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Ab initio geometry and anharmonic vibrational spectra of PbX_2 halides and $PbX_2\cdots L$ ($X=F$, Cl, Br, I; $L=CO$, N_2) complexes

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Abstract

Equilibrium geometries of PbX_2 halides and $PbX_2\cdots L$ ($X=F$, Cl, Br, I; $L=CO$, N_2) complexes have been determined at ab initio level with second order perturbative (MP2) treatment of electron correlation using Stevens–Basch–Krauss–Jasien–Cundari (SBKJC) relativistic effective core potentials (RECP) and basis sets. Optimized structures of $PbX_2\cdots L$ complexes have C_s symmetry with end-on coordination of the ligand, and are characterized by $Pb\cdots C$ bond length within 279.9–281.6 pm, $Pb\cdots N$ distance of 273.9–278.0 pm, and $Pb\cdots L$–L angle of 163.3–173.5°. Anharmonic vibrational spectra of PbX_2 halides and $PbX_2\cdots L$ complexes have been determined from ab initio MP2/SBKJC+(d) potential energy surfaces using vibrational self-consistent field (VSCF) and correlation-corrected vibrational self-consistent field (CC-VSCF) methods. Sensitivity of ν(Pb–X) and ν(L–L) stretching modes to complex formation, established from CC-VSCF anharmonic spectra, closely follows that observed in low temperature Ar matrix infrared spectra of these complexes. Anharmonic estimates of $\nu(Pb\cdots C)$ and $\nu(Pb\cdots N)$ stretching modes were computed at 137–131 and 149–150 cm^{-1}, respectively.

Keywords: Ab initio; VSCF; Vibrational self-consistent field; Anharmonic; Lead(II)-halide; Carbon monoxide; Dinitrogen

1. Introduction

Complexes of divalent fourth row metal halides (M = Ca, Cr, Mn, Ni, Cu, Zn) [1,2] and divalent Group 14 metal halides (M = Sn, Pb) [3] with σ-donors like carbon monoxide, nitrogen monoxide, and dinitrogen have attracted considerable attention because of the blue shift of intra-ligand stretching vibration frequency occurring upon complex formation. Frequency shifts of intra-ligand stretching mode observed in the infrared spectra of SnX_2 and PbX_2 ($X=F$, Cl, Br, I) complexes with CO, NO, and N_2 in low temperature Ar matrices [3] have been attributed to the strengthening of intra-ligand bond resulting from electron density transfer from σ* anti-bonding orbital of the ligand to empty d orbitals of the metal. The most probable geometry of $SnX_2\cdots L$ and $PbX_2\cdots L$ (where $L=CO$, NO, N_2) complexes has been inferred from their infrared spectra [3] and depicted as L molecule end-on coordinated to the bent MX_2 halide. Ground state properties of lead(II) halides have been investigated in detail by experimental techniques such as gas phase electron diffraction [4] and theoretical methods at Hartree–Fock [5], multireference singles and doubles configuration interaction (MRSDCI) [6,7], and density functional theory (DFT) [8] levels of theory. Both ab initio [5–7] and DFT [8] calculations employed quasirelativistic effective core potentials on lead atoms, accounting for scalar relativistic effects. On the other hand, structural information concerning lead or lead(II) halide complexes with small inorganic ligands appears rather scarce and has been derived from either low temperature matrix spectroscopic studies or quantum chemical calculations. Thus, the structure and vibrational transitions of lead carbonyls $Pb_n(CO)$ ($n=1$–4) [9], lead hydrides PbH_n ($n=1$–3) [10], and dioxygen lead complexes $Pb(O_2)$, $OPb(O_2)$ [11] have been deduced from their low temperature inert matrix spectra, whereas scalar relativistic DFT and coupled cluster (CCSD(T)) calculations provided insight into geometry and spectroscopic properties of lead compounds of environmental importance, namely PbOH, HPbO [12], $Pb(H_2)$, Pb(OH), $Pb(H_2O)$, $Pb(HO_2)$ [13], and $Pb(O_n)$ ($n=1$–3) [14].

Vibrational spectra routinely calculated in the harmonic approximation within many electronic structure programs by means of ab initio or DFT methods are commonly used to assist the assignment of the observed spectral features. Computed transition energies usually overestimate the experimental spectrum by as much as several hundred wavenumbers and

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require method/basis set dependent scaling in order to achieve agreement between computed and observed spectrum. However, because of a rapid increase in computing power of an average processor/workstation, anharmonic ab initio evaluation of the vibrational spectrum of moderately sized molecule (10–15 atoms) becomes feasible alternative to standard harmonic calculations.

Vibrational self-consistent field (VSCF) [15–19] and its correlation corrected extension (CC-VSCF), which accounts for mutual coupling of vibrational modes [20–22], provide conceptually simple and effective way of obtaining vibrational characteristics of a molecule in anharmonic approximation. Direct VSCF approach employing potential energy surfaces (PES) evaluated at MP2 or coupled cluster CCSD(T) level has successfully been used to assign vibrational spectra of strongly anharmonic species, including these formed by heavy elements, HRgF (Rg = He, Ne, Ar, Kr, Xe, Rn) [23], HXeI [24], HXeOH [25], and GdF_3, $GdCl_3$ [26]. Replacement of all-electron basis set by relativistic effective core potential (RECP)/valence basis [27–29] offers considerable reduction of the computational burden involved in PES evaluation [30], while providing basis set level treatment of scalar relativistic effects, indispensable in case of heavy elements. Moreover, it has been shown that ECPs can effectively be applied to the computation of equilibrium geometry and vibrational spectra of 2nd and 3rd row element compounds without significant loss of accuracy [31] with relation to all-electron basis sets.

Present work reports on application of SBKJC [27–29] RECP/valence basis set, within MP2 level of electron correlation, to the evaluation of equilibrium geometry and VSCF anharmonic spectra of lead(II) halide complexes with carbon monoxide and dinitrogen. Influence of basis set type on r(L–L) distances and wavenumbers of ν(L–L) stretching mode is analyzed along $PbX_2\cdots L$ (X = F, Cl, Br, I) series for SBKJC+(d) and TZV(d) bases. Sensitivity of intra-ligand ν(L–L), ν_a(Pb–X), and ν_s(Pb–X) stretching modes to complex formation has been determined from anharmonic spectra of $PbX_2\cdots L$ (X = F, Cl, Br, I) complexes and compared with that observed in low temperature Ar matrix spectra. Revised assignment of ν_a(Pb–Br) and ν_s(Pb–Br) stretching modes of lead(II) bromide, consistent with HF/ECP computed [5] wavenumbers of these modes is proposed.

2. Methods

All ab initio calculations were carried out using electronic structure program GAMESS [32]. Equilibrium geometries, harmonic vibrational spectra, and VSCF anharmonic spectra were computed on MP2 level in two different basis sets. In the first set, the effective core potentials and valence basis sets of Stevens, Basch, Krauss, Jasien, and Cundari (SBKJC) [27–29], augmented with single d type polarization function and sp type diffuse function, denoted as SBKJC+(d), were used on all atoms. Scalar relativistic effects have been accounted for in the effective core potentials [29]. In the second set, SBKJC+(d) basis was used on Pb, F, Cl, Br, and I atoms and triple-zeta valence basis augmented with single d-type polarization function, TZV(d) [33], on C, N, and O atoms. Equilibrium geometries of PbX_2 halides and $PbX_2\cdots L$ complexes were determined under C_{2v} and C_s point group symmetry, respectively, using analytical gradients of energy. Equilibrium geometry searches on $PbX_2\cdots L$ species performed under C_1 symmetry invariably converged to C_s symmetry structures, thus providing support for the $PbX_2\cdots L$ point group selection. Hessian matrices and harmonic vibrational wavenumbers were computed numerically from analytically calculated energy gradients. Geometries and vibrational frequencies of CO and N_2 were also computed in SBKJC+(d) and TZV(d) basis sets to facilitate direct comparison to the complexes. VSCF system potential has been approximated by the sum of single mode $V_j^{\text{diag}}(Q_j)$ (diagonal) and pair coupling (mode-mode) $V_{i,j}^{\text{coup}}(Q_i, Q_j)$ terms and neglecting higher order interactions between normal modes (e.g. mode triples) [20–22]:

$$V(Q_1, \ldots Q_N) = \sum_{j}^{N} V_j^{\text{diag}}(Q_j) + \sum_{i}^{N-1} \sum_{j>i}^{N} V_{ij}^{\text{coup}}(Q_i, Q_j)$$

where Q_i denotes ith normal coordinate, and N is the number of normal modes. Such 2-mode coupling representation of the system potential proved adequate in the description of anharmonicity of heavy element complexes studied to date [23–26], and its application to weakly anharmonic $PbX_2\cdots L$ species appears properly justified. Ab initio potential energy surfaces and dipole moment surfaces were evaluated in both basis sets on a 16 point grid (single mode) or 16×16 square grid (mode pair) across $[-4*\omega_i^{-0.5}, +4*\omega_i^{-0.5}]$ range (where ω_i is the harmonic frequency of ith normal mode) in the normal coordinate space, giving rise to 816 (PbX_2) and 9360 ($PbX_2\cdots L$) PES points. Anharmonic VSCF and CC-VSCF wavenumbers of the fundamental transitions of lead(II) halides and their complexes with CO and N_2 were computed directly from ab initio potential energy surfaces. Intensities of fundamentals were evaluated using MP2 dipole moment surfaces and VSCF wavefunctions of the corresponding states,

$$I_i = \frac{8\pi^3 N_a}{3hc}\,\omega_i \left|\left\langle \Psi_i^{(0)}(Q_i) \middle| \vec{\mu}(Q_i) \middle| \Psi_i^{(m)}(Q_i) \right\rangle\right|^2$$

where $\Psi_i^{(0)}$ and $\Psi_i^{(m)}$ denote VSCF wavefunctions of the ground and the mth excited vibrational states of ith normal mode, ω_i is the CC-VSCF vibrational frequency of this mode, and the remaining symbols have their usual meaning [21].

3. Results and discussion

3.1. Equilibrium geometries

Calculated geometry parameters of lead(II) halides and $PbX_2\cdots L$ complexes are listed in Tables 1 and 1a together with available PbX_2 experimental data. Interestingly, the computed Pb–X equilibrium distances of the halides are very close (within 1.0%) to the gas phase r_g bond lengths determined from electron diffraction [4], which implies slight overestimation of Pb–X r_e distances, as $r_e < r_g$. Nonetheless, the length of Pb–X bond computed at MP2/SBKJC+(d) level appears