ICl

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130: 316884k Potential energy curves of ICl and non-adiabatic interactions studied by the spin-orbit CI method. Yabushita, Satoshi (Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama, Japan). *THEOCHEM* **1999,** 461-462, 523-532 (Eng), Elsevier Science B.V.. Excited state potential curves of ICl were obtained by the spin-orbit CI method to describe the non-adiabatic interactions. Variations of each wave function were analyzed and three avoided crossings were characterized between 0^+(III)/0^+(IV), 0^+(II)/0^+(IV), and 0^+(II)/0^+(III) at R = 2.85, 3.14 and 3.62 Å, resp. The second avoided crossing, that was suggested before by Tiemann et al., was obtained here for the first time. Our $^1\Pi_1$, 1(II) state crosses with the B state just inside the second avoided crossing, supporting the exptl. analyses made by Gordon et al. and Tiemann et al. Applied to the B state photodissocn., our potential curves yield the wave-length dependence of the branching ratios, I($^2P_{3/2}$) + Cl($^2P_{3/2}$)/I($^2P_{3/2}$) + Cl($^2P_{1/2}$), in good agreement with exptl. results. Photodissocn. from the second absorption band is also discussed based on our theor. and recent exptl. results.

C.A., 1999, 130, N23

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F: ICl
P: 3

131:162640 Quasirelativistic transition moment calculations using the mul partitioning perturbation theory: B0+(3.PI.) X0+(1.SIGMA.+) transitions i and ICl. Zaitsevskii, A.; Teichteil, C.; Vigue, J.; Bazalgette, G. (Department of Chemistry, Laboratory of Molecular Structure and Quantum Mechanics, M. Lomonossov Moscow State University, Moscow 119899, Russia). Phys. Lett., 307(3,4), 277-282 (English) 1999 A simple method of ab initio quasi-relativistic calcns. on electronic transition moments in mols. is presented. The description of relativisti effects through effective core potentials is combined using the 2nd-order body multi-partitioning perturbation theory for correlation treatment. Transition moment ests. were obtained by the finite-field technique. Pil applications to the B0+(3.PI.) X0+(1.SIGMA.+) transitions in IF and ICl a reported and the results are compared to exptl. data. A new fit of the o visible absorption spectra of ICl gives results in excellent agreement wi ab initio results.

F: ICl
P: 3

2000

133:273649 Threshold photoelectron spectroscopy of iodine monochloride. Yencha, A. J.; Lopes, M. C. A.; King, G. C. Department of Chemistry, State University of New York at Albany . Albany, NY 12222, USA Chem. Phys. Lett., 325(5,6), 559-567 (English) 2000. A high-resoln. (1-11 meV) threshold photoelectron spectroscopic study of ICl was performed using synchrotron radiation and a penetrating- field electron spectrometer over the valence ionization region of the mol. Accurate vibrational consts. were obtained for both spin-orbit components of the ICl+ (X 2.PI.i) state through the observation of extended vibrational bands in the Franck-Condon gap regions of the mol. ion. The appearance of these vibrational bands is attributed to resonant autoionization of Rydberg states residing in this energy region of the ionic state. The adiabatic (v+=0) ionization potentials for formation of the ground state of the ICl+ ion are 10.076 .+-. 0.002 eV for (X 2.PI.3/2) and 10.655 .+-. 0.002 eV for (X 2.PI.1/2) yielding a spin-orbit splitting in this state of 0.579 .+-. 0.002 eV. The adiabatic (v+=0) ionization potential for formation of the (A 2.PI.i) state of ICl+ is at ~12.5 eV. Addnl. autoionization effects are noted in the formation of the (A 2.PI.i) and (B 2.SIGMA.+) band systems in ICl+.

F: ICl
P: 3

2001

135:24954 **Theoretical Calculation of Bond Dissociation Energies and Enthalpies of Formation for Halogenated Molecules.** Lazarou, Yannis G.; Prosmitis, Alexandros V.; Papadimitriou, Vassileios C.; Papagiannakopoulos, Panos. Institute of Physical Chemistry, National Center for Scientific Research Demokritos, Aghia Paraskevi, Greece. J. Phys. Chem. A (2001), 105(27), 6729-6742. in English.

The bond dissocn. energies and the enthalpies of formation of halogenated mols. were theor. calcd., and the results were compared with the corresponding exptl. values in order to examine the reliability of a large no. of levels of theory in thermochem. calcns. D. functional theory using a multitude of exchange and correlation functionals, Moller-Plesset perturbation theory, and QCISD(T) and CCSD(T) methods were employed, with all-electron and effective-core potential basis sets of varying complexity. A small set of 19 mols. was selected, consisting of X2, HX, and CH3X (X = F, Cl, Br, and I), the mixed-halogen mols. ClF, BrF, BrCl, IF, and ICl, and H2 and CH4. The calcd.

bond dissocn. energies were cor. for basis set superposition errors and the first-order spin-orbit coupling in the 2P state of halogen atoms. In addn., the enthalpies of formation of all mols. in the set as well as those of Me (CH3) and halomethyl radicals (CH2X) were also calcd. by using the corresponding atomization reactions, cor. for the spin-orbit coupling in the 3P state of carbon atom and the 2P state of halogen atoms. Levels of theory employing the B3P86 functional with moderately large basis sets, augmented with diffusion and polarization functions, were found to be sufficiently reliable in the calcn. of bond dissocn. energies of closed-shell halogenated mols. In particular, the B3P86/6-311++G(2df,p) level of theory was found to be the most accurate, with an RMS deviation of 6 kJ·mol-1 for 23 bond dissocn. energies, with a negligible dependence of the accuracy on the level of theory chosen for the geometry optimization. In addn., the B3P86 functional in combination with small basis sets was found to be superior to B3LYP and MP2 in the calcn. of mol. structures. Regarding the calcd. enthalpies of formation, G2 theory was the most accurate, with an RMS deviation of 9 kJ·mol-1, followed by several combinations of the B3PW91 and B3LYP functionals with mostly large basis sets. However, the B3P86 functional tends to overbind open-shell species, resulting in an underestimation of the enthalpies of formation for polyat. mols. Extension of the bond dissocn. energy calcns. at levels of theory employing the B3P86 functional to a larger set of 60 bonds in 41 halogen-contg. mols. revealed systematic errors dependent on the mol. size. Therefore, the calcd. bond dissocn. energies at the B3P86/6-311++G(2df,p) level of theory were empirically improved by increasing the abs. energies of the radicals by the quantity 9 × 10-5·Ne Hartrees (Ne = total no. of electrons of the radical), with a subsequent lowering of the RMS deviation in the larger set to 8.0 kJ·mol-1.