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A morphed intermolecular bending potential of OC–HCl

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Abstract

A morphed intermolecular bending potential energy surface (PES) has been generated for the dimer OC–HCl. This morphed potential is determined from gas phase spectroscopic data and found to have a global minimum with a well depth of 694.9 cm^{-1} and linear OC–HCl geometry having $R_{CM} = 4.25$ Å, $\theta_{CO} = 180.0°$, $\theta_{HCl} = 180.0°$, and $\phi = 0.0°$. The isomer CO–HCl is predicted with a well depth of 375.9 cm^{-1} and geometry $R_{CM} = 4.05$ Å, $\theta_{CO} = 0.0°$, $\theta_{HCl} = 180.0°$, and $\phi = 0.0°$, which corresponds to a $\Delta E = 319.0$ cm^{-1} between these potential energy minima.

1. Introduction

Previous *ab initio* calculations report that carbon monoxide can form stable isomeric complexes with hydrogen chloride [1–4]. Initial experimental work using pulse-nozzle Fourier-transform microwave spectroscopy [5,6] provided a precise ground state molecular structure for the OC–HCl isomer. A Rabi-type molecular beam electric resonance spectrometer gave additional microwave and radiofrequency data [7]. The values of the v_1, v_2, and v_4^1 vibrational frequencies modes were initially determined to be 2815.2(3), 2154.3(3) and 247.1(5) cm^{-1}, using infrared spectra in solid argon matrices [8]. Analysis of the intramolecular bands v_1 and v_2 located at 2851.761(2) and 2155.500(2) cm^{-1} were reported using diode-laser [9] and Fourier transform supersonic-jet spectroscopy [10]. Subsequently, the static gas-phase FTIR spectrum was recorded [11] and used to evaluate [12] the v_5^1 bending band to be 48.9944(2) cm^{-1}. Recently, a gas phase study of the OC–HCl dimer using synchrotron radiation was reported [13]. The high-resolution gas-phase FTIR spectrum of the v_4^1 intermolecular vibrational frequencies of OC–HCl was analyzed and a Morse potential constructed for the stretching of the intermolecular distance between OC and HCl monomers.

Experiment and theory concur that the hydrogen-bonded complex OC–HCl has a linear equilibrium geometry [1–14]. *Ab initio* calculations [1–4] also suggest that the CO–HCl isomer has a linear equilibrium geometry, although experimentally it has not yet been observed. Microwave rotational studies for each of the homologous series OC–HX (X = F, Cl, Br, I) are consistent with linear equilibrium geometries [5–7,15–17]. This is in contrast to the homologous series CO_2–HX (X = F, Cl, Br, I) where the complexes with X = F and Cl have the linear equilibrium geometry OCO–HX [18,19] but the complexes CO_2–HBr [20] and CO_2–HI [21] are found to be non-linear [20–22].

Morphed potential energy functions now exist for a range of Rg–HX (Rg = Ne, Ar, Kr; X = F, Br, I) complexes [23–26]. This approach has been extended to He–OCS [27] and more recently to hydrogen-bonded dimers [28]. The objective behind current studies is to calculate *ab initio* PESs for dimensionally larger systems and transform them so that a morphed potential is generated giving an optimized fit to the available experimental data. We now generate a 4D morphed intermolecular bending potential for the OC–HCl dimer for comparison with previous models of its bending potential.

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2. Theoretical methods

2.1. Ab initio calculation of the intermolecular potential

In the two-angle embedded frame, the interaction potential of OC–HCl dimer can be expressed in terms of the Jacobi coordinates (R_{CM}, θ_{CO}, θ_{HCl}, ϕ) [29,30] (Fig. 1). R_{CM} is the distance between the centers of mass of the two monomers, the angles θ_{CO} and θ_{HCl} describe the orientation of the monomers CO and HCl respectively, and the dihedral angle ϕ describes the relative internal orientation of both monomers. In all calculations, the bond lengths of both monomer components were fixed at experimental r_e 1.128323 Å for CO and 1.27455 Å for HCl [31]. The interaction energy of the OC–HCl dimer was calculated using the MOLPRO 2002 electronic structure package [32] at CCSD(T)/aug-cc-pVTZ level of theory. Every calculated point was corrected for the basis set superposition error (BSSE) using the counterpoise correction of Boys and Bernardi [33], and the PES was calculated on a grid of 2298 points. This potential has a global minimum with well depth determined to be 653.11 cm^{-1} at the geometry $R_{CM} = 4.25$ Å, $\theta_{CO} = 180.0°$, $\theta_{HCl} = 180.0°$, and $\phi = 0.0°$.

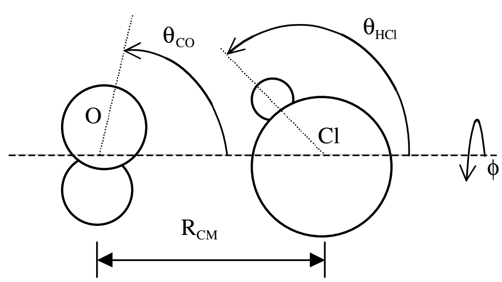

Fig. 1. Geometry of OC–HCl dimer in Jacobi coordinates.

2.2. Fitting of the ab initio potential

In order to have a global representation of the PES, the calculated 2298 *ab initio* points at each value of R_j were fitted to the spherical expansion [29,30]

$$V(R_j, \theta_{CO}, \theta_{HCl}, \phi) = \sum_{\Lambda} v_{\Lambda j} A_{\Lambda}(\theta_{CO}, \theta_{HCl}, \phi), \qquad (1)$$

where Λ is a collective symbol for the quantum numbers $\{L_{CO}, L_{HCl}, L\}$, $v_{\Lambda j}$ are the expansion coefficients [29] and $A_{\Lambda}(\theta_{CO}, \theta_{HCl}, \phi)$ is given by Eq. (2):

$$A_{\Lambda}(\theta_{CO}, \theta_{HCl}, \phi) = \sum_{M=0}^{\min(L_{CO},L_{HCl})} (-1)^M (2 - \delta_{M,0}) \times \langle L_{CO}, M; L_{HCl}, -M | L, 0 \rangle \times \left[\frac{(L_{CO} - M)!(L_{HCl} - M)!}{(L_{CO} + M)!(L_{HCl} + M)!} \right]^{1/2} \times P_{L_{CO}}^{|M|}(\cos\theta_{CO}) P_{L_{HCl}}^{|M|}(\cos\theta_{HCl}) \cos(M\phi) \qquad (2)$$

In Eq. (2) $P_L^{|M|}(\cos\theta)$ stands for the associated Legendre polynomials, and the symbol $\langle L_{CO}, M; L_{HCl}, -M | L, 0\rangle$ is the Clebsch–Gordan coefficient. The expansion coefficients $v_{\Lambda j}$ were evaluated using a linear least-squares procedure [29]. A weighting factor $F_w = 25$ cm^{-1} is used in order to have an absolute average difference less than 6 cm^{-1} between the values of the points in the *ab initio* and fitted potentials, for the points within 250 cm^{-1} of the minimum of the potential [29,30]. The four-dimensional potential was

Table 1
Experimental data used in the fits and fitted values with the uncertainties used

Observable	Units	Isotopomer	$V_{ab\,initio}$	$V_{morphed}$	Exp.	σ_k
B (ground state)	10^{-2} cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	5.50	5.60	5.58[a]	0.01
D (ground state)	10^{-8} cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	17.2	15.8	16.0[a]	0.5
B (ground state)	10^{-2} cm^{-1}	$^{16}O^{12}C–H^{37}Cl$	5.37	5.47	5.58[a]	0.01
D (ground state)	10^{-8} cm^{-1}	$^{16}O^{12}C–H^{37}Cl$	16.4	15.1	15.3[a]	0.5
B (ground state)	10^{-2} cm^{-1}	$^{16}O^{13}C–H^{35}Cl$	5.44	5.54	5.52[a]	0.01
D (ground state)	10^{-8} cm^{-1}	$^{16}O^{13}C–H^{35}Cl$	16.9	15.5	15.6[a]	0.5
B (ground state)	10^{-2} cm^{-1}	$^{16}O^{12}C–D^{35}Cl$	5.51	5.61	5.59[a]	0.01
D (ground state)	10^{-8} cm^{-1}	$^{16}O^{12}C–D^{35}Cl$	15.9	14.7	15.0[a]	0.5
$B\ (v_5^1)$	10^{-2} cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	5.57	5.67	5.66[b]	0.01
$D\ (v_5^1)$	10^{-8} cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	20.5	18.6	19.1[b]	0.5
$B\ (v_4^1)$	10^{-2} cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	5.36	5.47	5.43[c]	0.01
$D\ (v_4^1)$	10^{-8} cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	25.5	21.5	21.4[c]	0.5
$\langle P_2(\cos\theta)\rangle(H^{35}Cl)\ (0,0,0)$		$^{16}O^{12}C–H^{35}Cl$	0.81	0.81	0.77[a]	0.05
$\langle P_2(\cos\theta)\rangle(H^{37}Cl)\ (0,0,0)$		$^{16}O^{12}C–H^{37}Cl$	0.81	0.81	0.77[a]	0.05
$\langle P_2(\cos\theta)\rangle(H^{35}Cl)\ (0,0,0)$		$^{16}O^{13}C–H^{35}Cl$	0.81	0.81	0.77[a]	0.05
$\langle P_2(\cos\theta)\rangle(D^{35}Cl)\ (0,0,0)$		$^{16}O^{12}C–D^{35}Cl$	0.86	0.86	0.82[a]	0.05
v_5^1	cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	48.59	48.99	48.99[b]	0.01
v_4^1	cm^{-1}	$^{16}O^{12}C–H^{35}Cl$	191.80	201.20	201.20[c]	0.01
G			222.04	2.86		

[a] From Ref. [6].
[b] From Ref. [12].
[c] From Ref. [13].