Bound states of positron with simple carbonyl and aldehyde species with configuration interaction multi-component molecular orbital and local vibrational approaches

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Abstract. Characteristic features of the positron-binding structure of some carbonyl and aldehyde species such as formaldehyde, acetaldehyde, acetone and propionaldehyde are discussed with the configuration interaction scheme of multi-component molecular orbital (MC_MO) calculations. This method can take the electron–positron correlation contribution into account through single electronic–single positronic excitation configurations. Our vertical positron affinity (PA) values of acetaldehyde and acetone with electronic 6-31++G(2df,2pd) and positronic [15s15p3d2f1g] basis sets are as 52 and 92 meV, which can be compared to the recent experimental values of 90 and 173 meV by Danielson \textit{et al} (2010 \textit{Phys. Rev. Lett.} 104 233201). For formaldehyde we have also found that the PA values are enhanced by including the local C=O vibrational contribution from the vertical PA value of 15 meV to 17, 21 and 25 meV after averaging over the zeroth, first and second vibrational states, respectively, due to the anharmonicity of the potential.

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1. Introduction

Positrons are of both scientific and technological use in many areas such as physics, chemistry, material science, medicine and their interdisciplinary areas [1–5]. Binding energies of positrons to molecules have now been experimentally measured for more than 30 species such as some hydrocarbons (alkanes, alkenes and aromatics), alcohols and halogenated hydrocarbons [6, 7]. Very recently, Danielson et al [8] have experimentally measured positron binding to acetaldehyde and acetone and estimated these PA values as 90 and 173 meV. In the present study, we will thus focus on the characteristic features of the positron binding to carbonyl and aldehyde species using our theoretical approach.

A positron should be able to form an infinite number of bound states with non-rotating molecules if the molecule has a dipole moment with a value greater than 1.625 Debye (the critical dipole moment, \(D_c\)) [9]. Nowadays, the understanding of positron attachment processes is expected to provide useful information on the interaction of positrons with surfaces and bulk materials, as investigated using techniques such as positron emission tomography (PET), angular correlation of annihilation radiation (ACAR) and positron lifetime spectroscopy (PALS).

In order to investigate positronic compounds with a theoretical approach, it is necessary to develop a computational method that treats both electron and positron (multi-components) on an equal footing quantum mechanically. There have been some theoretical attempts to investigate a possible formation of positron-bound states based on mean-field [10–13], many-body perturbation [14, 15], configuration interaction (CI) [16–26], variational calculations using explicitly correlated Gaussian (ECG) wave functions [27–29] and quantum Monte Carlo (QMC) [30–36] techniques. Most calculations have shown that molecules with strong dipole moments (>3–4 Debye) can indeed bind a positron. Recently, we elucidated the positron-binding structure of some nitrile molecules with the CI scheme of MC_MO calculations [26]. For example, our computed PA value for acetonitrile is 135 meV, which agrees to within 25% of Danielson et al’s recent experimental value of 180 meV [8].

In this paper, we will demonstrate the binding of a positron to some carbonyl molecules, and propose a possibility for positronic bound states of such species. In the calculation of positronic compounds, the effect of long-range interactions and the electron–positron correlation play an important role in obtaining a bound state. However, QMC calculations for such larger carbonyl molecules are not realistic due to the limitations of our computational
facilities. In this paper, we have therefore employed the less time-consuming MC_MO calculation for some larger carbonyl molecules at the double excitation of the single electronic–single positronic excitation CI level to include the electron–positron correlation.

In section 2, we provide a brief outline of the numerical calculation for positronic compounds using the HF and CI levels of the MC_MO treatment. In section 3, we present computational details of various carbonyl molecules. In section 4, the results and discussion of some carbonyl molecules are considered. Finally, in section 5, concluding remarks are presented.

2. Theory

We show here a brief outline of the MC_MO method. The details are provided in [17]. The non-relativistic Hamiltonian operator for a molecular system containing \(N_e\) electrons, \(N_{\text{nuc}}\) fixed nuclei and a positron (p) is

\[
H = -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \nabla_p^2 + \sum_i \sum_{j>i} \frac{1}{r_{ij}} - \sum_i \sum_{I} \frac{Z_I}{r_{iI}} - \sum_i \sum_{I} \frac{1}{r_{ip}} + \sum_{I} \frac{Z_I}{r_{pI}},
\]

where the first and second terms are the kinetic energy operators for the electrons and positron, respectively. The other terms are the Coulomb interaction: \(Z_I\) is the charge of the \(I\)th nucleus and the variables of \(r_{ij}, r_{ip}, \) etc are the distances between particles.

The total wave function (\(|\Psi_{\text{tot}}(R)\rangle\)) of the positronic compound is given as a CI formalism of

\[
|\Psi_{\text{tot}}(R)\rangle = \sum_L |\Psi_L(R)\rangle C_L
= |\Phi^e_0(R_e)\rangle |\phi^p_0(r_p)\rangle C_{(0,0)} + \left( \sum_{L_e} \sum_{L_p} \right)' |\Phi^e_{L_e}(R_e)\rangle |\phi^p_{L_p}(r_p)\rangle C_{(L_e,L_p)},
\]

where \(C_L(C_{(L_e,L_p)})\) is the CI coefficient of the \(L\)th configuration (\(|\Psi_L(R)\rangle\)), which consists of products of the \(L_e\)th electronic configuration of the Slater determinant (\(|\Phi^e_{L_e}(R_e)\rangle\)) and the \(L_p\)th positronic orbital (\(|\phi^p_{L_p}(r_p)\rangle\)).

If one treats only the first term of equation (2), one can easily derive the mean-field Hartree–Fock (HF) equations of the MC_MO method. Considering a closed shell electronic structure, the one-particle electronic and positronic Fock operators are

\[
f^e(r_e) = h^e(r_e) + \sum_i \left[ 2 J_i(r_e) - K_i(r_e) \right] - J_p(r_e),
\]

\[
f^p(r_p) = h^p(r_p) - \sum_i \left( J_i(r_p) \right),
\]

where \(h^e(r_e)\) is the one-particle operator, which contains the kinetic energy and Coulomb interaction potential with the nuclei, \(J_i\) is the Coulomb operator and \(K_i\) is the exchange operator. Expanding the molecular orbitals of the electrons and the positron as linear combinations of basis functions, one can obtain the multi-component electronic and positronic wave functions.
by solving the Roothaan equations simultaneously and also obtain the HF energy. We have implemented these schemes in the GAUSSIAN 03 program package [37].

The CI matrix element is calculated by modification of the graphical unitary group approximation (GUGA) technique [38] for the positronic compound of

\[ H_{LL'} = \langle \Psi_L(R) | H | \Psi_{L'}(R) \rangle \]

\[ = \langle \Phi^e_{Lz}(R_e) \rangle - \frac{1}{2} \sum_{i}^{N_e} \nabla^2_i + \sum_{i}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} - \sum_{i}^{N_e} \sum_{l}^{N_{nucl}} \frac{Z_l}{r_{il}} \langle \Phi^e_{L_{z'}}(R_{e'}) \rangle \langle \Phi^p_{L_{z'}}(r_p) | \Phi^p_{L_{z'}}(r_p) \rangle \]

\[ + \langle \Phi^p_{L_{z'}}(R_{e'}) \rangle \langle \Phi^p_{L_{z'}}(R_{e'}) \rangle \langle \phi^p_{L_{z'}}(r_p) | - \frac{1}{2} \nabla^2_p + \sum_{l}^{N_{nucl}} \frac{Z_l}{r_{pl}} | \phi^p_{L_{z'}}(r_p) \rangle \]

\[ - \langle \Phi^p_{L_{z'}}(R_{e'}) \rangle | \phi^p_{L_{z'}}(r_p) \rangle \sum_{i}^{N_e} \frac{1}{r_{ip}} | \Phi^e_{L_{z}}(R_e) \rangle | \phi^p_{L_{z'}}(r_p) \rangle, \] (5)

where the first, second and third terms denote the contributions of electronic, positronic and simultaneous electronic–positronic correlations, respectively. After diagonalization of the CI matrix of equation (5), one can obtain the CI wave function and its energy. Such CI calculations are performed using our own program package of the MC_MO [39].

3. Numerical calculations

Firstly, we have optimized the geometry of some parent species of carbonyl and aldehyde molecules such as formaldehyde (H\(_2\)CO), acetaldehyde (CH\(_3\)CHO), acetone ((CH\(_3\))\(_2\)CO) and propionaldehyde (C\(_2\)H\(_3\)CHO) at the HF/6-31++G(2df,2pd) level of calculation. Secondly, we have employed the single-point calculation for positron-attached complexes at the optimized equilibrium structures of the parent species. An even-tempered [15s15p3d2f1g] GTF positronic basis set is employed with \(\alpha_{i+1} = c \times \alpha_i\), where \(c = 3.1623\) and \(\alpha_i = 1.0 \times 10^{-6}\) for \(s\)- and \(p\)-type GTFs. This choice is important in defining the diffuse-type GTFs that need to be included in the positronic basis set in order to accurately describe the charge distribution of this particle. The other positronic polarized GTF exponents are 0.31623, 0.1, 0.031623 for \(d\)-type, 0.31623, 0.01 for \(f\)-type and 0.31623 for \(g\)-type GTFs. All positronic GTFs are centered at the oxygen nucleus.

The PA is defined as the difference between the energies of the parent species and its positron-attached complexes. We have employed the HF and the truncated singly and doubly excited configuration interaction (CISD) levels, where three types of excitations, single electronic, single positronic and both single electronic–single positronic excitation configurations are included. We note here that our CISD level of calculation includes no pure electronic correlation contributions (no double electronic excitation terms) [16, 22, 26]. Strictly speaking, further extension of the configuration space and the polarized basis functions will definitely improve the total energy and properties, since the CI expansion for positronic systems is known to converge slowly. Recently, however, we have already shown that the PA value for the HCN molecule obtained with our CISD calculations can be qualitatively compared to our previous QMC result, although our variational energy for the [HCN; \(e^+\)] species is still higher than that obtained by QMC [26]. Thus, we have decided to employ our truncated CISD level for the larger carbonyl and aldehyde molecules due to the limitations of our computational facilities.
For formaldehyde, we have also evaluated the vibrational averaged PA values in the Born–Oppenheimer framework. Following the paper [25], first we calculated the potential energy curve (PEC) with respect to the pure C=O stretching coordinate and numerically calculated the vibrational wave functions of local C=O stretching mode, since the polarization of the C=O stretching coordinate is strongest. Then, we evaluated both the ground (zero-point) and the excited νth vibrational averaged PA (PA_{ν}^{BO}) values as

$$PA_{ν}^{BO} = \int_{0}^{\infty} \left\{ E^X(R) - E^{[X,e^+]}(R) \right\} \left| \psi^X_ν(R) \right|^2 dR,$$

where $R$ is the local C=O stretching coordinate, $E^X(R)$ is the energy of $X$ ([X; $e^+$]) and $\psi^X_ν(R)$ the νth normalized vibrational wave function of $X$, respectively.

4. Results and discussion

4.1. Vertical positron affinity (PA) values for some carbonyl and aldehyde molecules

Figure 1 summarizes the optimized equilibrium geometries of some carbonyl and aldehyde molecules, formaldehyde (H_2CO), acetaldehyde (CH_3CHO), acetone ((CH_3)_2CO) and propionaldehyde (C_2H_5CHO) at the HF/6-31++G(2df,2pd) level of approximation. We note here that electrons are drawn toward the oxygen atom from the carbon atom in these CO groups. We have employed single-point calculations for the positronic complexes of these carbonyl molecules with the fixed equilibrium geometries as shown in figure 1.

Table 1 summarizes the CO distances, dipole moments and energies of the carbonyl (and aldehyde) parent molecules (H_2CO, CH_3CHO, (CH_3)_2CO and C_2H_5CHO) at the HF/6-31++G(2df,2pd) level, and energies of each positronic species obtained with our CISD
Table 1. CO distances ($R_{CO}$; Å), dipole moments ($\mu$; Debye), energies of X species with HF level ($E_X$(HF); Hartree) and energies of [X; $e^+$] species with our CISD levels ($E_{[X,e^+]$(CI); Hartree} using electronic 6-31++G(2df,2pd) and [15s15p3d2f1g] positronic basis sets. The corresponding positron affinities (PA; meV) are also shown.

| X          | $R_{CO}$ | $\mu$ | $E_X$(HF)   | $E_{[X,e^+]$(CI) | PA  |
|------------|----------|-------|-------------|-------------------|-----|
| H$_2$CO    | 1.179    | 2.76  | $-113.886206$ | $-113.886768$     | 15  |
| CH$_3$CHO  | 1.182    | 3.13  | $-152.941825$ | $-152.943740$     | 52  |
| CH$_3$COCH$_3$ | 1.182 | 3.27  | $-191.993936$ | $-191.997312$     | 92  |
| C$_2$H$_5$CHO | 1.182 | 3.01  | $-191.983165$ | $-191.985290$     | 58  |

Figure 2. (a) Valence electronic and (b) positronic densities on the molecular plane of [H$_2$CO; $e^+$] species. Positions of nuclei are also shown schematically. The x–y spatial scales are given in units of bohr.

calculations. The corresponding vertical PA values are also shown. All PAs in table 1 are positive, which indicates that stable positronic bound states exist for these species.

As expected, a huge dependence on positronic basis sets was observed; that is, the PA values of H$_2$CO with the [15s15p] and [15s15p3d2f1g] positronic basis sets were 6 and 15 meV, respectively. The polarization functions with higher angular momentum are indispensable for adequately taking into account the electron–positron correlation, as well as for the evaluation of PAs. Strasburger [21] obtained 15 meV with their electronic 6–311G plus a more diffuse function and a positronic [10s6p1d] plus diffuse function.

Figure 2 shows the (a) valence electronic and (b) positronic densities on the molecular plane of [H$_2$CO; $e^+$] species. The positron is attached to the electronic negative charge cloud on the oxygen atom, since the CO group of these molecules tends to form an ionic configuration. In these molecules, a positron is captured on the tail of a long-range dipole potential due to the Coulomb interaction between the positron and the electrons on the oxygen atom.
Table 2. Dipole moments ($\mu$; Debye) and positron affinities (PA; meV) at various CO distances ($R_{CO}$; Å) in the H$_2$CO molecule.

| $R_{CO}$ | $\mu$ | PA |
|---------|-------|----|
| 0.914   | 0.97  | 0  |
| 0.967   | 1.38  | 0  |
| 1.020   | 1.76  | 0  |
| 1.073   | 2.12  | 1  |
| 1.126   | 2.45  | 5  |
| 1.178   | 2.75  | 15 |
| 1.231   | 3.04  | 30 |
| 1.284   | 3.31  | 50 |
| 1.337   | 3.56  | 73 |
| 1.390   | 3.80  | 99 |
| 1.443   | 4.03  | 128|
| 1.496   | 4.26  | 160|

The dipole moments are 2.76, 3.13, 3.27 and 3.01 Debye for parent H$_2$CO, CH$_3$CHO, (CH$_3$)$_2$CO and C$_2$H$_5$CHO species. The PAs for CH$_3$CHO, (CH$_3$)$_2$CO and C$_2$H$_5$CHO are greater than those of H$_2$CO, which is consistent with their larger dipole moments. Very recently, Danielson et al [8] have experimentally estimated the PA values for CH$_3$CHO and (CH$_3$)$_2$CO as 90 and 173 meV, which can be compared with the present computed vertical PA values of 52 and 92 meV, respectively.

4.2. Vibrational averaged PA values for the formaldehyde molecule

To discuss one of the reasons for the above differences between experimental and our calculated PA values, we have taken into account the vibrational contributions. Because of the limitations of our computational resources, we have calculated the H$_2$CO molecule considering only the C=O local stretching mode. Following [25], we have evaluated the averaged PA values in the Born–Oppenheimer framework, i.e. within the model of an immediate positron attachment to the H$_2$CO molecule at a given geometry, modulated by the vibrational wave function of the initial parent species before the relaxation process occurs.

In table 2, first, we show the dipole moments and the vertical PA values ($E^{H_2CO}(R) - E^{[H_2CO,e^+]}(R)$) at various C=O distances for the H$_2$CO molecule. Table 2 clearly demonstrates that the PA value increases as the C=O distance increases. This result correlates with the corresponding dipole moment values.

Next, we solved the one-dimensional (1D) Schrödinger equation for nuclear wave functions on the PEC of the C=O stretching coordinate. Figure 3 shows the PEC (on a left-hand side scale in eV), PA (on a right-hand side scale in meV) values and zeroth, first and second vibrational wave functions with respect to the local C=O stretching coordinate. Our 0→1 vibrational excitation energy is 1878 cm$^{-1}$, which is slightly smaller than the corresponding C=O normal mode of 1994 cm$^{-1}$, mainly due to the anharmonic effect and neglecting the motions of hydrogen nuclei. The energies of the zeroth, first and second vibrational states are 943, 2821 and 4680 cm$^{-1}$ (116.9, 349.8 and 580.3 meV), respectively. The expectation values
The 1D PEC (on a left-hand side scale in eV) and PA (on a right-hand side scale in meV) values with respect to the local C═O stretching coordinate. The corresponding zeroth, first and second vibrational wave functions are also shown.

of CO distance for these vibrational states are calculated to be 1.182, 1.189 and 1.197 Å, respectively. It should be noted that these values are longer than the corresponding equilibrium one of 1.179 Å, due to the anharmonicity of the potential energy curve.

Using equation (6) we have numerically estimated the PA$^\text{BO}$ values as 17, 21 and 25 meV for $\nu = 0$, 1 and 2, respectively. Contrary to the alkali-halide cases [25], our PA$^\text{BO}$ value of 17 meV is greater than the pure vertical PA value of 15 meV in table 1. Interestingly, the PA$^\text{BO}$ value increases quickly with $\nu$, since the expectation values of C═O distance for $\nu = 1$ and 2 are greater than those for $\nu = 0$ due to the anharmonicity of the C═O potential in figure 3. This result implies that the experimental PA values should be greater than the vertical PA ones, since vibrationally excited states are included in forming positron–molecule bound states via Feshbach resonances in which a vibrational mode absorbs the excess energy [8].

We found that the positron is trapped in the field of the dipole potential and the corresponding vertical PA values are all positive for H$_2$CO, CH$_3$CHO, (CH$_3$)$_2$CO and C$_2$H$_5$CHO molecules. For the H$_2$CO molecule we also found that the PA values are enhanced by including the local C═O vibrational contribution. The inclusion of other vibrational degrees of freedom such as the C–H anti-symmetric coordinate and application to other molecules are quite interesting topics. Such studies are currently in progress by our group.

5. Conclusion

We have elucidated the positron-binding structure of some carbonyl and aldehyde molecules with the CI scheme of MC$^\text{MO}$ calculations. Our vertical PA values for H$_2$CO, CH$_3$CHO, (CH$_3$)$_2$CO and C$_2$H$_5$CHO molecules with electronic 6-31++G(2df,2pd) and positronic [15s15p3d2f1g] basis sets are calculated to be 15, 52, 92 and 58 meV, respectively. We have also determined that the PA values are enhanced by including the local C═O vibrational contribution for the H$_2$CO molecule from 15 meV to 17, 21 and 25 meV after averaging over the zeroth,
first and second vibrational states, respectively. We can conclude that the contribution of the nuclear vibrational effect is indispensable for comparing the calculated PA values with the corresponding experimental results.

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References

[1] Charlton M and Humberston J W 2001 Positron Physics (Cambridge: Cambridge University Press)
[2] Coleman P G 2000 Positron Beams and Their Applications (Singapore: World Scientific)
[3] Gidley D W, Chi D Z, Wang W D and Vallery R S 2006 Annu. Rev. Mater. Sci. 36 49
[4] Surko C M, Gribakin G F and Buckman S J 2005 J. Phys. B: At. Mol. Opt. Phys. 38 R57
[5] Danielson J R, Young J A and Surko C M 2009 J. Phys. B: At. Mol. Opt. Phys. 42 235203
[6] Young J A and Surko C M 2008 Phys. Rev. A 77 052704
[7] Young J A and Surko C M 2008 Phys. Rev. A 78 032702
[8] Danielson J R, Gosselin J J and Surko C M 2010 Phys. Rev. Lett. 104 233201
[9] Crawford O H 1967 Proc. Phys. Soc. 91 279
[10] Cade P E and Farazdel A 1977 J. Chem. Phys. 66 2598
[11] Kao C M and Cade P E 1984 J. Chem. Phys. 80 3234
[12] Tachikawa M, Mori K, Suzuki K and Iguchi K 1998 Int. J. Quantum Chem. 70 491
[13] Tachikawa M, Mori K, Nakai H and Iguchi K 1998 Chem. Phys. Lett. 290 437
[14] Tachikawa M, Sainowo H, Iguchi K and Suzuki K 1994 J. Chem. Phys. 101 5925
[15] Saito T, Tachikawa M, Ohe C, Iguchi K and Suzuki K 1994 J. Phys. Chem. 100 6057
[16] Saito S L and Sasaki F 1995 J. Chem. Phys. 102 8040
[17] Tachikawa M 2001 Chem. Phys. Lett. 350 269
[18] Bromley M W J and Mitroy J 2002 Phys. Rev. A 65 062505
[19] Tachikawa M, Bueren R J and Kimura M 2003 J. Chem. Phys. 119 5005
[20] Tachikawa M, Bueren R J and Kimura M 2004 J. Chem. Phys. 121 9191
[21] Strasburger K 2004 Struct. Chem. 15 415
[22] Chojnacki H and Strasburger K 2006 Mol. Phys. 104 2273
[23] Saito S L 2005 J. Chem. Phys. 122 054302
[24] Bueren R J, Liebermann H-P, Melnikov V, Tachikawa M, Pichl L and Kimura M 2005 J. Phys. Chem. A 109 5956
[25] Gianturco F A, Franz J, Bueren R J, Liebermann H-P, Pichl L, Rost J-M, Tachikawa M and Kimura M 2006 Phys. Rev. A 73 022705
[26] Tachikawa M, Kita Y and Bueren R J 2011 Phys. Chem. Chem. Phys. 13 2701–5
[27] Strasburger K 2001 J. Chem. Phys. 114 00615
[28] Bubin S and Adamowicz L 2004 J. Chem. Phys. 120 6051
[29] Mitroy J 2006 Phys. Rev. A 73 054502
[30] Schrader D M, Yoshida T and Iguchi K 1992 Phys. Rev. Lett. 68 3281
[31] Schrader D M, Yoshida T and Iguchi K 1993 J. Chem. Phys. 98 7185
[32] Jiang N and Schrader D M 1998 J. Chem. Phys. 109 9430
[33] Bressanini D, Mella M and Morosi G 1998 J. Chem. Phys. 108 4756

New Journal of Physics 14 (2012) 035004 (http://www.njp.org/)
[34] Mella M, Casalegno M and Morosi G 2002 J. Chem. Phys. 117 1450
[35] Kita Y, Maezono R, Tachikawa M, Towler M and Needs R J 2009 J. Chem. Phys. 131 134310
[36] Kita Y, Maezono R, Tachikawa M, Towler M and Needs R J 2011 J. Chem. Phys. 135 054108
[37] Frisch M J et al 2003 GAUSSIAN 03, Revision B.05 (Pittsburgh, PA: Gaussian)
[38] Shavitt I 1981 The Unitary Group for the Evaluation of Electronic Energy Matrix Elements (Berlin: Springer)
[39] Tachikawa M 2010 Ab initio multi-component molecular orbital (MC_MO) code (http://www-user.yokohama-cu.ac.jp/~tachi/index.html)