-cm^{-1} resolution. The Raman scattering source was a Spectra Physics Model 164 Ar+ laser operating at 514.5 nm. Peak positions obtained in the Raman FTIR spectra refer to the maximum datum point. As the peak position properly should be obtained by more sophisticated procedures such as center-of-gravity, this paper discusses only band shifts greater than 4 cm^{-1}.

XRD spectra were obtained on a Nicolet powder X-ray diffractometer at constant humidity, by using thin clay films sedimented onto a ceramic filter.

Methods. Adsorption of the DMMP onto the clay was by vapor deposition at 40 °C.

Raman spectra of the clay deposited on a glass slide were obtained before and after DMMP adsorption. These spectra provide information on the organic–clay mineral completely unaffected by any manipulation such as size separation or KBr pelletization.

The use of the KBr disk technique in an adsorption study using a swelling clay is addressed in separate papers (15–17). Preliminary results indicate no substantive changes in the spectra of the DMMP–clay complex due to exchange of potassium ions from the KBr disk.

KBr pellets were manufactured by mixing the samples with spectral-grade KBr to form a 0.5–1% w/w mixture, pressed at 10 000 psi for 20 s to form 10 mm diameter disks of a nominal thickness of 0.3 mm. Untreated SAZ-1 clay in KBr was used to provide the reference for spectral subtraction from the spectra of the adsorbed complex to produce the difference spectra shown in this study.

Variations in adsorption and desorption of DMMP with time were studied by removing small amounts of the sample from the reaction container at different times of exposure and monitoring them with FTIR and Raman spectra.

Identification of the emission quenching was done by inspection of the Raman spectra of the clay minerals before and after adsorption. Care was taken to filter out plasma emission lines in the Raman spectra arising from the laser itself with the use of Pellin–Broka optics.

Results and Discussion

Adsorption Behavior of DMMP on SAZ-1 with Respect to Time. The vapor-phase adsorption of DMMP was assumed to be subject to equilibrium and kinetic restraints; thus, preliminary experiments were designed to determine the adsorption behavior of DMMP onto the montmorillonite clay (SAZ-1) with respect to time. The results of the adsorption at different times are shown in Figure 2. The DMMP bands can be seen to increase in intensity during the first 2 h, at which time the adsorption is essentially complete. One obvious change in the clay spectrum that appears during the adsorption of the DMMP is a marked decrease in the broad band in the OH stretching region centered at 3430 cm^{-1} and the 1635-cm^{-1} HOH bend. This montmorillonite OH stretching region can be confidently divided into a non-hydrogen-bonded region comprising the 3624-cm^{-1} band and a complex series of bands maximizing at 3430 cm^{-1} (18), which represent
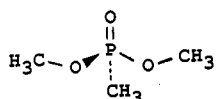
Figure 1. Structure of dimethyl methylphosphonate.
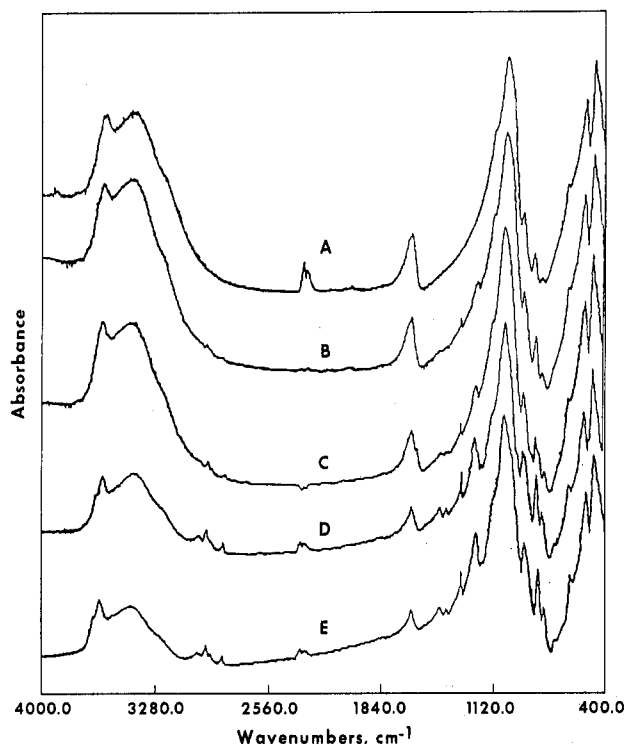

Figure 2. FTIR spectra of the adsorption of DMMP onto SAZ-1 at various exposure times: (a) 0.0 h, (b) 0.5 h, (c) 1.0 h, (d) 2.0 h, (e) 16 h.
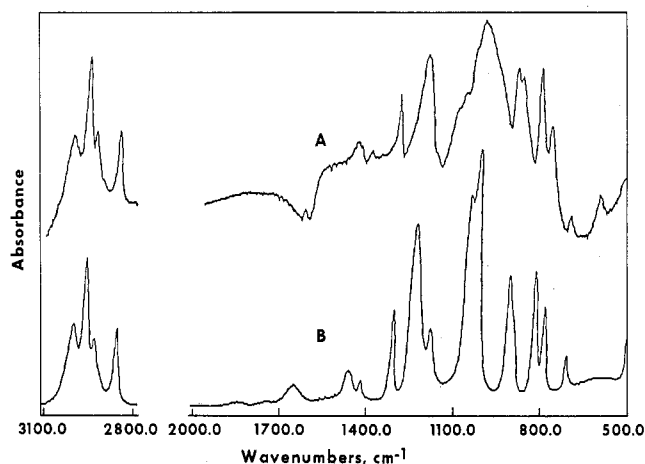

Figure 3. (a) Detail of the FTIR difference spectrum of DMMP-SAZ-1 complex compared with (b) a FTIR spectrum of pure DMMP. The negative feature in (a) at 1635 cm^{-1} is the HOH bending mode, indicating that there was more water in the clay before the adsorption of DMMP.
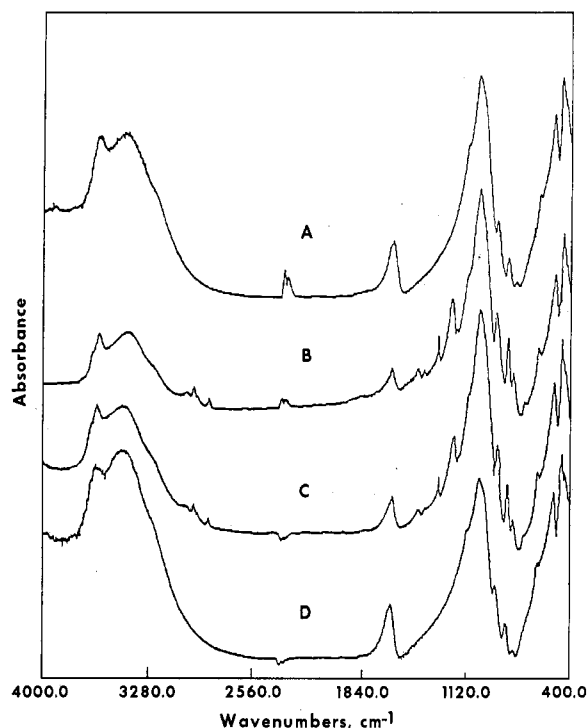

Figure 4. Effect on the DMMP-clay complex when exposed to water. (a) Ca SAZ-1, (b) DMMP-SAZ-1 complex, (c) 20-h exposure to water vapor, (d) after a single wash with liquid water followed by filtration.

hydrogen-bonded water and which can be attributed in large part to interlamellar water (waters of hydration for the exchangeable cations). Although both the 3624- and 3430-cm^{-1} bands decrease in intensity when ratioed against the 1000-cm^{-1} clay Si–O stretch, during the dehydration accompanying the adsorption of DMMP, the decrease is greatest for the 3430-cm^{-1} as well as the 1635-cm^{-1} band, indicating that it is mostly hydrogen-bonded water, held primarily in the interlamellar spaces of the clay mineral (3) that is lost during the adsorption process. Further corroboration for this conclusion is seen in the negative intensity of the 1635-cm^{-1} HOH bending band in the difference spectrum of the DMMP-clay complex (Figure 3). This is a subtraction artifact indicating that there was more water in the clay before the adsorption process than after, suggesting the displacement of water during the adsorption of the organophosphonate.

The conclusion from these data is that the DMMP displaces water from the interlamellar spaces during the process of adsorption.

Effect of Water on the DMMP–Clay Complex. The results of exposing the DMMP–clay complex to a water wash and to a water vapor atmosphere are shown in Figure 4. The absence of any loss of DMMP–clay complex bands when the complex is exposed to a water vapor atmosphere indicates that water in the vapor state has no affect on the DMMP–clay complex. However, upon exposure to liquid water the DMMP is quickly and completely displaced, indicated by the loss of the Raman and FTIR DMMP–clay bands and accompanied by a large increase in the intensity of the 3430-cm^{-1} OH stretching bands. This suggests that the DMMP, with a dipole moment of 3.62 D (19) is displaced only with liquid water, which has a lower dipole

moment of 1.08 D (20). That the more polar DMMP is displaced by water suggests that equilibrium thermodynamics play an important role in the sorption of the organophosphonate pesticides similar to DMMP by the swelling clay soil components. These data also indicate that the sorption interaction is likely polar in nature rather than resulting from some nonspecific hydrophobic interaction. The only available positively charged polar substituents in the clay mineral are the interlamellar cations.

XRD Analysis. If DMMP occupies the interlamellar clay spaces, there should be a corresponding expansion of the lattice. XRD spectra of SAZ-1 were run before and after adsorption, at constant humidity. The diffraction patterns show that in response to the DMMP atmosphere the SAZ-1 expanded reproducibly an average interlamellar spacing of 3.3 Å, which is similar to the calculated thickness of the DMMP molecule if it is constrained to the flattened disk-shaped configuration corresponding to the electronic

Table I. IR and Raman Bands of DMMP and DMMP Adsorbed onto Calcium Montmorillonite (Numbers in Wavenumbers)[a]

reference			complex	
IR	Raman	assignments	IR	Raman
	507	δ(POC)		511
714	715	ν(PC)	722	719
791	791?	ν(PO$_2$)	795	798?
824	823?	ν(PO$_2$)	831	839?
895	ρ(CH$_3$P)	897*		
916		ρ(CH$_3$P)	914*	
1034		ν(CO)	1028	
1057		ν(CO)	1059*	
1186		ρ(CH$_3$O)	1188* sh	
1244		ν(P=O)	1223	
1316		δ_s(CH$_3$P)	1320	
1420	1425	δ_a(CH$_3$P)	1416	1423*
1464	1474	$\delta_s\delta_a$(CH$_3$O)	1470	1463
2855	2862	2δ_s(CH$_3$O)	2858*	2865*
2930	2936	ν_s(CH$_3$P)	2936	2942
2959	2966	ν_s(CH$_3$O)	2965	2969*
2998	3007	ν_a(CH$_3$P)	3013	3015

[a] (*) = bands with wavenumber shifts less than 4 cm^{-1}. (sh) = shoulder. (?) = bands with S/N less than 1.5 such that wavenumber cannot be confidently determined. IR reference bands from a neet DMMP smear on a KBr disk. Raman reference bands from the pure liquid.

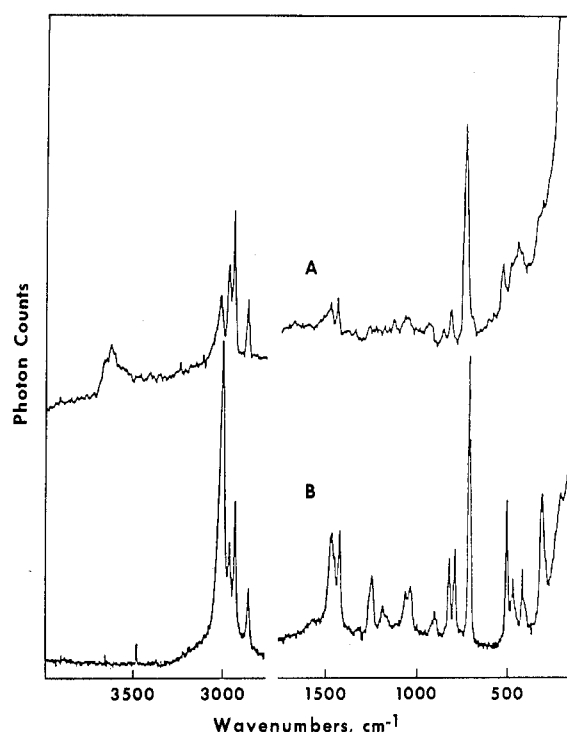**Figure 5.** Detail of the Raman spectrum of (a) the DMMP–clay complex compared with (b) pure DMMP.

ground state. These data provide independent corroboration of the results observed by FTIR and Raman that DMMP does undergo interlamellar insertion.

Bonding Analysis from Spectral Shift Data. Our results indicate that the DMMP–montmorillonite interaction is between the organophosphonate and the interlamellar cations in the clay mineral. In this case, two monodentate bonding mechanisms are possible. The first is a direct coordination of the DMMP to the cation by an ion-induced dipole interaction, and the second, an indirect coordination through a water molecule in the first coordination sphere of the cation (21). These two possibilities can be distinguished by an analysis of the bonding-induced shifts in the vibrational spectra as detailed below.

The infrared and Raman spectra of the DMMP–clay mineral complex are similar to those of the pure DMMP spectra, but a number of bands are slightly shifted in wavenumber. Several of the more important infrared DMMP bands appear near the intense clay mineral Si–O stretch near 1000 cm^{-1}, making their analysis difficult. This is an intense asymmetric band and so does not appear in the Raman spectra of the clay mineral, making analysis of the complex with this method more simple. Both the IR and Raman bands with their assignments (15) and their observed shifts are summarized in Table I. The FTIR difference spectra and the Raman spectra are shown in Figures 3 and 5.

The DMMP band that undergoes the largest frequency shift after adsorption is the P=O stretching band at 1244 cm^{-1}. This bond must therefore be the site of the major specific interaction between the clay mineral and DMMP. This shift of 21 cm^{-1} to a lower wavenumber for the calcium clay indicates a decrease in the strength of the P=O bond, which would be consistent with an interaction between a nonbonding orbital of the doubly bonded oxygen and some positive center, either the first hydration sphere around the interlamellar cation or the exchangeable interlamellar cation itself. It must be noted that although this band is prominent in the IR spectra of the DMMP–clay complex it is lost in the noise of the Raman spectra.

Farmer (21) suggested that the magnitude of the spectral shift should be dependent on the polarizing power of cation

if the interaction of the sorbate with the cation is not through a "water bridge". If it is through the first hydration sphere, the shift should be small and little affected by the polarizing power of the cation. To establish this, the calcium ions in the SAZ-1 were exchanged for potassium ions and the band shifts remeasured. The P=O shift in the potassium-exchanged SAZ-1 was found to be only 6 cm^{-1} toward lower wavenumbers, compared with the 21-cm^{-1} downshift found with the calcium-containing SAZ-1. It can be concluded, therefore, that the interaction is a direct ion–dipole coordination between the DMMP P=O functional group and the exchangeable calcium ion rather than through a water of hydration sphere.

This was the only interaction found, no other band is similarly shifted so far in frequency. If one of the singly bonded DMMP oxygens also contributed to the interaction between the clay minerals and the DMMP to form a bidentate interaction, one should expect to observe a second large frequency shift associated with that oxygen bond.

The result of the bonding of the DMMP to the clay mineral through the P=O oxygen nonbonding electrons is that the resultant electronic rearrangement should leave the P atom with a partial positive charge. This should result in a back-bonding effect of a nonbonding electron from a singly bonded oxygen to an unoccupied phosphorous p orbital, essentially strenghtening the P–O and P–C bonds and causing a shift in these bands to higher frequencies (Table I). The other shifts observed in Table I support this conclusion by similar logic.

Emission Quenching Followed by Raman Spectroscopy. In the course of this work, it was noticed that the Raman spectra were superimposed on a broad-emission background centered at 600 cm^{-1} (Figure 6). Emission is found in some minerals (22) and is also thought to be associated with acene moieties in natural soil organic material (23, 24) such as humic acids. The breadth of these bands and their lack of vibronic structure seem to indicate very large, high molecular weight aromatic structures. However without additional studies, broad-band emission from emission centers in minerals cannot be ruled out.
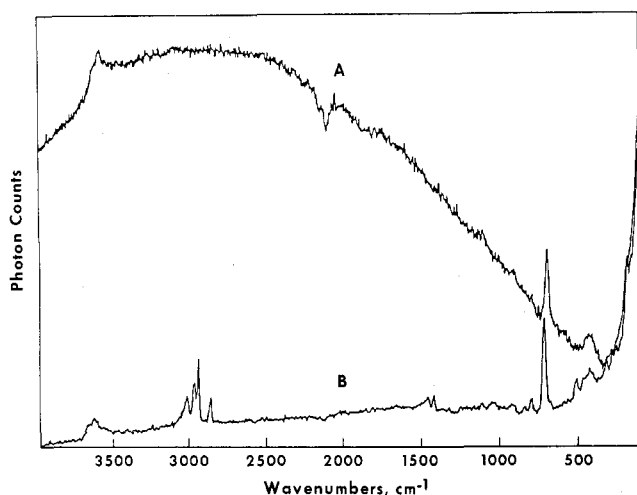
Figure 6. Raman spectra of (a) Ca SAZ-1 and (b) DMMP-SAZ-1 complex showing the loss of broad-band emission after the adsorption process.

This emission was noticeably quenched by addition of DMMP in a time shorter than that indicated by the FTIR time study. The fact that the quenching takes place and that quenching by charge–transfer or Forster dipole–dipole mechanisms are short-range effects does suggest that the emission originates from the exterior surface or from the interlamellar spaces. If the emission is due to soil organic material, standard emission procedures should provide a useful means for studying sorbate–soil organic matter interactions. This quenching effect represents a second interaction of the DMMP with the clay, but detailed mechanistic understanding of this interaction awaits more experimentation.

Conclusions

It has been shown that the specific interactions between DMMP, a pesticide-like organic compound, and a natural montmorillonite clay mineral can be determined directly and rapidly by using Raman and FTIR techniques, even when the bands of interest are near the intense clay mineral bands associated with the Si–O stretch.

An analysis of the spectral shifting of the DMMP vibrational bands after adsorption indicated that the major interaction between the clay mineral used here and the DMMP molecule is an ion-induced dipole interaction of the phosphonate oxygen (P=O) with the interlamellar cationic species and not through an intervening hydration sphere. It was also found that this interaction drives off the interlamellar water molecules as the adsorption proceeds and that the adsorbed DMMP can be displaced by liquid water as expected from equilibrium considerations. Further, an interaction of DMMP with what may be natural organic material was seen in the Raman spectra of the natural clay minerals by the quenching of the emission seen in the clay spectra as the DMMP adsorption proceeded.

Acknowledgments

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