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Commentationes

Effect of Ionic Lattices on Electronic Structures of Polyatomic Ions

II. Sulphate

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The effect of the electrostatic environment of the lattice upon the electronic structure of the sulphate ion is studied by carrying through VESCF calculations of the free sulphate ion and the ion in K_2SO_4, $CaSO_4$ and $BaSO_4$. The ion is treated as a 24 electron system, the basis functions being oxygen $2p$, sulphur $3s$ and $3p$ orbitals.

The effect of the lattices is to increase the electron population on the sulphur at the expense of the oxygen populations. Oxygens that are crystallographically inequivalent are found to vary perceptibly in net charge. The lattices are also found to lead to a pronounced lowering in the total electronic energy of the anion and to more negative bond energy values for all SO bonds.

The most interesting prediction is of a measurable splitting of degenerate excited spectroscopic states of the ion in the lattices. In particular splittings of several hundred wavenumbers for the longest wavelength ${}^1A_1 \rightarrow {}^1T_2$ band, differing for each of the lattices, are predicted. Comparisons of these predictions with observation could provide a valuable testing of various wave functions for sulphates, and indeed other polyatomic ions in general.

Der Einfluß, der vom elektrostatischen Feld eines umgebenden Gitters auf die Elektronenstruktur des Sulfations herrührt, wird mittels des Vergleichs von vier VESCF-Rechnungen (freies Ion, Ion in K_2SO_4, $CaSO_4$, $BaSO_4$) verfolgt. 24 Elektronen werden in die Rechnung miteinbezogen; als Basis fungieren die $2p$-Zustände des Sauerstoffs und die $3s$- und $3p$-Zustände des Schwefels.

Die Existenz der Gitter-Umgebung bewirkt eine Wanderung der Elektronen vom Sauerstoff zum Schwefel. Kristallographisch inäquivalente Sauerstoffatome zeigen deutlich verschiedene Nettoladungen. Außerdem wird die Gesamtenergie des Anions kräftig gesenkt, desgleichen die Bindungsenergie aller SO-Bindungen.

Das interessanteste Ergebnis ist aber eine Aufspaltung der entarteten angeregten Zustände, die von einer meßbaren Größenordnung sein sollte. Insbesondere ergibt sich eine Aufspaltung von mehreren hundert Wellenzahlen für die längste ${}^1A_1 \rightarrow {}^1T_2$-Bande, und zwar für jede Gitterstruktur eine andere. Vergleicht man diese Ergebnisse mit dem Experiment, so ergibt sich die Möglichkeit, verschiedene Wellenfunktionen auf ihre Güte hin zu testen.

L'effet de l'environnement électrostatique du réseau sur la structure électronique de l'ion sulfate est étudié à l'aide de calculs VESCF de l'ion sulfate libre et de l'ion dans K_2SO_4, $CaSO_4$ et $BaSO_4$.

L'ion est traité comme un système de 24 électrons dans une base d'orbitales $2p$ sur l'oxygène, $3s$ et $3p$ sur le soufre.

Les réseaux ont pour effet d'augmenter la population électronique sur le soufre au dépens des atomes d'oxygène. Les oxygènes non équivalents du point de vue cristallographique ont des charges nettes différentes. Les réseaux conduisent aussi à un abaissement prononcé de l'énergie électronique totale de l'anion et à une énergie de liaison plus négative pour toutes les liaisons S–O.

La prédiction la plus intéressante concerne une séparation mesurable des états spectroscopiques excités dégénérés de l'ion, dans les réseaux. En particulier on prévoit des séparations de plusieurs

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centaines de nombres d'onde pour la bande la plus lointaine ${}^1A_1 \rightarrow {}^1T_2$, différentes selon les réseaux. La comparaison de ces prédictions à l'expérience serait un test intéressant pour les différentes fonctions d'onde des sulfates et des ions polyatomiques en général.

Introduction

From time to time quantum-mechanical calculations of the electronic structures of ions have been performed. In all cases the ions have been considered in isolation. The comparison of the theoretical results with experimental data is attended by some uncertainty because all experimental data relate to measurements on solvated ions in solution or on ions arranged in a crystal lattice. Either environment would be expected to produce a substantial distortion of the electronic structure of the ion. It is not easy to assess quantitatively the effect of solvation but the effect of the electrostatic field of an ionic lattice is more amenable to treatment. In the present paper we report on such lattice effects for the sulphate anion. There is no reason to believe that this case is exceptional. We expect analogous perturbations to arise quite generally for ions in crystal lattices. A preliminary study of triiodides has already been published [1].

Our initial aim is to discern those experimentally accessible properties of ions that will best reveal the influence of lattice effects. In the study of I_3^- we considered several properties of the ground state, primarily internuclear distances (although vibrational frequencies, when experimentally accessible, would appear to be more sensitive to lattice effects). It seemed probable however that it might be easier to detect the lattice effect on the energies and symmetries of excited electronic states and so these are the prime concern of the present study.

Method

For a proper discussion of electronic excited states of molecules it is necessary to use antisymmetrical electronic wave functions and to give direct recognition, in the Hamiltonian, of electron repulsion. In the case of tetrahedral anions like sulphate this has almost never been done although recently some steps have been taken to rectify this [2]. Some technical difficulties arise but these have been discussed elsewhere [3]. For the present study we shall be content with a relatively simple ASMO procedure and with simple approximations to various integrals so that attention can be focussed on the effect of the lattice.

We have used a simple form of the VESCF method to derive molecular orbitals. The sulphate ion was treated as a 24 electron problem, the basis functions being oxygen $2p$ orbitals (the $2s$ electrons being regarded as "inner shell") and the sulphur $3s$ and $3p$ orbitals[1]. The relevant valence state ionization potentials for these orbitals were taken to be

$$I(\mathrm{O}, 2p) = 0.0828\,Z_\mu^2 + 19.7376\,Z_\mu - 23.3640 \tag{1}$$

$$I(\mathrm{S}, 3s) = -0.1464\,Z_\mu^2 + 12.1288\,Z_\mu + 3.3176 \tag{2}$$

$$I(\mathrm{S}, 3p) = -0.1506\,Z_\mu^2 + 11.9015\,Z_\mu + 2.8369 \tag{3}$$

where Z_μ is the effective nuclear charge for the atomic orbital. These effective nuclear charges were derived from Burn's rules [4] and the atomic valence

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[1] We leave for subsequent consideration the possibility that sulphur $3d$ orbitals need to be included, noting that we have not yet found convincing evidence that one needs to go beyond $3s$ and $3p$ orbitals to obtain an adequate understanding of the electronic structure of the sulphate ion.

electron populations according to the formulation:

$$Z_\mu = Z_\mu^{\mathrm{core}} - (P_{\mu\mu} - 1)\sigma_{\mu\mu} - \sum_{\nu \neq \mu} P_{\nu\nu}\sigma_{\mu\nu} \tag{4}$$

the summation being over all of the valence orbitals considered on the atom in question. Z_μ^{core} is the effective nuclear charge arising from the nucleus and inner-shell electrons while $\sigma_{\mu\nu}$ represents the Burn's constant for the screening of orbital χ_μ by an electron in orbital χ_ν.

The formula for the required Hartree-Fock matrix elements in the CNDO approximation are those given by Pople, Santry and Segal [5]. Weighted averages of the theoretical values of nuclear attraction (V_{AA}, V_{AB}) and Coulomb electron repulsion integrals ($\gamma_{\mathrm{A}}, \gamma_{\mathrm{AB}}$) have been used. Some allowance has been made for Hartree-Fock corrections and electron correlation in choosing values of the latter. A comparison of overlap integrals calculated for Slater-type atomic orbitals with Burns exponents, and those calculated from true atomic Hartree-Fock orbitals indicated the need to scale the overlap integrals used in this work.

Core Hamiltonian integrals were obtained thus:

$$\alpha_\mu = -I_\mu + \sum_{\mathrm{B} \neq \mathrm{A}} X_{\mathrm{B}} V_{\mathrm{BA}} \tag{5}$$

$$\beta_{\mu\nu} = \frac{S_{\mu\nu}}{2}\left[\alpha_\mu + \alpha_\nu + \frac{1}{2}(X_{\mathrm{A}} V_{\mathrm{AA}} + X_{\mathrm{B}} V_{\mathrm{BB}} - X_{\mathrm{A}} V_{\mathrm{AB}} - X_{\mathrm{B}} V_{\mathrm{BA}})\right] \tag{6}$$

for orbital μ on centre A and orbital ν on centre B, X_{A} is the core charge on atom A, V_{AB} the average nuclear attraction integral for unit positive charge on atom A and an electron in any orbital on atom B. The Mulliken approximation has been used to obtain the expression for $\beta_{\mu\nu}$ from its complete theoretical definition.

Assuming a basis of Löwdin orthogonalized atomic orbitals in the CNDO method, the core Hamiltonian matrix H formed from the above elements was transformed for use with the CNDO repulsion integral approximations:

$$H^{\mathrm{CNDO}} = S^{-\frac{1}{2}} H S^{-\frac{1}{2}}. \tag{7}$$

The standard procedure was followed for setting up excited configuration functions, extracting appropriate combinations of Slater determinants belonging to different multiplicities and irreducible representations of the relevant point group and then carrying through a configuration-interaction treatment involving all singly excited configurations.

We do not set out here to justify the above procedures as being the best of various alternatives available because we are not concerned to claim that we have derived the best possible wave functions and energies. Rather we suggest that the above-described method is not unreasonable and thus serves as a convenient basis for exploring the influences of the surrounding lattice upon the electronic structure and properties of the sulphate ion.

The effect of the lattice was included via its contribution to each element of the core Hamiltonian matrix:

$$H_{\mu\nu} = H_{\mu\nu}^i + H_{\mu\nu}^l$$

where $H_{\mu\nu}^i$ is the matrix element for orbitals μ and ν in an isolated sulphate ion and $H^l_{\mu\nu}$ is the contribution from the lattice given by:

$$H^l_{\mu\mu} = V^l_{\mathrm{A}} \tag{8}$$

$$H^l_{\mu\nu} = \frac{S_{\mu\nu}}{2}(V^l_{\mathrm{A}} + V^l_{\mathrm{B}}) \tag{9}$$

for orbital μ on centre A, orbital ν on centre B and V^l_{A} the potential at atom A due to the lattice. Since in the VESCF method, the effect of an adjacent core B *within* the molecular system is included in the terms $X_{\mathrm{B}} V_{\mathrm{BA}}$, for charges *outside* the system the appropriate point-charge approximation is

$$V^l_{\mathrm{A}} = -\sum_c Q_c/R_{\mathrm{AC}}, \tag{10}$$

the summation being over all charges throughout the lattice external to the sulphate ion. Other sulphate ions in the lattice are regarded as collections of five point charges on the five nuclei.

To perform the summations in (10) for each of the five nuclei of the reference sulphate ion, one needs the coordinates of all nuclei in the unit cell. The relevant data for the sulphates studied was obtained from Wyckoff's tables [6], and bond lengths calculated from this data are summarised in Table 1. The appropriate charges Q_c for the five charges over the sulphate anion have, of course, to be derived iteratively, i.e. the VESCF procedure has to be applied to the lattice as a whole.

Table 1. *Bond lengths in crystalline sulphates (Å)*

Bond	Free SO_4^{2-}	K_2SO_4	$CaSO_4$	$BaSO_4$
S–O_1	1.49	1.534	1.482	1.492
S–O_2	1.49	1.506	1.482	1.515
S–O_3	1.49	1.463	1.471	1.476
S–O_4	1.49 (Assumed)	1.463	1.471	1.476

The Ewald method was used for the lattice summation[2], following the derivation of Slater and DeCicco [7]. The optimum value of the convergence factor was found to be 0.2 for the crystals studied here. For a particular reference atom, a separate potential sum was carried out for each symmetry type of ion in the unit cell placing a unit positive charge at each ion point. Then in the molecular orbital program the lattice potential V^l_{A} is given by:

$$V^l_{\mathrm{A}} = \sum Q_{\mathrm{cation}} V^{\mathrm{Ewald}}_{\mathrm{cation,A}} + \sum_{\mathrm{B}} Q_{\mathrm{B}} \left[V^{\mathrm{Ewald}}_{\mathrm{BA}} - \frac{14.4}{R_{\mathrm{AB}}} \right] \tag{11}$$

where $V^{\mathrm{Ewald}}_{\mathrm{BA}}$ is the Ewald potential at reference atom A due to ions B throughout the lattice, the first sum is over all cations present, the second over all atoms B in the sulphate anion and the term $\frac{14.4}{R_{\mathrm{AB}}}$ takes out the potential due to adjacent cores within the molecular system.

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[2] A suitable computer program for the lattices involved in the present work was kindly made available by Dr. I. D. Campbell of the Division of Chemical Physics, C.S.I.R.O.

Results and Discussion

Table 2 shows the redistribution of electron density that occurs when the effects of the different crystal lattices are added to a calculation for the isolated sulphate anion. In each case, the gross electron population on the sulphur atom (obtained from a Mulliken population analysis) increases, corresponding to a reduction of the sulphur net charge. Both the sulphur $3s$ and $3p$ orbital populations increase. There is also some redistribution of charge among the oxygen atoms and the oxygen orbital occupations vary from case to case, being 0.7 ± 0.02 for the $2p_\sigma$ orbital [directed along the O–S internuclear axis] and 1.91 ± 0.01 for each of the $2p_\pi$ and $2p_\pi$-orbitals.

Table 2. *Crystal lattice effect on electron density in the sulphate anion*

	Free SO_4^{2-}	K_2SO_4	$CaSO_4$	$BaSO_4$
Atomic Charges				
S	+0.13	+0.11	+0.06	+0.05
O_1	−0.53	−0.50	−0.53	−0.48
O_2	−0.53	−0.54	−0.53	−0.50
O_3	−0.53	−0.53	−0.50	−0.53
O_4	−0.53	−0.53	−0.50	−0.53
Sulphur Orbital Occupations				
S, $3s$	1.701	1.704	1.711	1.713
S, each $3p$	1.390	1.397	1.410	1.413
S, total $3p$	4.169	4.190	4.230	4.239

Table 3. *Crystal lattice effect on bond and total energies in the sulphate anion*

	Free SO_4^{2-}	K_2SO_4	$CaSO_4$	$BaSO_4$
Total Energy (eV)	−958.7	−1269.2	−1319.6	−1311.9
Bond Energy, E_{SO_1}, (eV)	− 56.66	− 59.41	− 59.21	− 59.30
Bond Energy, E_{SO_2}, (eV)	− 56.66	− 59.02	− 59.21	− 59.17
Bond Energy, E_{SO_3}, (eV)	− 56.66	− 59.08	− 59.42	− 58.87
Bond Energy, E_{SO_4}, (eV)	− 56.66	− 59.08	− 59.42	− 58.87

A lowering of both the total energy and the sulphur-oxygen electronic "bond energy" occurs, as shown in Table 3. The bond energy is defined by:

$$E_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} \frac{1}{2} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \tag{12}$$

and acts as an indication of the amount of binding interaction, in a similar way to the bond order concept for π-electron conjugated hydrocarbons.

It is when we consider the effect of the lattice on the UV spectrum that a most interesting and potentially observable effect is seen. Electrostatic splittings of the free ion spectrum of up to 400 cm^{-1} are shown in Fig. 1[3], together with an overall

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[3] The inability to distinguish between singlet and triplet T_1 and E spectroscopic states is a particular shortcoming of the CNDO method.

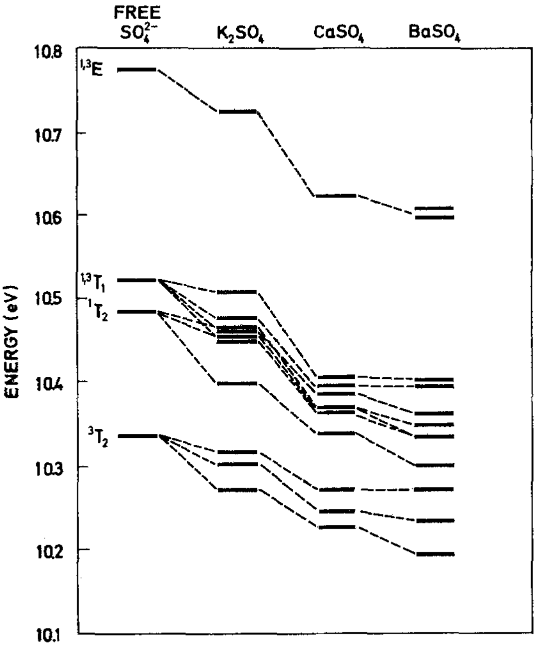

Fig. 1. Calculated splittings of free sulphate anion spectroscopic states in several sulphate crystals

lowering of the calculated transition energies. The particular splitting for the first symmetry allowed $^1A_1 \rightarrow {}^1T_2$ band is shown in greater detail in Fig. 2. The different crystalline environments cause both different amounts of lowering of the transition energy, and different degrees of splitting of the band.

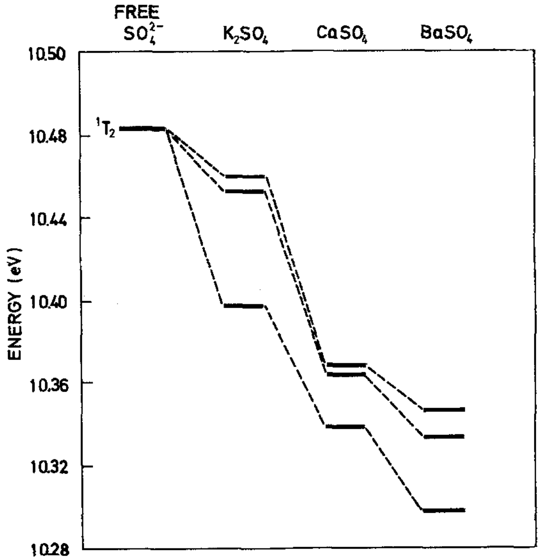

Fig. 2. Calculated splittings of lowest singlet excited state of a free sulphate anion in several sulphate crystals

Other recent studies of the sulphate ion have been made by Manne [8], Bishop [9] and Santry and Segal [10]. These studies however took no account of the effect of the lattice on the electronic structure (Manne made an *a posteriori* estimate of the lattice potential at the sulphate nucleus in K_2SO_4 but did not incorporate this potential in his Hamiltonian). Since our purpose in this paper was to focus attention on lattice effects we prefer to leave to a subsequent publication any comparison of our results for an isolated sulphate ion with those of the workers named above.

The quantitative predictions of splitting of degenerate spectroscopic states will be somewhat dependent upon the details of the MO procedure employed and may be appreciably changed if substantial participation of sulphur 3*d* orbitals is incorporated in the calculations. Other studies of sulphate and other tetrahedral ions that we have made and that we plan to report subsequently suggest that 3*d* orbital participation is not substantial. For the present we wish to emphasise that a careful experimental and theoretical study of lattice effects on excited states may prove to be a powerful method of testing wave functions proposed for such spectroscopic states.

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